INSTITUTE OF ORGANIC CHEMISTRY
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DISSERTATION

The synthesis of π-expanded *meso*-substituted porphyrins and corroles

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This 4-year-period has been extraordinarily important for me. I discovered how complex and fascinating life could be from both a scientific and personal viewpoint. The major part of this discovery was that I had a several occasions to meet people that have greatly influenced me. I would like to thank them all, however in view of the character of this *Thesis* and due to limited space, I must focus on chemistry related people.

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An invaluable gratitude goes to my beloved wife. Aga, your understanding and support have been of crucial importance to me. I wish I could find appropriate words to express how grateful I am to you. With you at my side, I feel I can face whatever the future may hold.

Warsaw, Jan Paweł Lewtak

Contents

1 Introduction and the aim of work.

Porphyrin scaffold has been chosen by Nature to play two important roles: in photosynthesis and in reversible oxygen binding. Its aromatic, planar structure, rich coordination chemistry and reasonable stability all played roles in this choice. Although porphyrins themselves are so interesting object of research, for many years already there is a tendency to alter the porphyrin chromophore. Countless number of new structures was prepared, especially in last 20 years.

The modifications of the porphyrin core include, but they are not limited to: replacing central nitrogen atom(s) with sulfur,[1] oxygen,[1] carbon,[2] selenium, tellurium[3] etc.; reducing number of pyrrole units,[4] increasing the number of pyrrole units,[5] altering the number of direct pyrrole-pyrrole linkages,[6] removing certain pyrrole units,[7] adding additional conjugated double and triple bonds, aromatic rings etc.[8] All these modifications change the optical, physicochemical and coordination properties of resulting macrocycles.

In addition to purely academic interest in answering the fundamental questions about structure, aromaticity and photophysical properties of these new functional dyes, there is also significant interest streaming from the fact that these compounds can

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[1] L. Latos-Grażyński, In *The Porphyrin Handbook*; , K. M. Kadish, K. M. Smith and R. Guilard, Eds., Academic Press: New-York, 2000, Vol.**2**, Chapter 14.

[2] (a) M. Pawlicki and L. Latos-Grażyński, In *Handbook of Porphyrin Science*, K. M. Kadish, K. M. Smith and R. Guilard, Eds., *World Scientific,* Singapore, 2010, Vol. **2**, Chapter 8; (b) P. J. Chmielewski and L. Latos-Grażyński, *J. Chem. Soc., Perkin Trans. 2*, 1995, **3**, 503.

[3] L. Latos-Grażyński, E. Pacholska, P. J. Chmielewski, M. M. Olmstead and A. J. Balch, *Angew. Chem. Int. Ed*. 1995, **34**, 2252.

[4] Y. Inokuma, J. H. Kwon, T. K. Ahn, M.-C. Yoon, D. Kim and A. Osuka, *Angew. Chem. Int. Ed.* 2006, **45**, 961.

[5] J. L. Sessler and D. Seidel, *Angew. Chem. Int. Ed*., 2003, **42**, 5134.

[6] I. Aviv-Harel and Z. Gross, *Chem. Eur. J*. 2009, **15**, 8382.

[7] E. Pacholska, L. Latos-Grażyński and Z. Ciunik, *Chem. Eur. J*., 2002, **8**, 5403.

[8] N. Ono, H. Yamada and T. Okujima, In *Handbook of Porphyrin Science*, K. M. Kadish, K. M. Smith and R. Guilard, Eds., *World Scientific*, Singapore, 2010, Vol. **2**, p.1.

serve as means in various applications. One of them is optical limiting of light based on two-photon absorption[9] and another is photovoltaics.[10]

In last decade, corroles became one of the most popular subject of research among core-modified porphyrinoids. Their scaffold is known since 1964, but these compounds became readily accessible only after the discovery of one-pot procedure for their synthesis in 1999.[11] Further improvements allowed to optimize the synthetic procedures and to obtain virtually any substitution pattern in corroles.[12] Still, there are only limited number of π-extension[13] of the corrole chromophore known up-to-date. Lower symmetry (in comparison to porphyrins) as well as stability issues obviously contribute to this situation.

Among various possibilities of modification of porphyrin scaffold, there is one relatively new trend to perform oxidative aromatic coupling on these macrocycles bearing at *meso*-positions additional aromatic units. This tendency is probably driven (among others) by the fact that this approach allows for significant bathochromic shift of absorption of both Soret and Q bands.

In compliance with current state of research in this field, main goals of my work can be delineated as follows:

- Investigation of different synthetic possibilities of π-extension of corrole chromophore
- Investigation of oxidative aromatic coupling of *meso*-substituted A_3B- and *trans*-A_2B_2-porphyrins bearing various aromatic units

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[9] (a) C. W. Spangler, *J. Mat. Chem*., 1999, **9**, 2013; (b) M. Calvete, G. Y. Yang. M. Hanack, *Synthetic Metals,* 2004, **1**, 231.

[10] Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka and E. Nakamura, *J. Am. Chem. Soc*., 2009, **131**, 16048.

[11] (a) Z. Gross, N. Galili and I. Saltsman, *Angew. Chem., Int. Ed*., 1999, **38**, 1427; (b) R. Paolesse, L. Jaquinod, D. J. Nurco, S. Mini, F. Sagone, T. Boschi and K. M. Smith, *Chem. Commun*., 1999, 1307.

[12] D. T. Gryko, *J. Porphyrins Phthalocyanines* 2008, **12**, 906.

[13] In their 2003 review Sessler and Seidel proposed a definition of 'expanded' porphyrin as 'macrocycles that contain pyrrole, furan, thiophene, or other heterocyclic units linked together either directly or through one or more spacer atoms in such way that the internal ring pathway contain a minimum of 17 atoms' (J. L. Sessler and D. Seidel, *Angew. Chem. Int. Ed*., 2003, **42**, 5134). Consequently to differentiate these expanded porphyrins from compounds with non-altered core, but possessing additional conjugated multiple carbon-carbon bonds, I propose to call the latter 'π-extended porphyrins'.

During my work I planned to study two general strategies leding to π-extension of both macrocycles: attaching an another aromatic unit *via* triple bondat position *meso* and attaching another aromatic unit at position *meso* and *β*. Since the first approach is relatively established for porphyrins and totally unknown for corroles I decided to focus on corroles in this regard. In order to accomplish this plan certain degree of methodological development was required in the chemistry of porphyrins and corroles. Obviously, during realization of these goals many interrelated trends occurred.

In the final stage of my work I planned to combine both strategies and obtain modified porphyrins bearing both *meso*-*β*-fused units as well as ethynyl substituents. During the research, attention was paid to corrole stability and in most cases electron-withdrawing substituents were employed.

During my experimental work numerous publications have been published on this topic by competing research groups. Needless to say, their results influenced my research directions to certain extent.

2 Literature review. Synthesis of π–extended porphyrins *via* intramolecular oxidative coupling.

2.1 Introduction

Porphyrins and other porphyrinoids, by nature of their electronic and redox properties, are extremely versatile architectures that figure prominently in applications ranging from materials[14] to biomedicine.[15] The relationship between the structure of porphyrinoids and their spectroscopic and photophysical properties is a complex and deeply intriguing issue.[16] Among other changes, π-extension of a porphyrin chromophore usually leads to a certain bathochromic shift in its absorption (and hence emission) spectrum. The magnitude of this alteration depends more on the type of conjugation than on the actual number of double or triple bonds added. The subtle nature of this relationship can be exemplified by Osuka's extended porphyrin which, in spite of possessing an extra double bond, displays hipsochromic shift.[17] The vast diversity of π-extended porphyrinoids[18] attracts attention not only because of the theoretical issues involved, but also because of the opportunities to

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[14] J. H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow and K. S. Suslick, *In Porphyrin Handbook*, K. M. Kadish, K. M. Smith and R. Guilard, Eds., *Academic Press*, San Diego, CA, 2000, **Vol. 6**, p. 43.

[15] R. W. Boyle and D. Dolphin, *Photochem. Photobiol.*, 1996, **64**, 469.

[16] (a) H. L. Anderson, Chem. *Commun.*, 1999, **23**, 2323; (b) P. F. Schwab, M. D. Levin and J. Michl, *Chem. Rev.*, 1999, **99**, 1863; (c) N.G. Pschirer, C. Kohl, F. Nolde, J. Qu and K. Müllen, *Angew. Chem. Int. Ed.*, 2006, **45**, 1401.

[17] A. K. Sahoo, S. Mori, H. Shinokubo and A. Osuka, *Angew. Chem. Int. Ed.*, 2006, **45**, 7972.

[18] Recent examples: (a) M. Nath, M. Pink and J. M. Zaleski, *J. Am. Chem. Soc.*, 2005, **127**, 478; (b) J.-Ch. Chang, Ch.-J. Ma, G.H. Lee, S. M. Peng and Ch. Y. Yeh, *Dalton Trans.*, 2005, **34**, 1504; (c) N. Sprutta, M. Swiderska and L. Latos-Grażyński, *J. Am. Chem. Soc.*, 2005, **127**, 13108; (d) V. G. Anand, S. Saito, S. Shimizu and A. Osuka, *Angew. Chem. Int. Ed.*, 2005, **44**, 7244; (e) T. Khoury and M. J. Crossley, *Chem. Commun.*, 2007, **46**, 4851; (f) T. D. Lash, D. A. Colby, A. S. Idate and R. N. Davis, *J. Am. Chem. Soc.*, 2007, **129**, 13800; (g) L. J. Esdaile, P. Jensen, J. C. McMurtrie and D. P. Arnold, *Angew. Chem. Int. Ed.*, 2007, **46**, 2090; (h) R. W. Boyle and S. Fox, *Chem. Commun.*, 2004, **40**, 1322; (i) H. S. Gill, M. Harujanz, J. Santamaria, I. Finger and M. J. Scott, *Angew. Chem. Int. Ed.*, 2004, **43**, 485; (j) F. R. Fronczek, E. Hao and M. G. H. Vicente, *J. Org. Chem.*, 2006, **71**, 1233.

explore their optical linear and non-linear properties in technology and medicine.[19] π-Extended porphyrins are potential precursors for building electron- and energy-transfer devices, and many such molecules have been reported. Geometry, distance and relative orientation between each chromophore, the nature of the bridges between aromatic components and the extent of steric interactions are to be considered for the design and development of such functional porphyrin–based dyes. These materials display significant changes in their optical and electrochemical properties when compared with native porphyrins. The bridging groups enhance direct conjugation between essentially coplanar chromophores, resulting often in split Soret band and intensively red shifted Q bands. Over the last two decades considerable attention has been devoted to study of extensive delocalized π-conjugation of such porphyrins.

Conceptually, there are many ways to extend a porphyrin chromophore without changing the actual number of pyrrole units and methine bridges. Some of these ideas have been intensively explored over the last 30 years. The first possible approach to modifying the porphyrin chromophore involves placement of one or more fused aromatic rings at adjacent *β* positions of the tetrapyrrolic macrocycle. The simplest example of this idea is tetrabenzoporphyrin (**1**, Chart 1).[20] Each additional benzene unit included in the macrocycle causes a bathochromic shift of about 30 nm. Further extension of the conjugated aromatic unit has been synthetically realized by Ono and Lash (**2**, Chart 1).[21] Along these lines Vicente and coworkers had demonstrated highly ordered porphyrin pentamer.[22]

Another interesting example are Crossley's porphyrins,[23] which contain one or more pyrazine units (**3**, Chart 1).

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[19] H. A. Collins, M. Khurana, E. H. Moriyama, A. Mariampillai, E. Dahlstedt, M. Balaz, M. K. Kuimova, M. Drobizhev, V. X. D. Yang, D. Phillips, A. Rebane, B. C. Wilson and H. L. Anderson, *Nature Photonics*, 2008, **2**, 420.

[20] (a) O. S. Finikova, S. E. Aleshchenkov, R. P. Brin, A. V. Cheprakov, P. J. Carroll and S. A. Vinogradov, *J. Org. Chem.*, 2005, **6**, 4617. (b) R. B. M. Koehorst, J. F. Kleibeuker, T. J. Schaafsma, D. A. de Bie, B. Geurtsen, R. N. Henrie and H. C. van der Plas, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1005. (c) S. Ito, T. Murashima, H. Uno and N. Ono, *Chem. Commun.*, 1998, **34**, 1661.

[21] J. D. Spence and T. D. Lash, *J. Org. Chem*. 2000, **65,** 1530.

[22] M. G. H. Vicente, M. T. Cancilla, C. B. Lebrilla and K. M. Smith, *Chem. Commun*., 1998, **34**, 2355.

[23] M. J. Crossley, P. L. Burn, S. S. Chew, F. B. Cuttance and I. A. Newson, *J. Chem. Soc., Chem.*

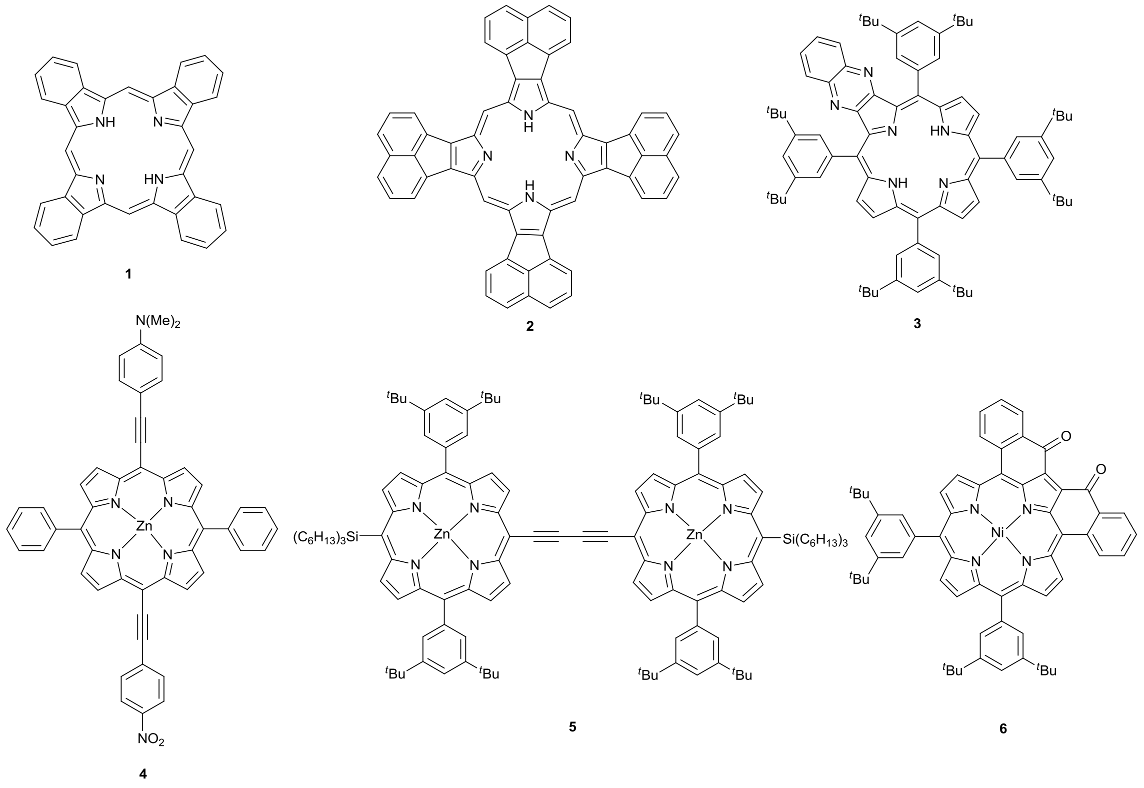

Chart 1

Porphyrins can also be extended by attaching other aromatic units *via* triple bonds,[24] and porphyrin dimers prepared for the first time by the Anderson group serve as capital examples of this approach (**4**, **5**, Chart 1).[25]

Callot and co-workers prepared a π-extended porphyrin chromophore containing a sequence of rings fused to one pyrrole (**6**, Chart 1).[26]

In addition to their varied coordination chemistry, topology, reversible electrochemistry and complex absorption of visible light, porphyrins also possess the property of being electron rich. This raises the obvious question about the possibility

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Commun., 1991, 1564.

[24] S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, 1996, **118**, 1497.

[25] P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams and H. L. Anderson, *Chem. Commun*., 1998, **34**, 909.

[26] S. Richeter, C. Jeandon, N. Kyritsakas, R. Ruppert and H. J. Callot, *J. Org. Chem.*, 2003, **68**, 9200.

of performing inter- and intramolecular oxidative aromatic coupling. In 1999,[27] 2000[28] and 2004,[29] three fundamental papers showed that it is possible to prepare porphyrins fused with other porphyrins or with aromatic hydrocarbons at both the *meso* and *β* positions. These discoveries opened new avenues which were quickly followed by other researchers. Over time, it was observed that the synthesis of π-extended porphyrins *via* intramolecular oxidative coupling usually requires activation of the aromatic subunits (for example by introducing alkoxy groups). Oxidative aromatic coupling has recently become a popular method for the π-extension of porphyrin chromophores because it results in the most significant redshift of absorption. It is well known that addition of many conjugated double bonds to a given aromatic system usually leads to a sharp decrease in solubility due to aggregation. Consequently, substantial bathochromic shift of absorption observed in *meso*- and *β*-fused porphyrins is advantageous for many applications which require compounds with reasonable solubility.

This *Literature review* offers a systematic presentation of current knowledge on π–extended porphyrins prepared *via* oxidative aromatic coupling. Special emphasis will be given to porphyrins fused at the *meso* and *β* positions with non-porphyrinoid units.

2.2 Porphyrins fused with porphyrins.

The first report describing diporphyrins comprised of two cores linked at the *meso* and *β* positions was published in 1999 by Sakata and co-workers.[15] These authors discovered that the nickel complex of *meso*-substituted A_2-porphyrin **7** reacted with $TeCl_4$ to give the corresponding *meso-β*, *meso-β* dimer **8** in 31% yield (Scheme 1). It was found that the lowest energy Q band is shifted to 743 nm. At the time of this first discovery, researchers noted that the bathochromic shift of **8** is considerably higher than that of the π-extended porphyrins reported by Therien,[12] Crossley[11] or Ono.[8c]

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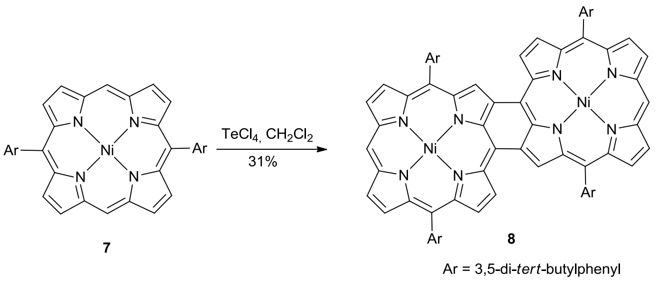
[27] K. Sugiura, T. Matsumoto, S. Ohkouchi, Y. Naitoh, T. Kawai, Y. Takai, K. Ushiroda and Y. Sakata, *Chem. Commun.*, 1999, **35**, 1957.

[28] A. Tsuda, H. Furuta and A.Osuka, *Angew. Chem. Int. Ed.*, 2000, **39**, 14.

[29] O. Yamane, K. Sugiura, H. Miyasaka, K. Nakamura, T. Fujimoto, T. Kaneda, Y. Sakata and M. Yamashita, *Chem. Lett.*, 2004, **33**, 40.

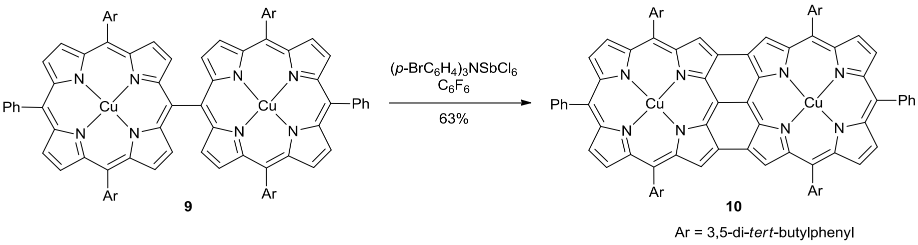


7 **8**

Scheme 1

The majority of the work in the field of porphyrin oxidative coupling has been done by Osuka and co-workers, with an emphasis on connecting porphyrin units *via* triple linkages.[30,31] In 2000, they noticed that transformation of the *meso-meso* singly linked diporphyrin copper complex **9** into *meso–meso, β–β, β–β* triply linked, fused diporphyrin **10**, can be achieved in 63% yield by using a strong oxidant, namely tris(4-bromophenyl)aminium hexachloroantimonate (Scheme 2).[16]

Interestingly, this different way of linking two porphyrin cores led to a different bathochromic shift compared to Sakata's dimer, **8**. Osuka and co-workers reported that diporphyrin **10** has the lowest energy band at 996 nm. They noticed extensive chlorination at the *β*-positions when the reaction was performed in $CHCl_3$. Both diporphyrins possess a planar geometry, leading to unprecedented delocalization of the π electrons.



9 **10**

Scheme 2

This report was quickly followed by the discovery that the combination of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) with scandium (III) triflate was a more

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[30] D. Kim and A. Osuka, *Acc. Chem. Res.,* 2004, **37**, 735.

[31] N. Ono, H. Yamada and T. Okujima, In *Handbook of Porphyrin Science*, K. M. Kadish, K. M. Smith and R. Guilard, Eds., *World Scientific*, Singapore, 2010, Vol. **2,** Chapter 7.

efficient oxidizing agent, which not only allowed the *meso-meso*, *β–β, β–β* dimer to be synthesized in 80% yield, but also enabled the use of zinc porphyrins as substrates in aromatic oxidative coupling reactions.[32] This finding culminated in the synthesis of porphyrin tape **11**, which is comprised of twelve porphyrin units and is 10 nm in length (Fig.1).[33] Further studies focused on zinc complexes since, in general, they exhibit longer excited state lifetimes. Altogether over 100 papers were published on this topic by Osuka's group.[34,35]

In addition to synthesis, the spectroscopic and photophysical properties for this family of complexes were studied in detail. It was found that elongation causes progressive red-shift reaching 2400 nm for 12-mer conjugated fused porphyrin array. These porphyrin tapes display very short S_1 excited state lifetimes but possess superb non-linear optical properties. The two-photon absorption cross-section of porphyrin tapes reaches 93600 GM (for 'tetraporphyrin tape').[36]

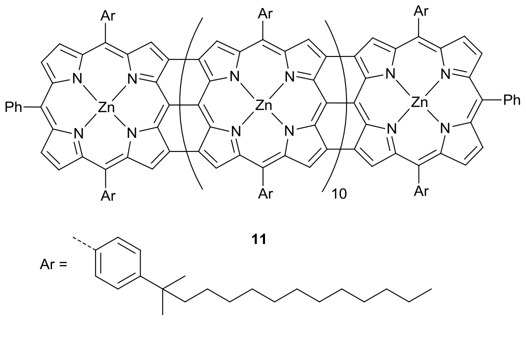

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Figure 1

Regioselectivity of the one-pot oxidative coupling was found to strongly depend on the metal present in the cavity.[37] Zinc complexes of A_2B-porphyrins subjected to DDQ/$Sc(OTf)_3$ gave exclusively *meso–meso, β–β, β–β* triply linked diporphyrins,

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[32] A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.

[33] A. Tsuda and A. Osuka, *Adv. Mat.*, 2002, **14**, 75.

[34] T. Tanaka, B. S. Lee, N. Aratani, M.-C. Yoon, D. Kim and A. Osuka, *Chem. Eur. J.*, 2011, **17**, 14400.

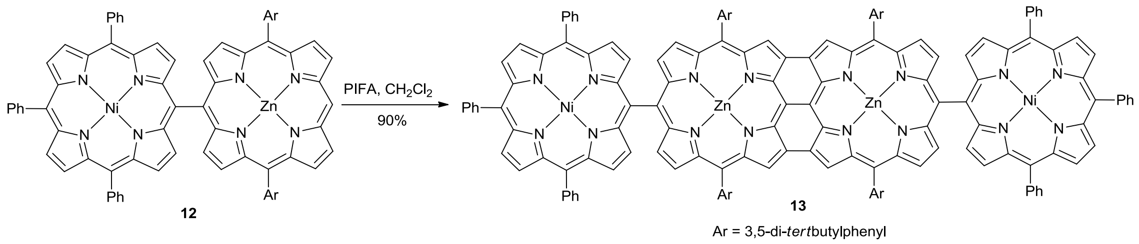
[35] T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Chem. Sci.*, 2011, **2**, 1414.

[36] T. K. Ahn, K. S. Kim, D. Y. Kim, S. B. Noh, N. Aratani, C. Ikeda, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2006, **128**, 1700.

[37] M. Kamo, A. Tsuda, Y. Nakamura, N. Aratani, K Furukawa, T. Kato and A.Osuka, *Org. Lett.*, 2003, **5**, 2079.

while analogous palladium porphyrins formed *meso-β, meso-β* dimers (analogous to compound **8** prepared by Sakata). Both dimer types were observed for nickel and copper porphyrins, albeit it different ratios.

Very recently,[38] it was found that by harnessing the different oxidation potentials of porphyrin complexes with different metals, one can selectively control the oxidative coupling process. Phenyliodine bis(trifluoroacetate) (PIFA), one of the most popular mediators in aromatic oxidative coupling,[39] can not only form *meso-meso* linked diporphyrins[40] but also triply *meso–meso, β–β, β–β* linked porphyrins, but only if zinc complexes are used as substrates (Scheme 4). The same reaction does not occur for nickel complexes (which typically have an oxidation potential that is 150 mV higher), which allows for regioselective control in the formation of larger arrays (**12** → **13**, Scheme 3).



Scheme 3

A variety of oxidants were found to be effective for aromatic oxidative coupling of smaller aromatic substrates.[41] Gust and co-workers found that *meso*-substituted A_3-porphyrins can be fused using certain copper salts.[42] Subjecting copper complex **14**

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[38] Q. Ouyang, Y.-Z. Zhu, C.-H. Zhang, K.-Q. Yan, Y.-Ch. Li and J.-Y. Zheng, *Org. Lett.*, 2009, **11**, 5266.

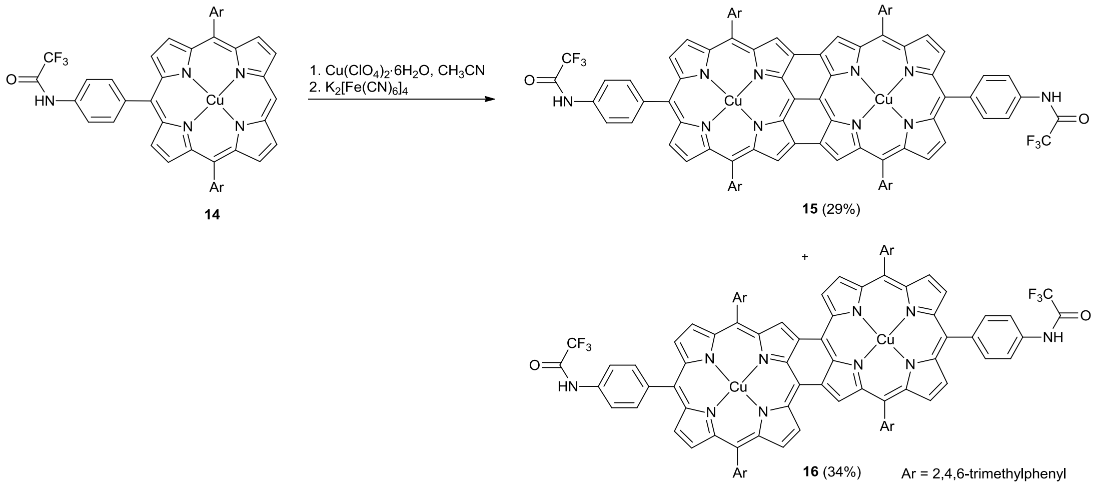
[39] (a) Y. Kita and H. Tohma, *Top. Curr. Chem.*, 2003, **224**, 209; (b) Y. Kita, T. Dohi and K. Morimoto, *J. Synth. Org. Chem.*, 2011, **69**, 47.

[40] L.-M. Jin, J.-J. Yin, L. Chen, C.-C. Guo and Q.-Y. Chen, *Synlett*, 2005, **19**, 2893.

[41] (a) W. I. Taylor and A. B. Battersby, *Oxidative coupling of phenols;* Arnold: London, 1967. (b) A. D. Whiting, *In Comprehensive organic synthesis*, B. M.Trost and I. Fleming, Eds., *Pergamon Exeter*, 1991, Vol**.** **3**, p. 659.

[42] B. J. Brennan, M. J. Kenney, P. A. Liddell, B. R. Cherry, J. Li, A. L. Moore, T. A. Moore and D. Gust, *Chem. Commun.*, 2011, **47**, 10034.

to $Cu(ClO_4)_2{\cdot}6H_2O$ gave a mixture of *meso–meso, β–β, β–β* diporphyrin **15** and *meso-β, meso-β* diporphyrin **16** in 29% and 34% yields respectively (Scheme 4). The absorption measurements for these compounds confirmed Osuka's report that triply linked porphyrins have considerably more shifted absorptions in the NIR region.



Scheme 4

2.3 Corrole dimers

In 2006 Osuka and co-workers reported the synthesis of the double linked corrole dimer **19**.[43] Palladium-catalyzed oxidative coupling of corrole **17** afforded 2,2'-linked corrole dimer **18**, which after oxidation and subsequent reduction gave doubly linked corrole dimer **19** (Scheme 5). Authors noticed that this compound exists in two forms: oxidized and reduced. The oxidized corrole dimer shows unusual biradical character. Independently, at the same time, Cavaleiro and co-workers obtained exactly the same final product by simple heating of tris-5,10,15-(pentafluorophenyl)corrole at 200 °C for six hours.[44]

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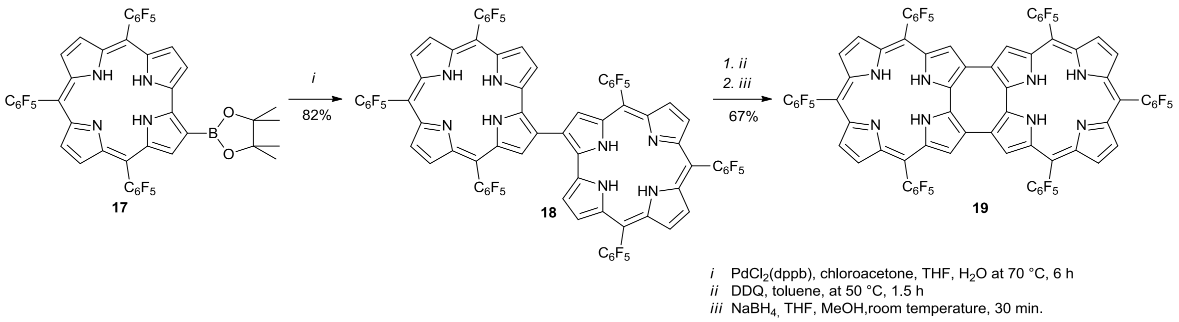
[43] S. Hiroto, K. Furukawa, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.***,** 2006, **128**, 12380

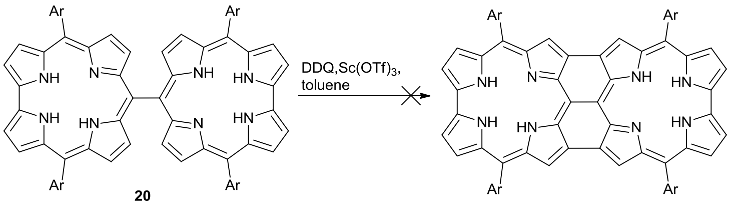
[44] J. F. B. Barata, A. M. G. Silva, M. G. P. M. S. Neves, A. C. Tome, A. M. S. Silva and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 2006, **47**, 8171.



i PdCl$_2$(dppb), chloroacetone, THF, H$_2$O at 70 °C, 6 h
ii DDQ, toluene, at 50 °C, 1.5 h
iii NaBH$_4$, THF, MeOH,room temperature, 30 min.

Scheme 5

An attempt to obtain *meso–meso, β–β, β–β* triply linked corrole was reported by Gryko and Koszarna.[45] *Meso–meso* corrole dimer **20** (prepared directly *via* condensation of 5-(2,6-dichlorophenyl)dipyrrane with formaldehyde, followed by oxidation with DDQ) was subjected to various oxidants; none of them, however, afforded the expected product (Scheme 6).



Ar = 2,6-dichlorophenyl

Scheme 6

2.4 Porphyrins fused with aromatic hydrocarbons containing two rings

The first example of a porphyrin fused with naphthalene was reported by Cammidge and co-workers in 2005.[46] They unexpectedly found that direct aromatic coupling occurs when zinc porphyrin **21** (which is substituted at the *meso* position by one naphthalene unit with a triflate group at position 8) is exposed to typical Suzuki reaction conditions in the presence of ferrocene bis(boronic)acid. Fused porphyrin

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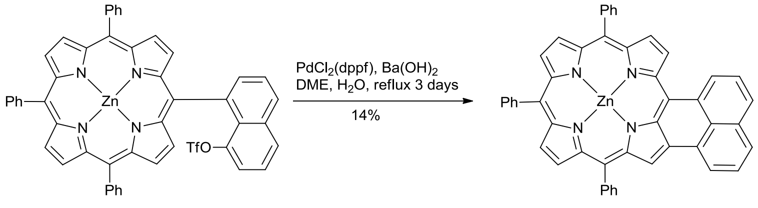
[45] B. Koszarna and D. T. Gryko, *Chem. Commun.*, 2007, **43**, 2994.
[46] D.L. Hughes, A.N. Cammidge and P.J. Scaife, *Org. Lett.*, 2005, **7**, 3413.

22, which lacks any substituents on the naphthalene moiety, was isolated in 14% yield (Scheme 7). This type of direct coupling reaction has recently become increasingly popular in heterocyclic chemistry.[47]



21 **22**

Scheme 7

Interestingly, using the same conditions but a different ratio of porphyrin **21** to ferrocene bis(boronic)acid the Suzuki reaction proceeded smoothly, yielding face-to-face ferrocenyl porphyrin. Product **22** possesses spectral changes that are comparable to related fused porphyrin systems.[48]

The broadening of the absorption spectrum and increased intensity of the Q bands for these porphyrins were caused not only by extension of the porphyrin chromophore, but also by a reduction in the HOMO-LUMO gap, which is a clear consequence of decreased symmetry. This observation inspired Imahori to further investigate the possibility of obtaining naphthalene-fused porphyrin derivatives *via* oxidative ring closure reactions.[49] In 2007, Imahori and co-workers noticed that Ni-porphyrin bearing an ester-containing naphthalene unit at the *meso*-position undergoes oxidative aromatic coupling in the presence of $FeCl_3$ to give fused-porphyrin **24** in 16% yield (Scheme 8).

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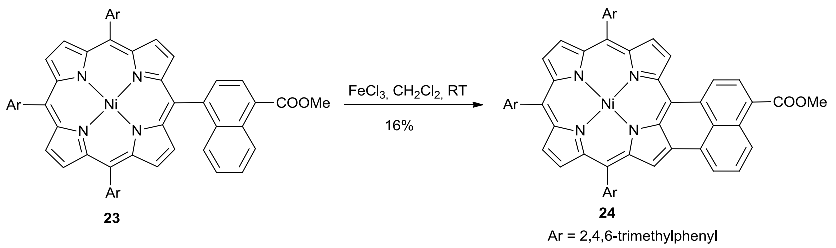
[47] D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174.
[48] M. Nath, J. C. Huffman and J. M. Zaleski, *J. Am. Chem. Soc.*, 2003, **125**, 11484.
[49] S. Eu, S. Hayashi, M. Tanaka, Y. Matano, T. Umeyama and H. Imahori, *Chem. Commun.*, 2007, **20**, 2069.



Scheme 8

The fact that this oxidation proceeds is rather surprising given that this particular naphthalene unit is not electron-rich. Apparently, the reaction begins with formation of a radical cation on the porphyrin complex which is sufficiently electrophilic to attack the naphthalene unit.

Spectroscopic measurements showed that the integrated value of the molar absorptivity at the Q band region (530–750 nm) of fused porphyrin **24** is two times larger than for its non-fused analog, even though the molar absorptivity at the Soret band is significantly lower. As for applications of these molecules, the power conversion efficiency of fused porphyrin-sensitized TiO_2 cells is improved by 50% compared to the non-fused porphyrin reference cell.

This illustrates that extension of a porphyrin π-system (with concomitant loss of symmetry) could be a useful tactic for collecting solar light in the visible region.

An entirely new approach towards the synthesis of *meso-β* fused porphyrins was published recently by Thompson and co-workers.[50] These authors focused on fusion of porphyrins with unsubstituted (hence non-activated) aromatic hydrocarbons. Zn-5,15-Bis(naphthalen-1-yl)porphyrin **25** was prepared *via* Suzuki coupling (as a mixture of atropoisomers) and subjected to very high temperatures (500-530 °C) under vacuum. A mixture of *meso-β*-linked regioisomers **26** and **27** were collectively obtained in 7% yield (Scheme 9).

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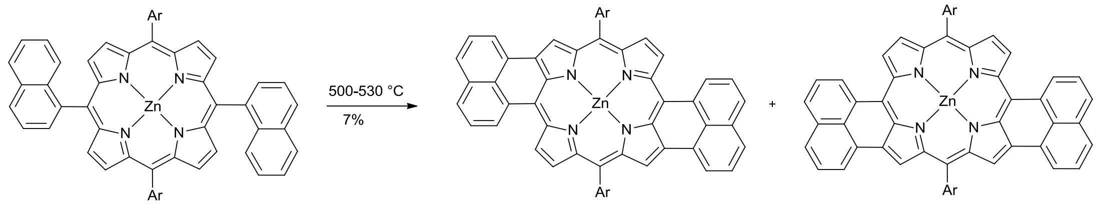
[50] V. V. Diev, C. W. Schlenker, K. Hanson, Q. Zhong, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *J. Org. Chem.*, 2012, **77**, 143.



25 **26** **27**

Ar = 3,5-di-*tert*-butylphenyl

Scheme 9

Thermal activation of C-H bonds in aromatic systems for direct C-C bond formation is known to proceed under flash vacuum pyrolysis conditions,[51] but it has not been used before in the context of porphyrins. Under these conditions formation of an additional bond between the porphyrin skeleton and the *meso*-substituted aromatic unit did not require addition of an oxidizing agent.

Although low-yielding, this procedure allows for the synthesis of porphyrins etended with other aromatic systems without additional substituents, which can be crucial in the interpretation of optical data for such compounds. This interesting concept was further expanded to include also other well-known homoaromatic systems.

Replacing naphthalene with its non-alternating hydrocarbon isomer, azulene, opens new possibilities in oxidative aromatic coupling of porphyrins. The different electronic character of both rings (five-membered ring is electron-rich while seven-membered ring is electron-poor) allows to predict that suitably substituted azulene derivatives will undergo intramolecular oxidative aromatic coupling without the presence of additional electron-donating substituents. Osuka and co-workers inserted a formyl group on the seven-membered ring to allow the oxidative aromatic coupling to occur at the five-membered ring.[52] Aldehyde **28** is rather complex and is prepared *via* a multistep synthesis. Condensation with other aromatic aldehydes affords porphyrins **29-31**. Compounds **32-34** were obtained in yields ranging from 60 to 84% using very mild conditions ($FeCl_3$, 5 min, RT). Interestingly, DDQ/$Sc(OTf)_3$ was not effective in this case. These results illustrate that porphyrins possessing varying

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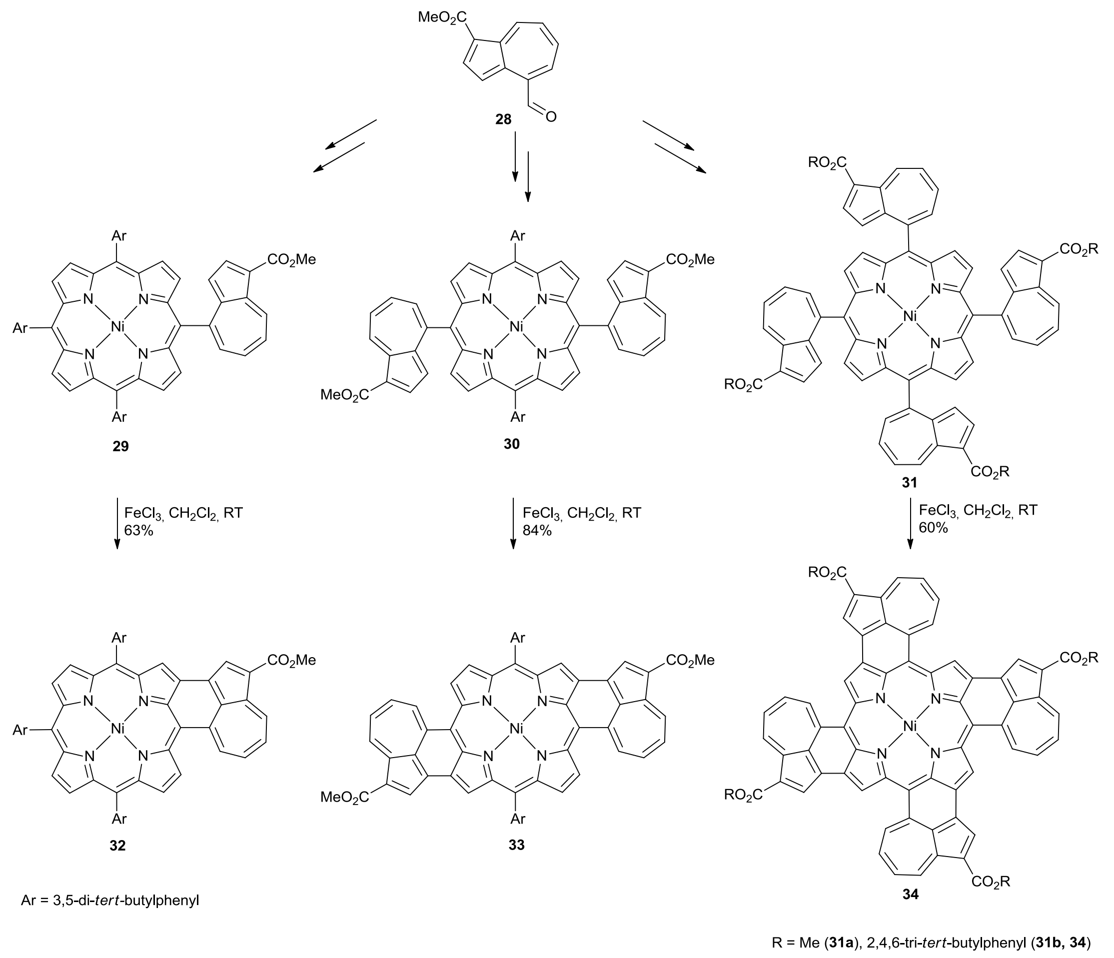
[51] V. M. Tserikas and L. T. Scott, *Chem. Rev.*, 2006, **106**, 4868.

[52] K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem.*, 2006, **118**, 4048; *Angew. Chem. Int. Ed.*, 2006, **45**, 3944.

numbers of azulenyl units can undergo one-, two-, or four-fold ring closure when exposed to certain oxidizing conditions. Curiously, the *syn*-isomer of porphyrin **33** is not detected, which may suggest that the regiochemistry of the second aromatic oxidative coupling is strongly influenced by the first.

The crystallographic data of the fused porphyrins **32, 33** and **34** confirm their planarity.[37] Needless to say, this has a strong influence on their physicochemical properties because it greatly lowers their solubility due to increased aggregation. The absorption spectrum of **32** features unprecedented bathochromic shifts: a broad Soret band at 467 nm and a fairly broad band near 1000 nm. Absorption spectra of porphyrins **33**-**34** exhibit a red-shift in Soret and Q bands that progresses with increasing number of azulenyl groups, covering the IR region up to 1200 nm in the case of quadruply fused **34**. Porphyrins **32**-**34** also possess a very high two-photon absorption cross section.

A mostly insoluble reaction mixture was obtained while treating **31a** with $FeCl_3$. Thus, changing the character of substrates was required. The porphyrin **31b** bearing 2,4,6-tri-*tert*-butylphenyl substituents was easily transformed into quadruply fused azulene porphyrin **34** in 60% yield.



Ar = 3,5-di-*tert*-butylphenyl

R = Me (**31a**), 2,4,6-tri-*tert*-butylphenyl (**31b, 34**)

Scheme 10

2.5 Porphyrins fused with aromatic hydrocarbon containing three rings - anthracene

The idea of synthesizing anthracene-fused porphyrin was suggested for the first time by Yen in 1975.[53] It was believed that fusion to an anthracene unit would strongly perturb the electronic structure of the porphyrin and was expected to shift absorption into the NIR region as well as reduce the HOMO-LUMO gap by making the macrocycles easier to oxidize.

It was not until 2008 when the first example of such a porphyrin was actually prepared by Anderson and co-workers.[54] The oxidative fusion of *meso*-(9-anthryl)porphyrin **35** was attempted using DDQ/Sc(OTf)$_3$, but no ring-fused products were detected. A possible explanation is that there is not enough electron density on the 9-anthryl unit (which does not contain any electron donating groups). Indeed, electron-rich alkoxyanthracenes gave more amenable results. Addition of two methoxy groups to the anthracene unit (**35**) followed by treatment with DDQ/Sc(OTf)$_3$ afforded the triply fused anthracene-porphyrin **37** (Scheme 11). Its purification, however, was difficult to perform since porphyrin **37** proved to be insoluble and was lost during chromatography. In order to increase the solubility of the final fused porphyrin, octyloxy- chains were introduced to the anthryl unit.

Intramolecular oxidative coupling of **36** gave triply linked porprhyrin **38**, which was isolated in 82% yield (Scheme 11). It is worth mentioning that anthryl-porphyrin **36** was prepared *via* Suzuki coupling from *meso*-bromoporphyrin and the corresponding anthracene-derived boronic acid.

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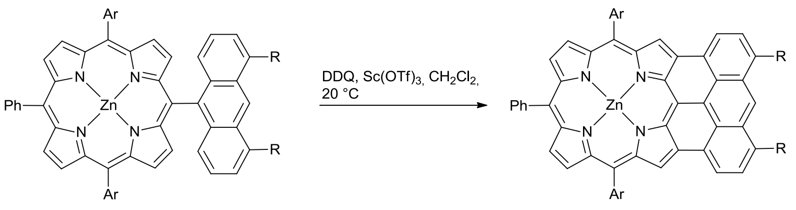
[53] T. F. Yen in *The Role of Trace Metals in Petroleum*; T. F. Yen, Ed., *Ann. Arbor Scientific*: Ann Arbor, 1975; p. 1.

[54] H. L. Anderson, N. L. S. Davis and M. Pawlicki, *Org. Lett.*, 2008, **10**, 3945.



35 R = OMe
36 R = OC_8H_{17}

37 R = OMe (not isolated)
38 R = OC_8H_{17}, 82%

Ar = 3,5-di-*tert*- butylphenyl

Scheme 11

In 2010, Anderson's group extended this study and reported the synthesis of a fused bis-anthracene-porphyrin monomer and dimer.[55] Interestingly, treatment of the zinc complex of *trans*-A_2B_2-porphyrin bearing *n*-octyl ether substituents on the anthryl units with DDQ/$Sc(OTf)_3$ resulted in only partial fusion. One would expect that the additional π-electrons from one dialkoxyanthryl unit should rather facilitate a second oxidative coupling by lowering the first oxidation potential of porphyrin.

In order to force the formation of fully fused bis-anthracene porphyrin, iron (III) chloride was used. Treatment of an analogous nickel porphyrin with an excess of $FeCl_3$ again resulted in only partially fused porphyrin. Subjection of this compound to a further equivalents of $FeCl_3$ at higher temperature led to the formation of fully fused bis-anthracene porphyrin.

Due to problems with purification (the product displays a strong tendency to aggregate), the octyloxy substituents located at positions 1 and 8 of the anthracene moiety were replaced with bulky 2,4,6–trimethyphenyl substituents. This methodology was earlier successfully employed in phthalocyanines[56] in order to limit their aggregation.

Oxidation of porphyrin **39** with $FeCl_3$ led again to a partially fused porphyrin product, which upon addition of further equivalent of $FeCl_3$, cleanly formed the non-aggregating fully fused porphyrin **40** (Scheme 12). Yet another problem was again observed, namely chlorination of the formed macrocycles.[40]

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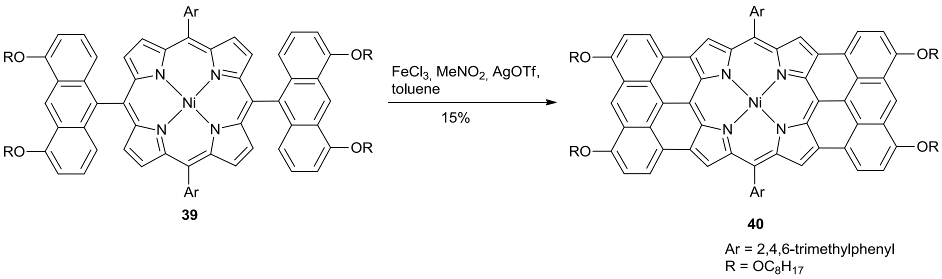
[55] H. L. Anderson, N. L. S. Davis and A. L. Thompson, *Org. Lett.*, 2010, **12**, 2124.

[56] N. B. McKeown, S. Makhseed, K. J. Msayib, L. L. Ooi, M. Helliwell and J. E. Warren, *Angew. Chem. Int. Ed.*, 2005, **44**, 7546.

Davis *et al*. attempted to suppress chlorination using Osuka's method (i.e. with the addition of AgOTf, which scavenges chlorine ions).[57] This strategy greatly reduced the degree of chlorination. Pure nickel porphyrin **40** was obtained in 15% yield. Fusion of two anthracene units to the ring of the porphyrin occurred without loss of planarity, which allows for generation of a highly delocalized π-system with a strong absorbtion in the NIR region. Indeed, the fused dimer displays extensive absorption in the NIR region, shifted up to 1000 nm compared to the substrate.



Scheme 12

In 2011, learning from their experience with aromatic oxidative coupling of one and two anthracene moieties, Anderson's group attempted to prepare porphyrins with four such units.[58]

Treatment of the *meso*-anthracenyl nickel(II) porphyrin **41** with $FeCl_3$ in CH_2Cl_2 gave the fully fused tetraanthracenyl porphyrin **42** in 49% yield (Scheme 13). Eightfold ring closure resulted in dramatic changes in the UV-vis spectrum. The Q band was observed at 1417 nm and it is extremely sharp due to the high symmetry of the chromophore. Also the Soret band is exceptional because it is located at 850 nm, which is the longest detected wavelength for Soret-bands of porphyrin monomers.

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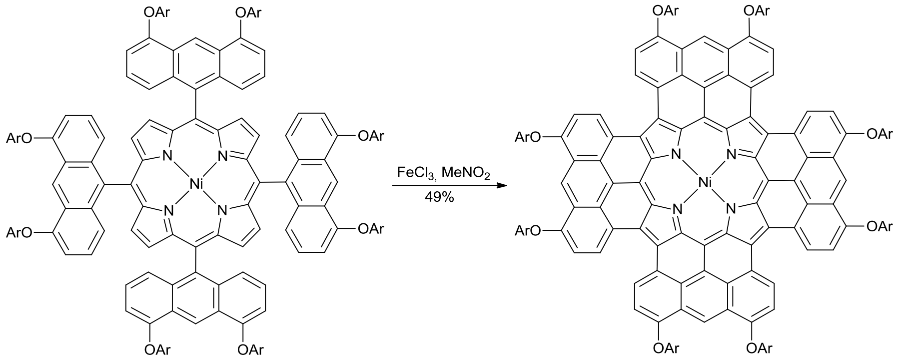
[57] K. Sahoo, Y Nakamura, N. Aratani, K. S. Kim, S. B. Noh, H. Shinokubo, D. Kim and A. Osuka, *Org. Lett.*, 2006, **8**, 4144.

[58] N. L. S. Davis, A. L. Thompson and H. L. Anderson, J. *Am. Chem. Soc.*, 2011, **133**, 30.

Porphyrins fused with anthracene units fascinate not only experimentalists but also theoretical chemists. Qi and Jiang performed advanced molecular calculations on a series of non-existing free-base porphyrins fused with four anthracene units (H_2(TAnP)).[59] By varying the electronic character of the substituents along the periphery of the H_2(TAnP) macrocycle, they observe that it is possible to design novel NIR dyes with regulated UV–vis–NIR absorption bands covering the full solar spectrum in the range of 300–2400 nm. These calculations made it possible to explain the nature of the broad and intense electronic absorptions of H_2(TAnP) in the range of 500–1700 nm is clearly revealed. Different types of $\pi \rightarrow \pi^*$ electronic transitions associated with various absorption bands seem to correspond to different electron density moving direction between peripherally fused 14-electron-π-conjugated anthracene units and the central 18-electron-π-conjugated porphyrin core. In a different study using advanced molecular calculations, Kowalski and co-workers demonstrated that fusion with anthracene or coronene significantly alters the electronic structure of the low-lying excited states of these π-extended dyes.[60] Instead of the multiconfigurational character of the lowest excited states of the *meso*-substitiuted porphyrins, it was shown that the lowest states of the variously fused anthracene-porphyrins are dominated by the HOMO–LUMO excitations.



41

42

Ar = 2,4,6-trimethylphenyl

Scheme 13

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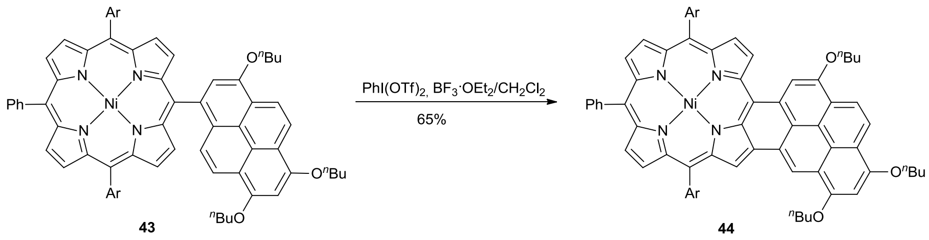
[59] D. Qi and J. Jiang, *J. Phys. Chem. A*, 2011, **115**, 13811.

[60] K. Kowalski, R. M. Olson, S. Krsihamoorthy, V. Tipparaju and E. Aprá, *J. Chem. Theory Comput.*, 2011, **7**, 2200.

2.6 Porphyrins fused with aromatic hydrocarbons comprising of >3 rings

2.6.1 Pyrene

Yamashita and co-workers were the first to present *meso-β* fusion of porphyrins with non-porphyrinoid chromophores. They chose pyrenyl-porphyrin as the molecule of study.[29] They carried out intramolecular oxidative coupling on a *meso*-pyrenyl-porphyrin bearing three alkoxy groups using PhI(OTf)$_2$ and BF$_3$·OEt$_2$[46] (Scheme 14). It was demonstrated that mono- and bis-alkoxy derivatives also afforded pyrene-fused porphyrin in acceptable yields. On the other hand, the precursor with no alkoxy groups did not undergo ring closure.



Ar = 3,5-di-*tert*-butylphenyl

Scheme 14

Fused product **44** was obtained in 65% yield and displays a bathochromically shifted UV-vis spectrum (compared to its precursor) with the lowest energy band located at 724 nm.

Synthetic difficulties and moderate yields of previously reported fused porphyrins led Thompson and co-workers to the conclusion, that one should start from the *meso–meso, β–β, β–β diporphyrin*, bearing pyrene moieties, as the appropriate substrate for intramolecular oxidation reactions.[61]

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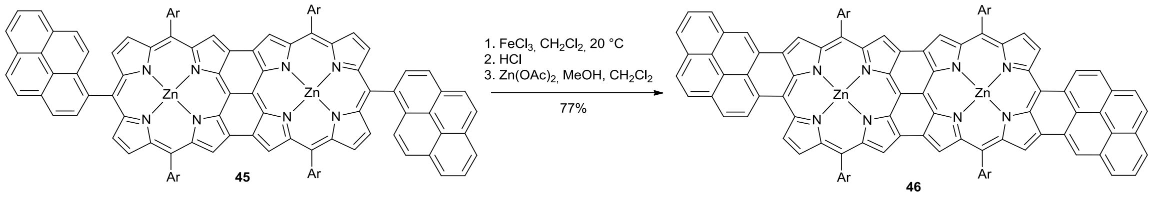
[61] V. V. Diev, K. Hanson, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *Angew. Chem. Int. Ed.*, 2010, **49**, 5523.

The crucial point in this approach is Suzuki coupling of *meso* free porphyrin with borolane pyrenyl derivative and subsequent oxidative fusion of two porphyrin rings gave the starting material for the aromatic oxidative coupling (**45**, Scheme 15). Previous attempts to perform an analogous oxidative coupling starting from monoporphyrins bearing unsubstituted pyrene rings were unsuccessful.[38] The difference in oxidation potential of porphyrin and *meso–meso, β–β, β–β* diporphyrin (~0.5V) is responsible for these strikingly different results.

Demetalation of the zinc complex occurs *in situ* but does not disturb the oxidation process, allowing one to first obtain the free base fused diporphyrin and subsequently metalate it to give the fully fused porphyrin **46** in 77% yield.

According to the authors, the lack of alkoxy substituents as well as the potential distortion of the final molecule **46** prevented undesirable aggregation *via* π-stacking and resulted in a comparatively more soluble product. The DFT calculations suggest that pyrene-(*meso-β*)–fused diporphyrin **46** displays out-of-plane distortion, that is known to improve solubility of conjugated aromatics.[62]

This reaction is the first example of an oxidative coupling of unsubstituted aromatic rings to a porphyrin without the need for activation of the aromatic rings with electron-donating groups. Not obviously, only one, '*anti*' isomer of doubly fused porphyrin was formed, according to authors.



Ar = 3,5-di-*tert*- butylphenyl

Scheme 15

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[62] (a) M. O. Senge, *Chem. Commun.*, 2006, **42**, 243; (b) A. Y. Lebedev, M. A. Filatov, A. V. Cheprakov and S. A. Vinogradov, *J. Phys. Chem. A*, 2008, **112**, 7723.

The fusion causes a strong shift of the UV-vis absorption spectrum into the NIR region. The Q band of **46** appears at 1323 nm. Remetalation of the fused free base with lead cation (derivatives of which, among the metalloporphyrins,[63] exhibit strong NIR shifts) resulted in an additional bathochromic shift of the Q band up to 1460 nm.

2.6.2 Perylene and larger hydrocarbons

The same authors attempted intramolecular oxidative coupling of *trans*-A_2B_2-porphyrins possessing pyrene or larger aromatic hydrocarbons (perylene or coronene) located at *meso*-positions. Among the porphyrins mentioned above, only the one possessing two perylene units could undergo oxidative coupling mediated by $FeCl_3$ (**47** → **48** + **49**, Scheme 16).[36]

This reaction was possible because perylene has the lowest oxidation potential among studied extended aromatic systems (+0.61 V vs. SCE). *Trans*-A_2B_2-porphyrin with pyrene units (having the next lowest oxidation potential of 0.89V vs. SCE), failed to undergo coupling under these conditions. Thus, the authors estimate that for this particular porphyrin core the upper limit oxidation potential lies somewhere between that of perylene and pyrene. Unfortunately, in analogy to naphthylporphyrin **25** the reaction is not regioselective; among the products we can observe both *anti* and *syn* isomers.

Since only the perylene-substituted porphyrin proved amenable to standard oxidative aromatic coupling conditions, a great effort was directed to fusion of other aromatic systems using thermal activation.[64] This approach is viable due to the relative stability of porphyrins at high temperatures. Experiments have shown that every *trans*-A_2B_2-porphyrin bearing two of the aforementioned substituents undergoes a thermal fusion reaction, resulting in a fused porphyrin displaying bathochromically shifted absorption spectra.[36] There is no way to enforce regioselectivity for these reactions, so in every case a mixture of both possible regioisomers was obtained. For

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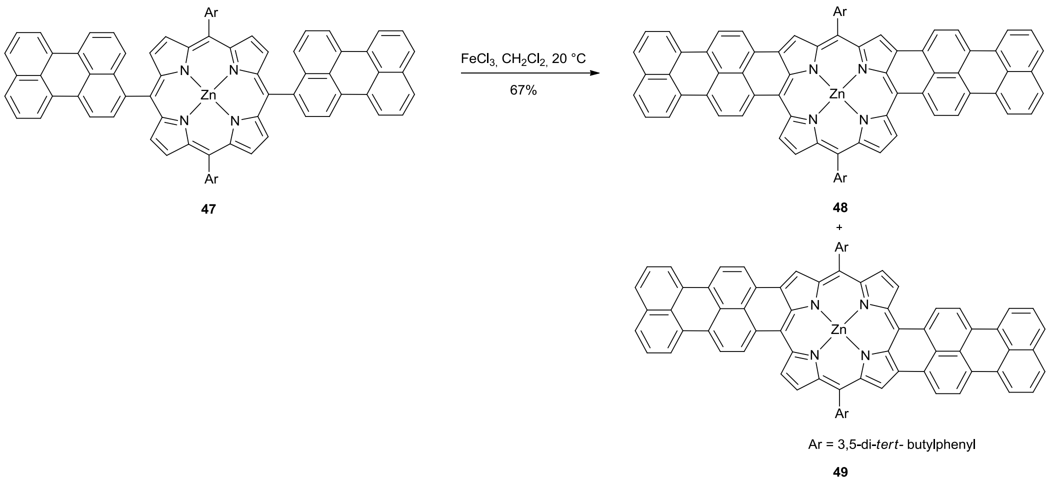
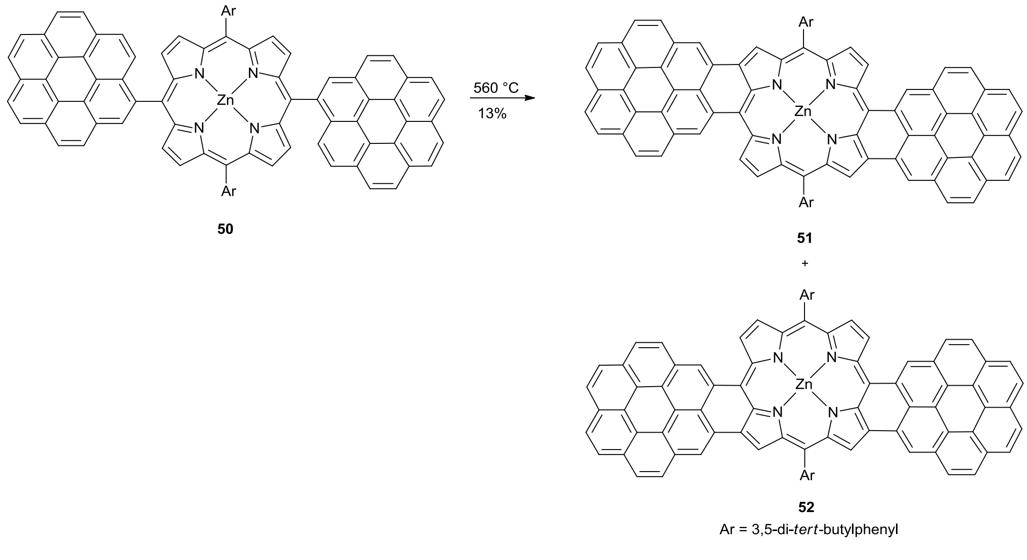
[63] *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith and R. Guilard, Eds. *Academic Press: San Diego*, CA, 2000, Vols. **1-10**.

[64] R. F. C. Brown, *Eur. J. Org. Chem.*, 1999, **64**, 3211.

example, in the case of the coronenyl-containing *trans*-A_2B_2-porphyrin **50**, thermal coupling gave an inseparable mixture of isomers **51** and **52** (Scheme 17).



Scheme 16



Scheme 17

Among all the doubly linked *meso-β* porphyrins obtained by the Thompson group, only regioisomers of doubly fused pyrenylporphyrins can be separated using column chromatography. The difference in the polarity between the two species can be explained by their different shapes, which is clearly visible in their calculated structures (Fig. 2).

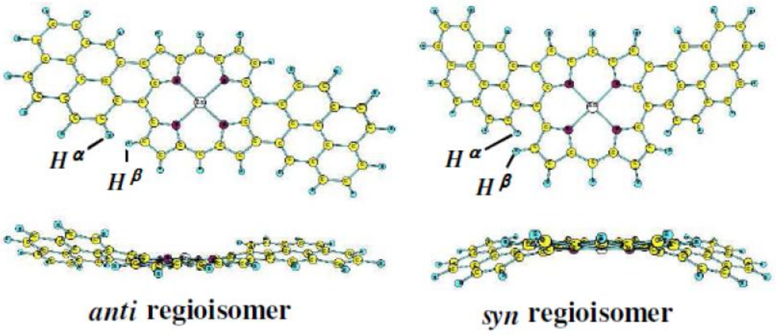


Figure 2. Calculated structures of doubly fused pyrenyl porphyrins.[50]

Intriguingly, among the expanded porphyrins synthesized by Thompson and co-workers, only bis-coronenyl fused porphyrins tend to aggregate in solution (similarly to non-distorted porphyrin tapes) and the solubility was improved comparing to the starting *trans*-A_2B_2-porphyrin. As for the rest, even the quadruply fused porphyrin is soluble, which is non-typical for such an extensively fused aromatic compound, even when decorated with multiple solubilizing groups.

At this time it is worth mentioning two publications which describe the synthesis of π-expanded porphyrins *via* intramolecular oxidative coupling, although products are not linked at *meso*-β positions. Wang and co-workers revealed an interesting example of oxidative coupling mediated by $FeCl_3$ (Scheme 18).[65]

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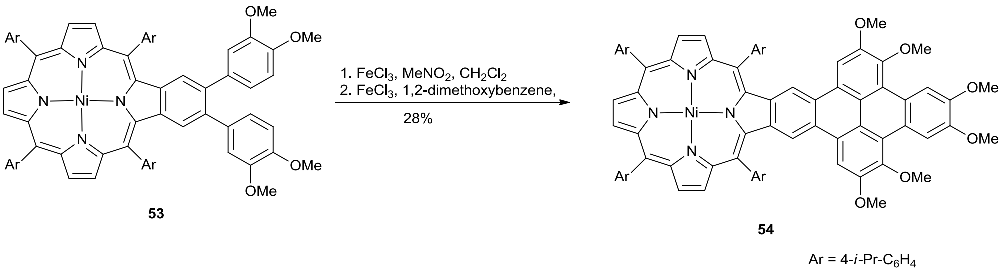
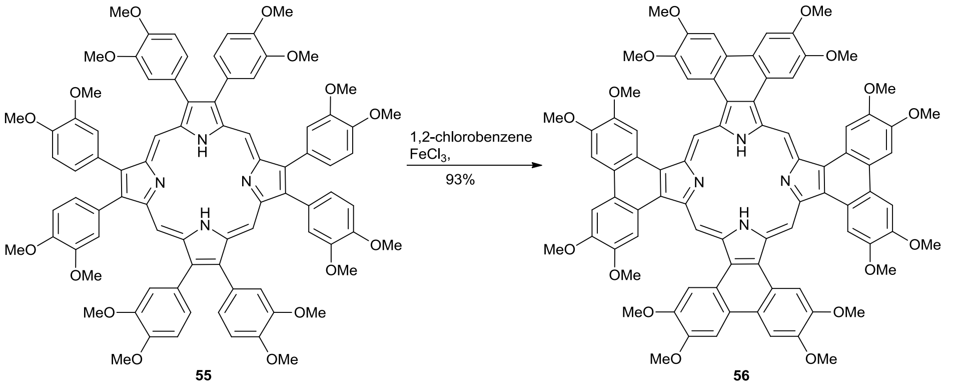
[65] L. Jiang, J. T. Eagle, L. Sirk, C. S. Hartley, C. J. Ziegler and H. Wang, *Org. Lett.*, 2011, **13**, 3020.



Scheme 18



Scheme 19

Suitably substituted mono-benzoporphyrin **53** bearing two electron-rich substituents at its periphery undergoes oxidative coupling under typical conditions ($FeCl_3/CH_2Cl_2/MeNO_2$) to give the corresponding phenanthro-porphyrin.

The authors report that this compound still possesses two electron-rich positions, and they attempted a second oxidation with excess of veratrole. This second oxidative coupling occured easily in 28% overall yield to give large porphyrin **54**.

A related yet different idea was presented very recently by Stępień and co-workers. Porphyrin **55**, substituted at all eight *β* positions with electron-rich 3,4-dimethoxyphenyl groups, was subjected to $FeCl_3$ in 1,2-dichlorobenzene to cleanly afford the π-expanded porphyrin **56** in 93% yield (Scheme 19).[66] To our knowledge, this is the first example of an oxidative aromatic coupling performed using free base

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[66] D. Myśliwiec, B. Donnio, P. J. Chmielewski, B. Heinrich and M. Stepień, *J. Am. Chem. Soc.*, 2012, **134**, 4822.

porphyrin. The authors extended this study to include benzo[*g*]chrysene units, which exhibit monoclinic 3D phases.

2.7 Porphyrins fused with aromatic heterocycles

It is rather obvious that aromatic hydrocarbons can be replaced with electron-rich heterocycles in a general scheme leading to *meso-β* linked π-extended porphyrins.

Perylene and its imides,[67] key chromophores in dye chemistry, have been intensively studied not only owing to their remarkable physical properties (large extinction coefficients and high fluorescence quantum yields), but also to the availability of their active sites, which allow for further chemical modifications. Although there are a few reported examples of porphyrins bearing the perylene moiety at the *meso* position,[68] there are still problems with fusion of this hydrocarbon system to the porphyrin core. A recent study by Thompson and co-workers showed that perylene can be oxidatively coupled with porphyrins both with $FeCl_3$ and under thermal conditions.

Still, one can envision that (in analogy to some previously described cases) some modification of the substituent could facilitate this reaction. In 2010, Wu and co-workers attached *N*-annulated perylene (phenanthro[1,10,9,8-*cdefg*]carbazole) to the porphyrin core.[69] An increase in the electron density of both components was required for efficient oxidative aromatic coupling (i.e. the use of a zinc porphyrin complex with a relatively low oxidation potential and a heterocyclic analogue of perylene). The latter is known for its capability to undergo self-fusion reactions that

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[67] A. Hermann and K. Müllen, *Chem. Lett.*, 2006, **35**, 978.

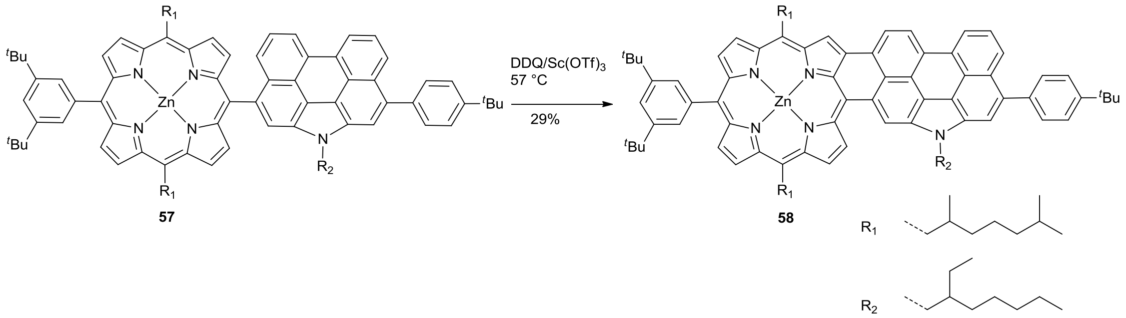
[68] (a) M. A. Miller, R. K. Lammi, P. Sreedharan, D. Holten and J. S. Lindsey, *J. Org. Chem.*, 2000, **65**, 6634; (b) C.-C. You and F. Würthner, *Org. Lett.*, 2004, **6**, 2401; (c) S. Xiao, M. E. El-Khouly, Y. Li, Z. Gan, H. Liu, L. Jiang, Y. Araki, O. Ito and D. Zhu, *J. Phys. Chem. B*, 2005, **109**, 3658; (d) A. Prodi, C. Chiorboli, F. Scandola, E. Iengo, E. Alessio, R. Dobrawa and F. Würthner, *J. Am. Chem. Soc.*, 2005, **127**, 1454; (e) R. F. Kelley, W. S. Shin, B. Rybtchinski, L. E. Sinks and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2007, **129**, 3173.

[69] C. Jiao, K. W. Huang, Z. Guan, Q.-H. Xu and J. Wu, *Org. Lett.*, 2010, **12**, 4046.

yield highly ordered quaterrylene and hexarylene derivatives upon treatment with $Sc(OTf)_3$/DDQ.[70]

The same technique has been applied to promote the intramolecular oxidative coupling reaction of porphyrin **57** possessing an *N*-annulated perylene at the *meso* position (Scheme 20). The stable π-extended product, **58**, was isolated in 29% yield, and featured intense absorption in NIR. These desirable properties inspired investigation of the perylene moiety as a linking fragment between two porphyrin cores. With this goal in mind, Suzuki coupling between two boronic ester porphyrin molecules and dibrominated *N*-annulated perylene gave the key intermediate **59** (Scheme 21). Subjection of this compound to the previously described oxidizing conditions gave, however, an inseparable mixture. This complication was attributed to the strong aggregation tendency of the prepared perylene-fused porphyrin. The problem was remedied by replacing branched alkyl chains with bulky 3,5-di-*tert*-butylphenyl groups, which facilitated the purification of the hybrid molecule **60**, allowing it to be isolated in 74% yield.

The color of compounds **58** and **60** is carmine and brown, respectively, which is the direct result of shifting absorption spectra into the NIR and simultaneously enhancing the Q band absorptivity.



Scheme 20

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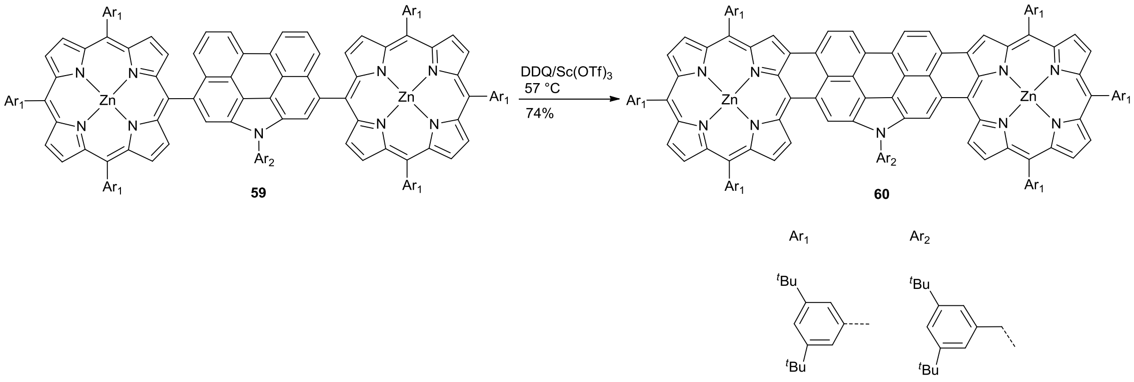
[70] (a) J. J. Hooker, *J. Org. Chem.*, 1972, **37**, 3379; (b) Y. Li and Z. Wang, *Org. Lett.*, 2009, **11**, 1385; (c) C. Jiao, K.-W. Huang, J. Luo, K. Zhang, C. Chi and J. Wu, *Org. Lett.*, 2009, **11**, 4508; (d) Y. Li, J. Gao, S. D. Motta, F. Negri and Z. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 4208.

The unusual photostability of the final compounds **58** and **60** must be highlighted. Even after exposing their solutions to visible light no decomposition is observed, despite the rather high electron density.



Scheme 21

However, solutions of **58** and **60** are not stable upon exposure to UV radiation. This is probably due to the high electron density in this conjugated systems. Subsequent efforts were directed towards enhancing the stability of these products by withdrawing electron density from the perylene skeleton. The final molecule should, however, still be sufficiently prone to oxidative aromatic coupling. An appropriate group which fulfills both these criteria is the imide group.[71]

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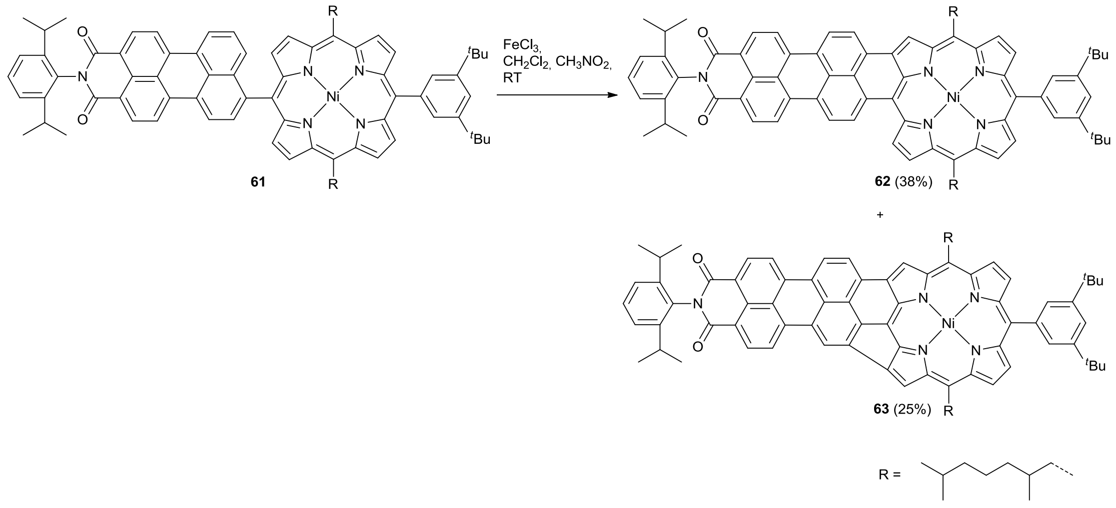
[71] Ch. Jiao, K.-W. Huang, Ch. Chunyan and J. Wu, *J. Org. Chem.*, 2011, **76**, 661.



Scheme 22

When the electron-rich *N*-annulated perylene was replaced with electron-withdrawing perylene-3,4-dicarboxylic acid imide at one of the *meso*-positions of the porphyrin and subjected to a ten-fold excess of $FeCl_3$, doubly fused product **62** was obtained in 38% yield (Scheme 22). Fused porphyrin **62** displayed significantly increased stability to UV light compared to products **58** and **60**. $FeCl_3$ was used because $Sc(OTf)_3$/DDQ was not effective for cyclization of such an electron-deficient porphyrin. The choice of oxidant was determined by the metal in the porphyrin cavity (the presence of Zn in the cavity precludes use of strong Lewis acids).

Enhanced reactivity of the nickel porphyrin is one possible explanation for the unexpected formation of triply fused porphyrin **63**, which was isolated in 25% yield. The third linkage, after the two in *peri-meso, peri-β,* was formed in the *meta-β* position.

The reaction required relatively harsh conditions (refluxing overnight), which were feasible due to the good stability of the starting material. It is noteworthy that although compounds **62** and **63** both have NIR shifted absorption spectra, this one-bond difference is enough for them to have completely different colors – purple and green, respectively.

Compound **62** displays the strongest Q band among aromatic ring fused monoporphyrins, with a molar extinction coefficient of ε = 91 000.

The derivatives of boron dipyrrin, known also as BODIPY or 'porphyrin's little sister', are extensively used as fluorescent probes.[72] Its remarkable properties, such as large molar extinction coefficients and high fluorescence quantum yield make it attractive for a variety of applications. The BODIPY family was first developed for applications in luminescent devices[73] and laser dyes.[74]

BODIPY chromophores generally possess visible absorption and fluorescence emission between 470 and 550 nm, and significant effort has been directed to both of them into 600-700 nm, or even NIR region. Various methods to access NIR BODIPY dyes have been developed, including extension of π-conjugation, introduction of intramolecular charge transfer (ICT) character and incorporation of a nitrogen atom into the skeleton.[75] To extend π-conjugation, introduction of π-conjugated fragments such as ethynyl and vinyl groups or fusion of BODIPYs with aryl groups is often employed.[60]

BODIPY has amphiphilic properties, and both electrophilic and nucleophilic and even vicarious nucleophilic substitutions[76] were performed on these compounds, suggesting that they posses rather moderate electron density.

These guidelines were considered by Wu while designing a new chromophore based on BODIPY.[77] The target molecule contains bulky 3,5-di-*tert*-butylphenyl substituents in order to suppress aggregation. Cyclization, carried out with $FeCl_3$ in CH_2Cl_2, gave the fused perylene-BODIPY dye in 23% yield.

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[72] N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev.,* 2012, **41**, 1130.

[73] R. Y. Lai and A. J. Bard, *J. Phys. Chem. B*, 2003, **107**, 5036.

[74] G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem. Int. Ed.*, 2008, **47**, 1184.

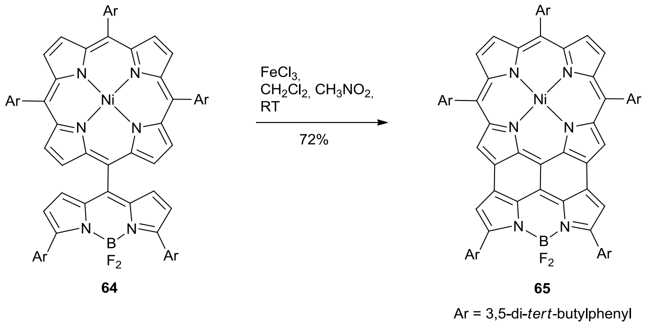
[75] (a) E. Deniz, G. C. Isbasar, O. A. Bozdemir; L. T.Yildirim, A. Siemiarczuk and E. U. Akkaya, *Org. Lett.*, 2008, **10**, 3401; (b) N. Adarsh, R. R. Avirah and D. Ramaiah, *Org. Lett.*, 2010, **12**, 5720; (c) S. Rihn, M. Erdem, A. De Nicola, P. Retailleau and R. Ziessel, *Org. Lett.*, 2011, **13**, 1926; (d) M. J. Hall, S. O. McDonnell, J. Killoran and D. F. O'Shea, *J. Org. Chem.*, 2005, **70**, 5571.

[76] (a) L. Jiao, W. Pang, J. Zhou, Y. Wei, X. Mu, G. Bai and E. Hao, *J. Org. Chem.*, 2011, **76**, 9988; (b) T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, **42**, 226; (c) V. Leen, M. van der Auweraer, N. Boens and W. Dehaen, *Org. Lett.*, 2011, **13**, 1470.

[77] C. Jiao, K.-W. Huang and J. Wu, *Org. Lett.*, 2011, **13**, 632.

Because of the largely delocalized π-system, the product displays absorption bands with an absorption maximum at 670 nm ($\varepsilon = 91\,000\ M^{-1}\ cm^{-1}$) and a shoulder around 780 nm. Equally importantly, in toluene this dye exhibits emission with a maximum at 830 nm, which is the longest NIR emission maximum ever observed for all BODIPY derivatives.

Due to the great stability of perylene-BODIPY dyes, one would expect similar stability for porphyrin-BODIPY fused dyes, despite the fact that the porphyrin core is electron-rich and BODIPY is relatively reactive. Actually, this high reactivity is beneficial for promoting the intramolecular oxidative coupling of the BODIPY unit with the porphyrin backbone.



Scheme 23

The A_3B-type BODIPY-porphyrin dyad **64** was successfully transformed into triply linked **65** in 72% yield using $FeCl_3$ as an oxidant (Scheme 23).[78] Problems occurred when applying the same oxidizing conditions to A_2B_2-type BODIPY-porphyrin derivative **66**. By increasing the temperature to 40 °C, it was possible to obtain the fully fused product **67** in 15% yield (Scheme 24). This low yield may be a result of the moderate electron density on the BODIPY unit. Interestingly, however, there is no undesired chlorination observed, which is very unusual when using $FeCl_3$ as an oxidant.

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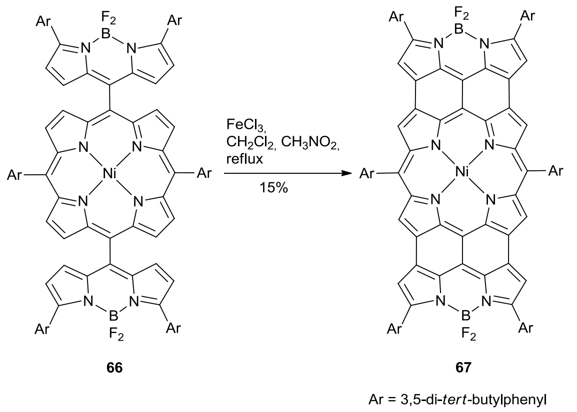
[78] C. Jiao, L. Zhu and J. Wu, *Chem. Eur. J.*, 2011, **17**, 6610.



Scheme 24

Compounds **65** and **67** display strong absorption bands in the visible region around 600 nm (which are responsible for the violet and blue color, respectively) and have a distinct absorption in NIR, with a maximum at 890 nm (ε = 49 000 $m^{-1}cm^{-1}$) and 1040 nm (ε = 68 000 $m^{-1}cm^{-1}$), respectively.

2.8 Summary of optical data

The linear optical data of diporphyrins and porphyrins fused with other aromatic units are summarized in Table 1. It is noteworthy to emphasize once more that *meso–meso, β–β, β–β* fusion gives larger bathochromic shifts than *meso–β*, *meso–β* linkages (**8** vs **10** and **16** vs **15**). The comparison of data for mono-naphthaleno fused porphyrins **18**, **20** and **22** clearly shows the small influence of peripheral substituents on absorption maxima (even after taking into consideration the effect of the central cation). The progressive bathochromic shift and hyperchromic effect can be observed when adding successive anthracene and azulene moieties to the porphyrin core (compounds **30-32**, **36**, **38** and **40**). Once again, comparing the position of the lowest energy Q band for *meso-β* fused porphyrins with those bearing large, fully conjugated subunits fused at two *β* positions (for example, **52** and **54**, with λ_{max} ~ 600-700 nm) emphasize the specific effect on HOMO-LUMO levels characteristic for *meso-β* fusion.

It is noteworthy, that despite the similar molecular size of BODIPY and anthracene, comparison of the NIR absorbance of bis-BODIPY-fused porphyrin **67** (λ=1040 nm) with bis-anthracene-fused porphyrin **38** (λ=973 nm) reveals the difference of 67 nm. These data suggest, that fusion of BODIPY to the porphyrin core appears to be an effective means to bathochromically shift the absorbance.

Table 1. Optical data of *meso-β* fused porphyrins

Compound	**Fused unit**	**λ_{max} (nm)**	ε x 10^{-3}	**Metal**
8	porphyrin	743	420	Ni
9	porphyrin	550	-	Cu
10	porphyrin	994	-	Cu
11	porphyrin	2400	-	Zn
13	porphyrin	1055	-	Zn, Ni
15	porphyrin	1002	-	Cu
16	porphyrin	768	-	Cu
19	corrole	720	117	-
22	naphthalene	660	20	Zn
24	naphthalene	682 (Zn)	24.6	Ni
26/27	naphthalene	730	-	Zn
32	azulene	700	15	Ni
33	azulene	1014	20	Ni
34	azulene	1146	55	Ni
38	anthracene	855	23	Zn
40	anthracene	973	140	Ni
42	anthracene	1417	120	Ni
44	pyrene	724	46	Ni
46	pyrene/porphyrin	1323	114	Zn
48/49	perylene	900	70	Zn
51/52	coronene	780	80	Zn
54	dibenzotetracene	615	-	Ni
56	phenanthrene	700	65	-
58	*N*-annulated	775	40	Zn
60	*N*-annulated	975	120	Zn
62	perylene imide	760	91	Ni
63	perylene imide	900	59	Ni
65	BODIPY	890	49	Ni
67	BODIPY	1040	68	Ni

2.9 Summary

The fact that majority of classical aromatic hydrocarbons have been already fused with porphyrins can give the wrong impression that this field is mature. Quite to the contrary - this is the beginning of an exciting new era in the area of porphyrin oxidative coupling chemistry. Until now, a very limited number of metal cations were utilized, with a heavy focus on nickel. Replacement of a zinc atom with nickel leads to better stability, but also has limitations such as fast deactivation of porphyrin excited states through low lying metal-based d-d-states,[79] thus limiting their utility in a range of optoelectronics and photovoltaic applications.[80] Moreover, in case of need, demetalation of zinc-porphyrins is very simple. DDQ/Sc(OTf)$_3$ and FeCl$_3$ are still the most popular oxidation methods, however the low oxidation potential of the first and the intrinsic problem with chlorination in the presence of the second will most likely result in the development of new reagents in the near future.

DFT calculations may help to predict certain optical properties before preparation at the same time inspiring and creating further challenges to porphyrin community.[59,60] Needles to say, some of fused anthracene-porphyrins suggested by Qi and Jiang[59] are impossible to synthesize with currently available methodology. The recent reports by Thompson and co-workers underline another intriguing issue, namely relationship between structure and tendency to form aggregates (hence solubility).[50] A possible explanation for his observation, that some of fused porphyrins display significantly better solubility than the others, is that distortion plays a key role in suppressing the aggregation of molecules.

Perhaps most importantly, a better understanding of the mechanism of these intramolecular oxidative couplings is needed, specifically which moiety (porphyrin or the second aromatic system) is first attacked by the oxidant to form an electrophilic radical cation.

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[79] M.-C. Yoon, S. B. Noh, A. Tsuda, Y. Nakamura, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 10080.

[80] (a) T. Katsu, K. Tamagake and Y. Fujita, *Chem. Lett.*, 1980, **9**, 289; (b) W. A. Nevin and G. A. Chamberlain, *J. Chem. Soc., Faraday Trans. 2,* 1989, **85**, 1747; (c) C.-Y. Lin, C.-F. Lo, M.-H. Hsieh, S.-J. Hsu, H.-P. Lu and E. W.-G. Diau, *J. Chin. Chem. Soc.*, 2010, **57**, 1136.

Proper answer to this and similar questions, will help explain the apparently contradictory observations such as: (a) participation of units which are by no means electron rich[49] (b) difficulties with carrying out oxidative aromatic coupling on already partially fused porphyrin, possessing first oxidation potential lower than starting material;[55] decomposition of product observed in cases when multiply electron-rich hydrocarbons are fused with central macrocyclic ring.[53]A set of rules describing the effects of (a) the metal cation in the cavity; (b) additional substituents at *meso*-positions (solubility, first oxidation potential, etc.) and (c) electron density of the key aromatic unit, on results of key reaction, have yet to emerge. The fact that rather limited number of porphyrinoids which were utilized as substrates in oxidative aromatic coupling (porphyrins, corroles[43,44,45] and [1.1.1.1.1.1]hexaphyrins[35]) suggests one of the directions of future development in this area. In addition to pure academic interest, the many potential applications of planar porphyrinoids in photovoltaic devices serve to motivate further development in this field.[10]

3 Results and discussion

3.1 Introduction

The growing interest in *meso-β*-fused porphyrinoids is well understandable, due to their interesting properties and promising potential applications. The wide spectrum of differently designed structures presented in the Chapter 2 indicates clearly, that the general knowledge of oxidative coupling reaction in case of porphyrins is quite established already. Observing this progressive development I came to conclusion that also corroles can react under oxidative conditions giving their *meso-β*-fused analogs.

Corroles[81,82] are aromatic tetrapyrrole macrocycles, one-carbon-shorter analogues of porphyrins. Instead of one *meso* carbon atom, corroles bear a direct pyrrole–pyrrole link. This leads to a smaller cavity than in the case of porphyrins. For this reason, the electron density is enhanced – the same number π-electrons is distributed over one less atom. Possibly, it could be a great advantage for oxidative coupling reaction, because corrole can more easily form electrophilic radical cation. Corroles possess three protons inside cavity whereas porphyrins contain two.

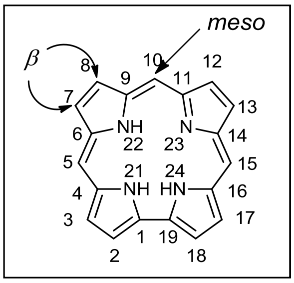

Figure 3

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[81] (a) A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, London 1964, p. 89. (b) A. W. Johnson, *Pure Appl. Chem.*, 1970, **23**, 375.

[82] R. Paolesse, *In The Porphyrin Handbook;* K. M. Kadish, K. M. Smith, R.Guilard, Eds.; *Academic Press: San Diego*, CA, 2000; Vol. **2**, p. 201.

The only known example of fused corrole has been reported independently by Osuka[43] and Cavaleiro,[44] but corrole dimer **19** prepared by them has linkages at position 2 and 18. My aim was to synthesize compounds with linkage between corrole position 13 and another aromatic unit. The oxidation potential of corroles[83] is significantly lower than that of porphyrin, so oxidative coupling should be in principle easier to perform. Limited number of π-extended corroles known in the literature[84] inclined me to attempt also the synthesis of corroles bearing arylethynyl substituents at *meso*-position. Such compounds are unknown to the best of my knowledge.

My investigation plan, was to pursue all three major directions in the parallel. For the sake of clearness, I have decided to present results of my studies starting from corroles.

3.2 Corroles

3.2.1 Synthesis of naphthalene-derived aldehydes and meso-substituted corroles

My first strategy to achieve the goal was as follows: the synthesis of a stable *meso*-substituted *trans*-A_2B-corrole,[85] bearing electron-rich aromatic substituent in position 10. Introducing at *meso* position suitably substituted moiety comprised of two aromatic rings, is crucial to provide required properties for oxidative coupling reaction.[55] Moderate stability of corroles requires, in turn, presence of electron-withdrawing substituents which are necessary to decrease the electron density on the macrocyclic ring and improve the overall stability of both substrate and potential product.

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[83] J. Shen, J. Shao, Z. Ou, W. E, B. Koszarna, D. T. Gryko and K. M. Kadish, *Inorg. Chem.*, 2006, **45**, 2251.

[84] (a) R. Ruppert, C. Jeandon and H. J. Callot, *J. Org. Chem.*, 2008, **73**, 694; (b), L. S. H. P. Vale, J. F. B. Barata, M. G. P. M. S. Neves, M. A. F. Faustino, *Tetrahedron Lett.,* 2007, **48**, 8904; (c) G. Pomarico, S. Nardis, R. Paolesse, O. C. Ongayi, B. H. Courtney, F. R. Fronczek and M. G. H. Vicente, *J. Org. Chem.*, 2011, **76**, 3765.

[85] I. Aviv and Z. Gross, *Chem. Commun.*, 2007, **43**, 1987.

In order to fulfill the latter condition, I chose two pentafluorophenyl moieties, since they already proved their capability to enhance the stability of corrole scaffold.[86]

Over the last two decades one could observe significant increase of interest in corroles' chemistry. Recent improvements in synthetic methodology of these macrocycles have made them readily available.[87] The most popular approach to afford corrole is to react dipyrrane with an aldehyde in acidic conditions. Among others[12] there are two typically used conditions for the synthesis of *trans*-A_2B-corroles from dipyrranes and aldehydes: 1. TFA, CH_2Cl_2; 2. HCl, MeOH, H_2O.[88] Especially aldehydes possessing electron-donating groups in skeleton, which are of moderate activity require stronger activation. This particular case I will discuss in my Thesis.

I started my research from the design of two naphthalene corroles, **77** and **78**. The two required aldehydes **70** and **73** were prepared according to literature procedures[89] (Schemes 25-26). I obtained two aldehydes: 2,7-dimethoxynaphthalene aldehyde (**70**) and 4,7-dimethoxynaphthalene aldehyde (**73**). They possess enhanced electron density in position 8, which is supposed to facilitate forming C-C bond between naphthalene unit and a β-position of corroles' skeleton. The aldehyde **70** was prepared from an easily available 2,7-dihydroxynaphthalene (**68**) by alkylation two hydroxyl groups with methyl iodide, followed by formylation under Vilsmeier conditions (Scheme 25). For the preparation of the aldehyde **73**, I used 1,6-dihydroxynaphthalene (**71**) as the substrate following the same pathway (Scheme 26).

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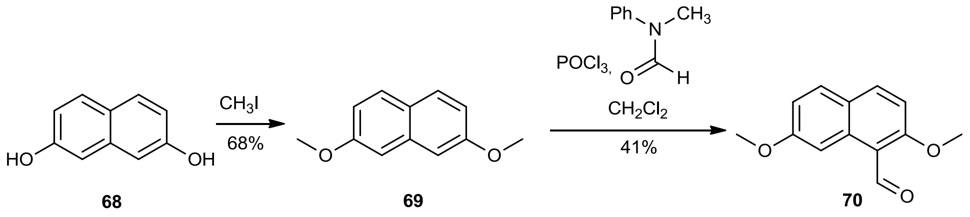
[86] D. T. Gryko and B. Koszarna, *Synthesis,* 2004, 2205.

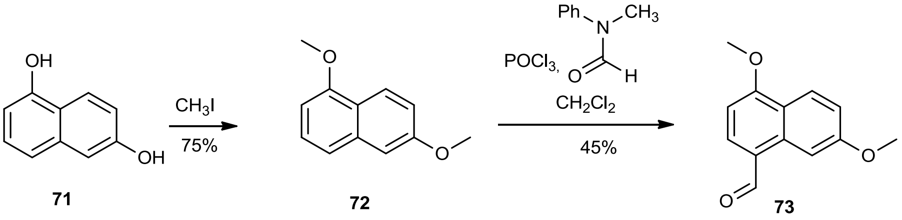
[87] (a) Z. Gross, N. Galili and I. Saltsman, *Angew. Chem., Int. Ed.* 1999, **38**, 1427. (b) D. T. Gryko, *Eur. J. Org. Chem.,* 2002, 1735.

[88] B. Koszarna and D.T. Gryko, *J. Org. Chem*., 2006, **71**, 3707.

[89] T. Mizutani, T. Murakami, T. Kurahashi and H Ogoshi, *J. Org. Chem.,* 1996, **61**, 539.



Scheme 25



Scheme 26

It is obvious, that there are four electron-rich positions, which can be active in the formylation reaction of 1,6-dimethoxynaphthalene (**72**). I observed in this case the formation of three blue-fluorescent regioisomeric aldehydes with slightly different R_f on TLC plate. This difference suggested column chromatography as a suitable technique for their separation. In both cases chromatography failed. In the light of this fact I had to find more effective way of purifying the required aldehydes. Eventually I found that crystallization from small amount of diethyl ether gave pure desired regioisomers **70** and **73** in 41% and 45% yield respectively. The advantage of this purification method is that crystallization can be easily used to work-up reactions performed in larger scale.

After confirmation of the aldehydes structures by using ^{1}H NMR analysis, the synthesis of corresponding corroles from 5-(pentafluorophenyl)dipyrrane (**75**)[90] was performed. The reaction of **70** with **75** was performed in HCl/MeOH/H_2O system, followed by extraction of bilane and oxidation with DDQ gave the desired corrole **77** in 4.5% yield. Such yield was not satisfying even in porphyrinoid chemistry. I decided to examine other conditions known from the literature. I performed the same

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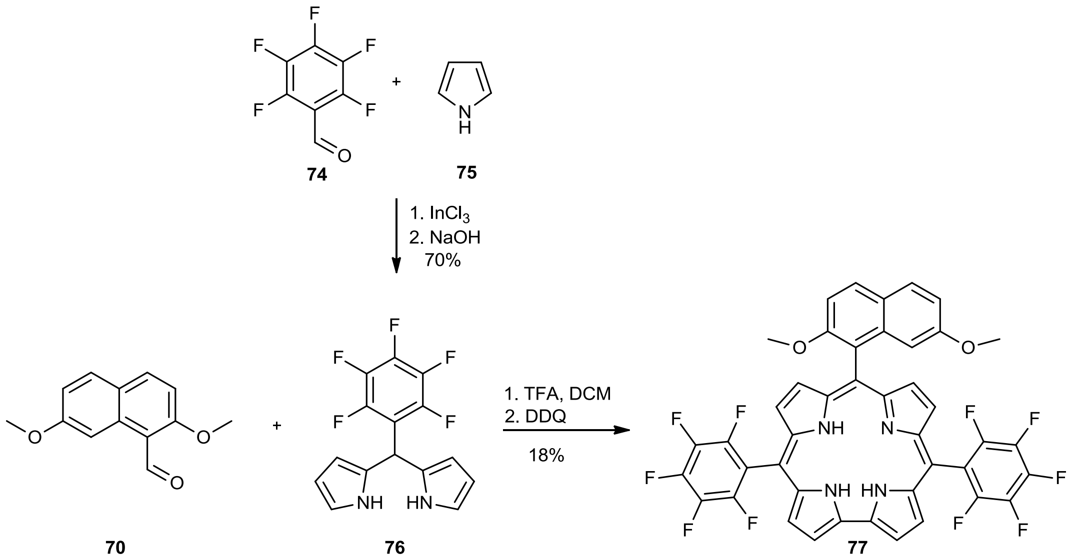
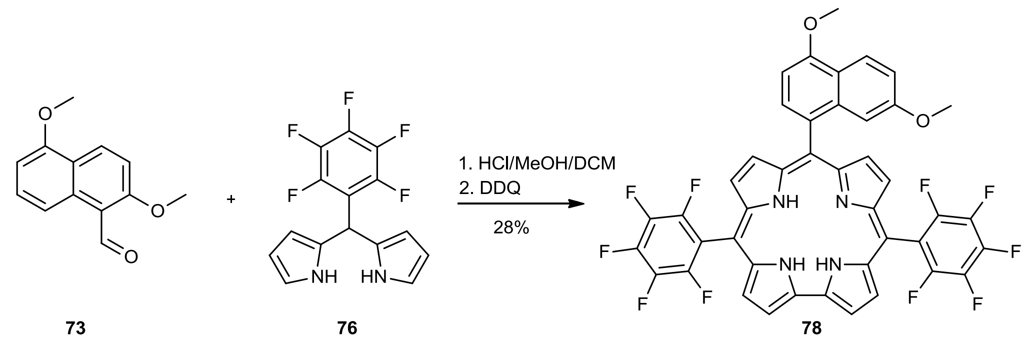
[90] J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Process Res. Dev.*, 2003, **7**, 799.

reaction in dichloromethane in the presence of TFA as a catalyst,[86] and subsequently oxidized the mixture of products with DDQ.

This is a typically used oxidant in the synthesis of corroles, especially for those bearing pentafluorophenyl groups.[88] Since these conditions proved to be far better than the first ones in terms of the yield (18%, Scheme 27), I applied them also to aldehyde **73**. Surprisingly the yield of corrole **78** was only 6%. Puzzled with this strikingly different result I resolved to return to HCl/MeOH/H_2O system. Corrole **78** was obtained in 28% yield under these modern conditions (Schemes 28). It is rather difficult to explain these trends in yields, since both aldehydes are similar in terms of electron-density on carbonyl group as well as from the point of view of steric hindrance.



Scheme 27



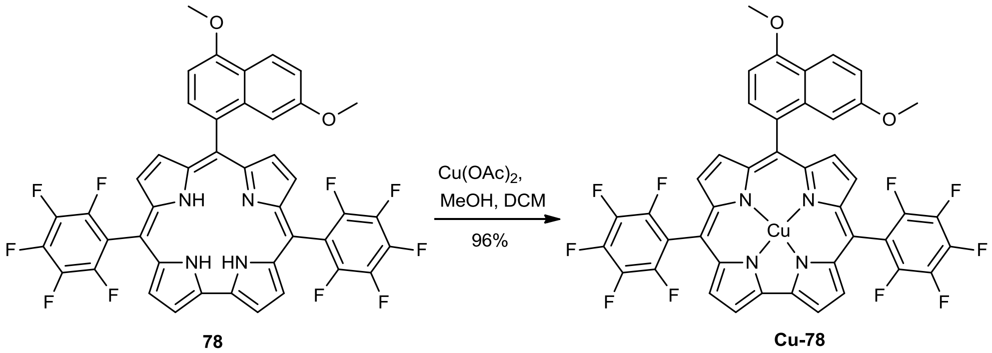
Scheme 28

The nitrogen atoms present inside such macrocycles as corrole or porphyrin are sensitive to oxidants like $FeCl_3$ and can react in an undesired way (for example coordinating of iron). Literature review shows (Chapter 2), that in order to perform oxidation coupling reaction on porphyrins, nitrogen atoms inside the core of porphyrin should be protected.

This can be easily achieved *via* complexation of Zn^{2+}, Cu^{2+}, Ni^{2+}. The same strategy should be applied to corrole. Moreover, inserting of metal cation into the macrocycle, substantially modulates the oxidation potential of final complex.

There is a variety of metals known in porphyrins coordination chemistry. One of them, copper, proved its usefulness in oxidative coupling of porphyrins.[46] This fact, as well as an ease in formation of copper corroles inclined me to utilize them in my research. Insertion of copper cation into the corrole is well-known and rather straightforward. Stirring of **78** with $Cu(OAc)_2$ in the mixture of DCM and MeOH overnight gave copper complex **Cu-78** in an excellent yield 96%.

In contrast to copper porphyrins, which are paramagnetic, (hence one cannot prove neither structure nor their purity using NMR), copper corroles are diamagnetic. I was able to transform corrole **78** into its copper complex **79** using standard conditions (Scheme 29). Surprisingly, corrole **77** subjected to the same reaction conditions decomposed entirely. The modifications of conditions by changing solvent, time of reaction or temperature did not help to form the desired complex.



Scheme 29

3.2.2 Oxidative coupling of naphthalene-corrole complexes

$FeCl_3$ is typically used oxidant in oxidative coupling reactions.[91] It also proved its usefulness in porphyrin chemistry.[49,52,92] One of its limitations is chlorination of electron-rich aromatic compounds.[93] On the other hand, its strong points are good yields, short time of reaction and relatively mild conditions. That is why I decided to use $FeCl_3/MeNO_2$ system to perform oxidative coupling of corrole **Cu-78** (Scheme 30). Subjecting of **Cu-78** solution in dry dichloromethane to these conditions caused distinct change of mixture's color from deep orange to dark green. After 5 min TLC plate showed complete consumption of substrate as well as new green spot's appearance.

The green color of a product is expected, due to the extending chromophore of corrole and, consequently, bathochromic shift of absorption spectrum. An elegant example of porphyrin reported by Anderson,[54] which displays similar absorption spectrum as corrole **Cu-79**, clearly shows that expecting the change of color into green after oxidative coupling is thoroughly justified.

Unfortunately, the product of the reaction turned out to be very unstable under light and air exposition. Quick submission to MS analysis proved, that reaction mixture contains product with desired mass, but further chromatographic purification was unsuccessfull because of complete decomposition. Performing chromatography in darkness and quick elution also did not help (Scheme 30).

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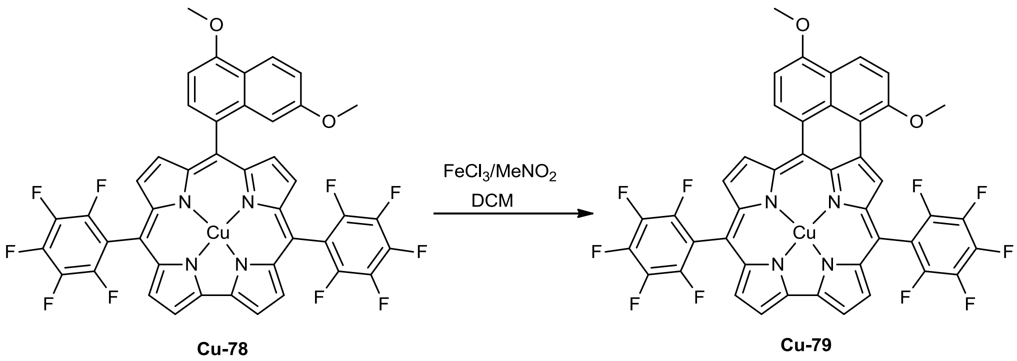
[91] (a) M. Müller, C. Kübel and K. Müllen, *Chem. Eur. J.*, 1998, **4**, 2099; (b) J. Wu, L. Gherghel, M. D. Watson, J. Li, Z. Wang, C. D. Simpson; U. Kolb and K. Müllen, *Macromolecules*, 2003, **36**, 7082.

[92] M. Tanaka, S. Hayashi, S. Eu, T. Umeyama, Y. Matano and H. Imahori, *Chem. Commun.,* 2007, **43**, 2069.

[93] L. T. Bratz and S. Niementowski, *Chem. Ber.*, 1919, **52**, 189.



Scheme 30

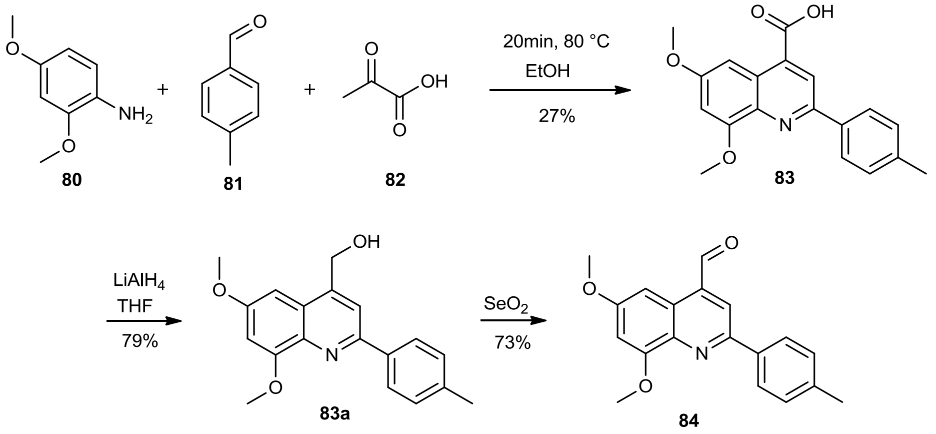
The only plausible rationale behind this result is as follows. It is well known, that corroles are less stable comparing to porphyrins. The hypothetical product **Cu-79** would possess the naphthalene moiety, rich in electrons due to the presence of two electron-donating methoxy groups, in the same plane as corrole core. Consequently, these methoxy groups would increase the electron density of the molecule which makes it even more prone to oxidative decomposition.

3.2.3 Quinoline-corroles

3.2.3.1 Synthesis of quinoline-aldehydes and corroles

Being aware of a fact, that the diminished stability of corroles bearing electron-donating substituent could be the factor responsible for above-described failure, I decided to modify the structure of the key aldehyde by making it less electron-rich. Diminishing electron donating character of *meso*-substituent at position 10 could increase stability of fused corrole. This idea has negative connotation from the viewpoint of the requirements of oxidative coupling, which generally proceeds better between two electron-rich components. One of the appropriate moieties to fulfill this idea, is quinoline skeleton possessing methoxy group(s) on benzene ring (the presence of pyridine ring lowers the electron density).

I designed three quinolinecarboxyaldehydes which possess one (**89** and **95**) or two (**84**) methoxy groups. Aldehyde **84** was synthesized according to the known procedure,[94] in 20% overall yield (Scheme 31).



Scheme 31

Subsequent reaction of an aldehyde **84** with dipyrrane **75** under acidic conditions optimized for aldehydes bearing basic nitrogen atoms,[95] followed by oxidation with the DDQ gave desired corrole **85** in 11% yield (Scheme 32). Attempts to prepare copper complex of corrole **85** resulted in its decomposition giving at least ten more polar products. None of them, according to FD-MS, was the desired product of complexation. I also could not detect the presence of *meso-β*-fused product, which might formed *via in situ* oxidative aromatic coupling, since Cu^{2+} salts can mediate this reaction.[42]

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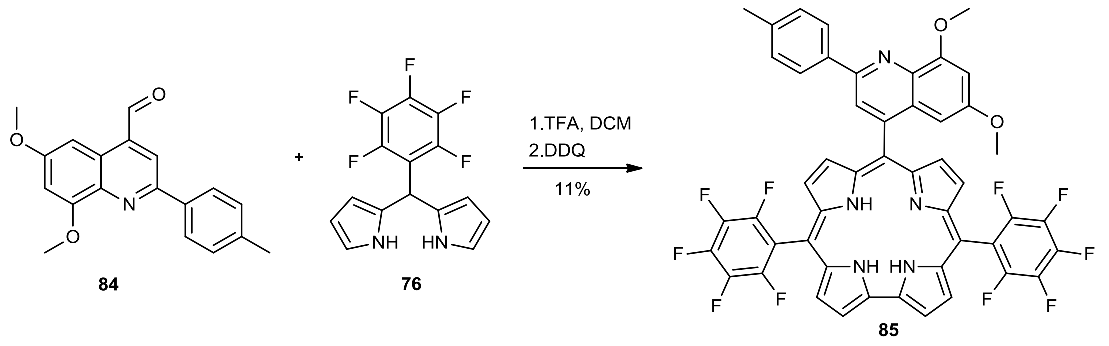
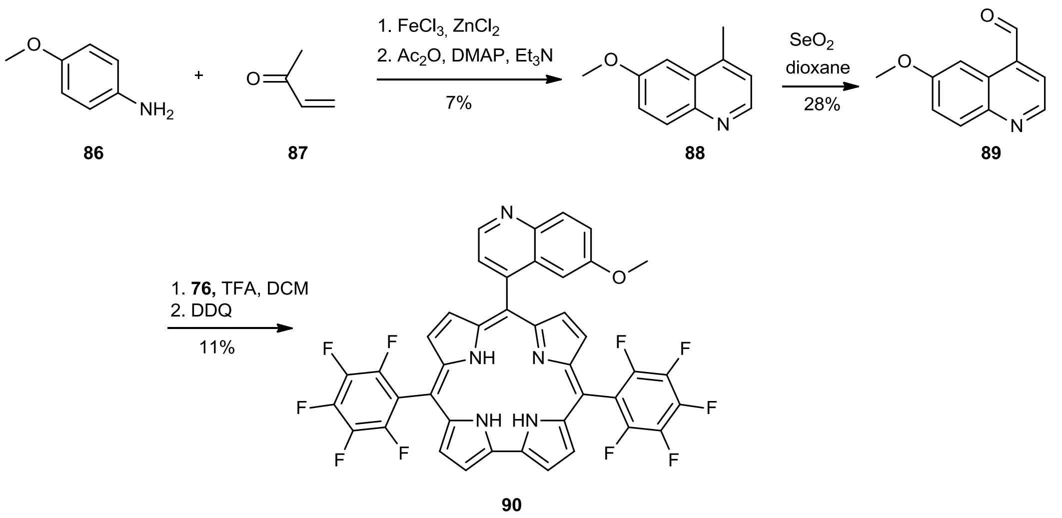
[94] (a) A. I. Vogel, *Preperatyka Organiczna*, WNT Warszawa 1984; Vol. **2**, p. 180; (b) G. A. Epling and K.-Y. Lin, *J. Het.Chem.*, 1987, **24**, 853.

[95] D. T. Gryko and K. Piechota, *J. Porphyrin Phthalocyanines*, 2002, **6**, 81.



Scheme 32

It seemed to me that the presence of two methoxy groups induced decomposition combined with ring-opening of corrole. In the light of this result I modified the structure of aldehyde by reducing the number of methoxy groups to one. Thus, the 4-formyl-6-methoxyquinoline (**89**) was synthesized according to the literature procedure in 28% yield (Scheme 33).[96]



Scheme 33

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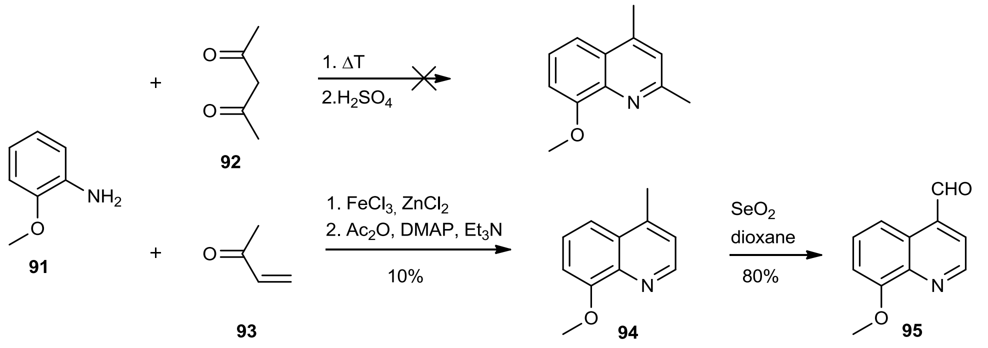
[96] D. M. Johns, M. Mori and R. Williams, *Org. Lett.*, 2006, **8**, 4051.

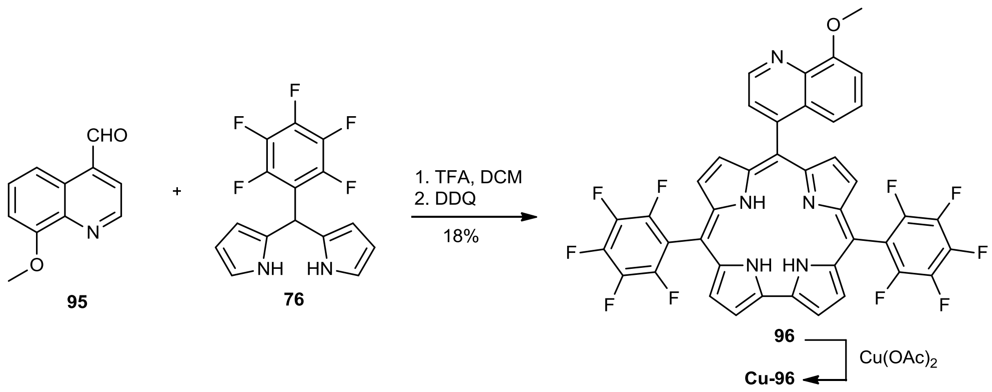
Aldehyde **89** submitted to the reaction with dipyrrane **76** under acidic conditions[95] followed by DDQ oxidation gave the corresponding corrole **90** in 11% yield, which was subsequently metalated using $Cu(OAc)_2$ in excellent 96% yield.

I also attempted the synthesis of the 4-formyl-8-methoxy-2-methylquinoline by reacting 4-methoxyaniline **91** and *β*-diketone **92** according to general Combes procedure.[97] The condensation failed despite of few attempts (Scheme 34).



Scheme 34

Finally, an analogous aldehyde **95** was obtained by the same type of reaction as for **89** in 8% yield for two steps (Scheme 34). Synthesis of corrole **96** from the aldehyde **95** was performed under previously used conditions in 18% yield (Scheme 35).



Scheme 35

The metalation of **96** with $Cu(OAc)_2$ gave the complex **Cu-96** in moderate 34% yield.

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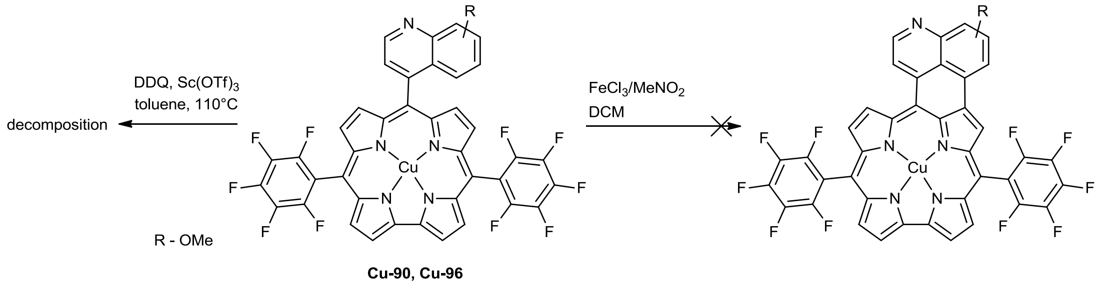
[97] A. Combes, *Bull. Chim. Soc.,* 1888, **49**, 89.

3.2.3.2 Oxidative coupling of quinoline corroles

Both complexes **Cu-90** and **Cu-96**, subjected to the 2.5 equiv. $FeCl_3$ in $MeNO_2$ showed no consumption of substrates. Even after adding the second portion (2.5 equiv.) of the oxidant and an additional half an hour, no product was observed. Since these conditions had no effect on substrate, I decided to use an another oxidant namely DDQ/$Sc(OTf)_3$.[32] The latter one is usually used in toluene, where the temperature could be increased up to 110 °C. The use of this oxidant with corroles **Cu-90** and **Cu-96**, induced the formation of some products (Scheme 36). TLC made when the entire substrate was consumed (30 min. in both cases) revealed the presence of a number of polar spots. None of them was a desired product as judged by FD-MS.



Scheme 36

3.2.4 Silver complexes of corroles

After a few unsuccessful attempts in oxidation of corrole copper complexes, I decided to change central metal cation. An inserted metal has a great impact on the oxidation potential of the porphyrynoids.[98] Among the variety of metals which are applicable in porphyrinoid chemistry, the zinc and nickel seem to be the best candidates.[99] (Fig. 4).Unfortunately, zinc complexes of corrole are unknown. The same situation is for nickel, unless all the β-positions in the core are occupied.[100]

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[98] In *The Porphyrin Handbook*; K. M. Kadish, K. M. Smith and R. Guilard, Eds.; *Academic Press: San Diego*, CA, 2000; Vol. **8**, p. 13.

[99] D.L. Hughes, A.N. Cammidge and P.J. Scaife, *Org. Lett.,* 2005, **7**, 3413.

[100] S. Will, J. Lex, E. Vogel, H. Schmickler, J. P. Gisselbrecht, C. Haubtmann, M. Bernard and M.

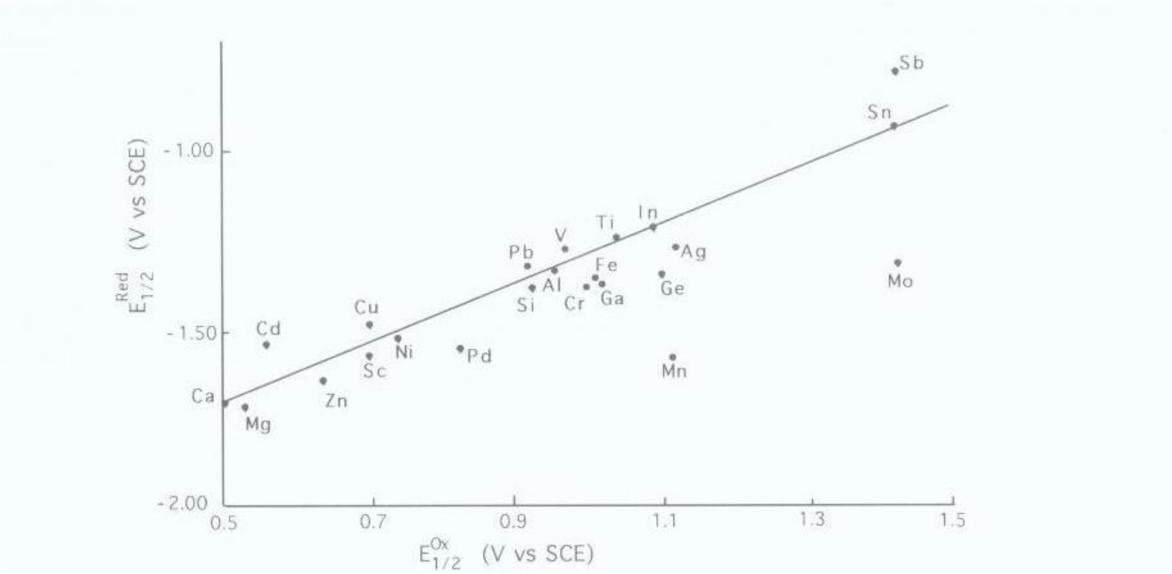


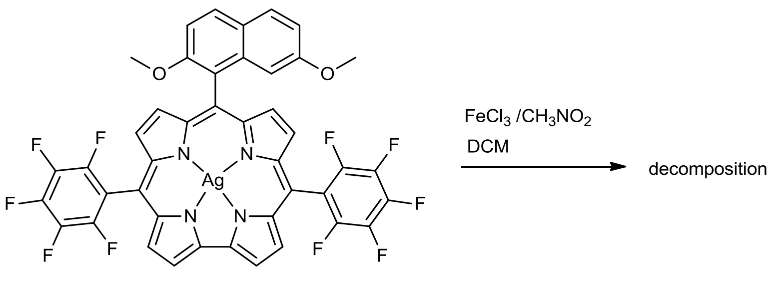
Figure 4. First oxidation potential of octaethylporphyrin for different metals inserted. (*The Porphyrin Handbook*; Vol. 8, p. 13)

Therefore, I chose silver complexes of corroles as a next model substrates to investigate oxidative coupling reactions. Silver complexes of corroles have slightly higher oxidation potential comparing to copper complexes so lower reactivity could be anticipated. At the end, however, they could display better stability which may allow the desired product to be stable.

There are several methods for synthesis of silver complexes described in the literature, among which the most effective is boiling a corrole in the pyridine in the presence of silver acetate.[101] Following this procedure I synthesized complexes **Ag-77** and **Ag-78** in 86% and 93% yields, respectively. The reaction of **Ag-77** and **Ag-78** with $FeCl_3$ in $MeNO_2$ gave, however, only products of decomposition (Scheme 37).

Gorss, *Angew. Chem., Int. Ed.*, 1997, **36**, 357.

[101] C. Brückner, C. A. Barta, R. P. Brin and J. A. Krause Bauer, *Inorg. Chem.*, 2003, **5**, 1673.



Ag-77

Scheme 37

Despite many attempts leading to oxidation of *trans*-A_2B-type complexes of corroles, I was not able to obtain desired *meso-β*-fused corrole. This could be probably due to limited stability and preferable formation of bonds in positions 2 and 18 rather than 8 and 12.[102]

3.2.5 *Cis*-A_2B corroles

Since I could not obtain stable *meso-β*-fused corroles, bearing additional bond between the position 8 of corrole and position 8 of naphthalene moiety, I decided to change the position of naphthalene substituent.

It is known from the literature, that the four *β* positions of corrole close to the direct pyrrole-pyrrole bond are richer in electrons than the remaining four *β* positions. Therefore, such reaction as bromination,[103] occurs preferentially at these positions.[43,104] Confronting the fact, that oxidative coupling seems to do not occur in position 8 (or it does but it leads to unstable product which decomposition is very fast), the question is raised what will happen if electron-rich aromatic moiety will be placed at position 5.

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[102] I. Saltsman, A. Mahammed, I. Goldberg, E. Tkachenko, M. Botoshansky and Z. Gross, *J. Am. Chem. Soc.,* 2002, **124**, 7411.

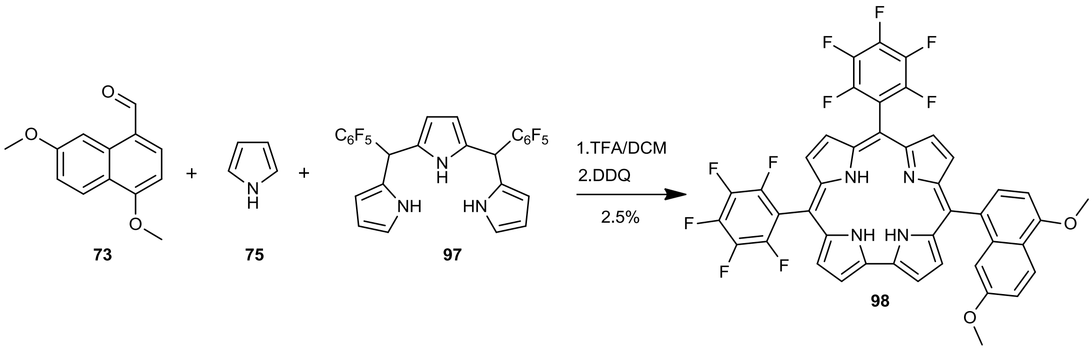
[103] R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti and K. M. Smith, *J. Porphyrins Phthalocyanines*, 2003, **7**, 25.

[104] M. Stefanelli, S. Nardis, L. Tortora, F. R. Fronczek, K. M. Smith, S. Licoccia and R. Paolesse, *Chem Commun.,* 2011, **47**, 4255.

I decided to introduce the electron-rich dimethoxynaphthalene moiety at the position 5 of corrole, hoping that position 3 of corrole will be more reactive in oxidative coupling. Obviously, there is still position 7 available for reaction, but forming a bond there is less probable due to the lower electron density.

There are two typically used strategies for introduction of the substituent at *meso* position of porphyrinoid. The first approach which is often applied to the porphyrin chemistry, is the synthesis of *meso* free porphyrin, from an aldehyde and dipyrrane lacking substituent at position 5 and subsequent mono- or dibromination followed by Suzuki coupling with boronic esters. This approach couldn't be applied in this case, because it is extremely difficult to synthesize a corrole with free *meso* position. There is an example of *meso*-free *trans*-A_2B-corrole in the literature; it was obtained earlier in our group starting from a formaldehyde, with yield as low as 2.4%.[45] Moreover, performing additional reaction on already generated corroles is rather avoided because of their limited stability.

Alternatively, the corrole **98** can be synthesized by reaction of tripyrrane **97** bearing two pentafluorophenyl substituents[105] with pyrrole (**75**) and aldehyde **73** under acidic conditions.[86] On TLC I observed many by-products and the desired corrole **98** was eventually purified after several chromatographies (Scheme 38).



Scheme 38

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[105] (a) J.-W. Ka and C.-H. Lee, *Tetrahedron Lett.*, 2000, **41**, 4609; (b) M. Gałęzowski, J. Jaźwiński, J. P. Lewtak and D. T. Gryko, *J. Org. Chem.*, 2009, **74**, 5610.

This low yield requires inventing a different, more efficient strategy. It is visible from the framework of corrole **98**, that one can divide it in three parts; one coming from 5-pentafluorophenyldipyrrane, second from 5-(4,7-dimethoxynaphthalen-1-yl)dipyrrane and the third from pentafluorophenylaldehyde (Fig. 5).

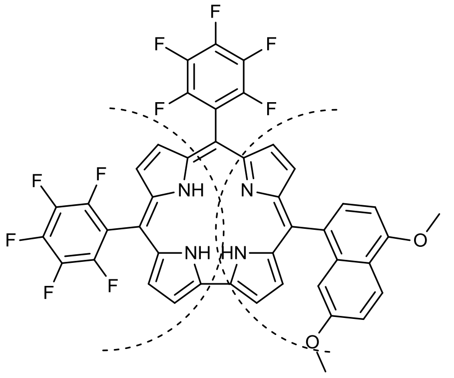

Figure 5.

I decided to carry out a mixed condensation with these two different dipyrranes and an aldehyde, which in principle should give three different corroles including the desired one. This approach to *cis*-A_2B corroles synthesis was reported only once by Paolesse and co-workers.[106]

Firstly, I performed synthesis of two necessary dipyrranes, among which pentafluorophenyldipyrrane (**76**) is known[107] but synthesis of the second one has never been reported. 5-(4,7-Dimethoxynaphthalen-1-yl)dipyrrane (**99**) was obtained under modified Lindsey's conditions in 90% yield (Scheme 39).

Having these two dipyrranes in hand, I performed synthesis of corrole **98**, using the literature method for preparation of *trans*-A_2B-corroles from sterically hindered dipyrranes.[108] The ratio of substrates was equimolar. As expected, three corroles were formed, however large amount of corrole bearing two naphthalene moieties at positions 5 and 15 was detected by TLC (Scheme 39). This explains unsatisfactory low yield of desired *cis*-A_2B corrole **98** (only 6%).

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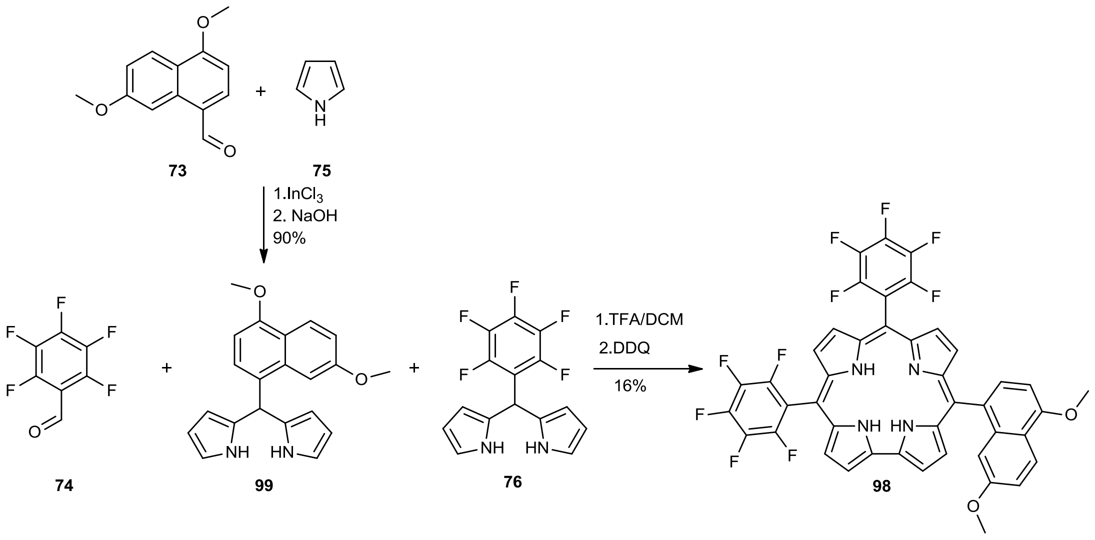
[106] R. Paolesse, A. Marini, S. Nardis, A. Froiio, F. Mandoj, D. J. Nurco, L. Prodi, M. Montalti and K. M. Smith, *J. Porphyrins Phthalocyanines*, 2003, **7**, 25.

[107] B. J. Littler, M. A. Miller, Ch. H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle and J. S. Lindsey, *J. Org. Chem.,* 1999**,** **64**, 1391.

[108] D. T. Gryko and K. Jadach, *J. Org. Chem.*, 2001**,** **66**, 4267.

This observation confirmed, that dipyrrane **99** is more reactive in the condensation with pentafluorobenzaldehyde (**74**).

The possibility to increase the yield is to use different ratio of substrates. Considering the statistic character of this reaction I came to the conclusion that increasing the amount of less reactive dipyrrane **76** (to **76**:**99** = 3:1) will enhance the yield of the desired product. This change caused increase in the yield of **98** up to satisfactory 16% (Scheme 39).



Scheme 39

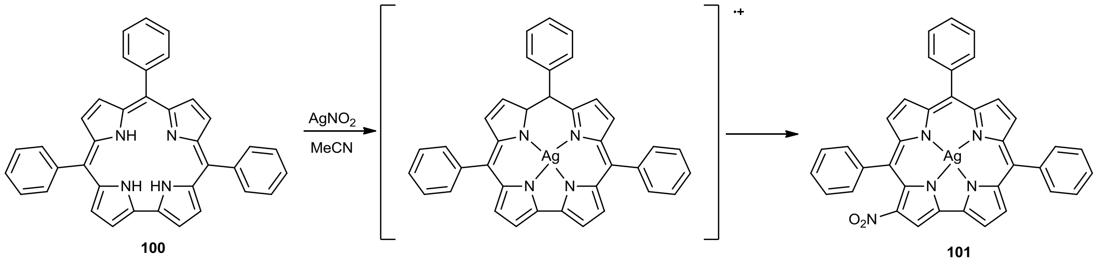
Having free-base corrole **98** in hand, I prepared its copper complex in 82% yield using standard method for synthesis of copper complexes. The reaction of **Cu-98** with $FeCl_3$, gave on TLC at least ten green spots with higher polarity, easily visible on TLC, but desired product could not be detected analyzing the crude reaction mixture by mass spectrometry.

Subsequently I focused on silver complex **Ag-98**, which was synthesized starting from **98** using standard procedure in 95% yield. Oxidative conditions ($FeCl_3/MeNO_2$) caused decomposition of silver complex as well.

Summing up this project, naphthalene *cis*-A_2B-corroles turned to be not suitable substrates for oxidative coupling. None of them gave desired *meso*-*β*-fused corrole.

3.2.6 Attempts with radical cations of corroles

The most probable mechanism of oxidative coupling reaction using $FeCl_3$ is the formation of radical cation located on one of the aromatic units. $FeCl_3$ is an one-electron oxidant, hence in order to abstract two hydrogens one would need to use at least two equivalents of it. I was curious if corrole deprivation of electron in different process could cause similar effect. In another word, if forming a radical from suitably substituted corrole could spontaneously lead to *meso-β*-fused corrole. Initially, I decided to use TEMPO to verify this hypothesis, hoping that this reagent will oxidize corroles to radical cations. After mixing of corrole **Ag-77** with 1 eq. of TEMPO neither conversion nor change of color appeared. It means, that radical was not even formed. Subsequently I moved to another idea based on the results published by Paolesse and co-workers in 2007.[109] They reported, that in the mechanism of corroles nitration, radical cation of corrole is a crucial intermediate (Scheme 40).



Scheme 40

This led me to the conclusion, that during nitration of naphthalene free base corrole **77** using $AgNO_2$ similar reaction can occur, potentially giving nitrated silver complexe(s). The formation of radical cation as an intermediate, however, could lead to one-pot oxidative coupling reaction without using an additional oxidant.

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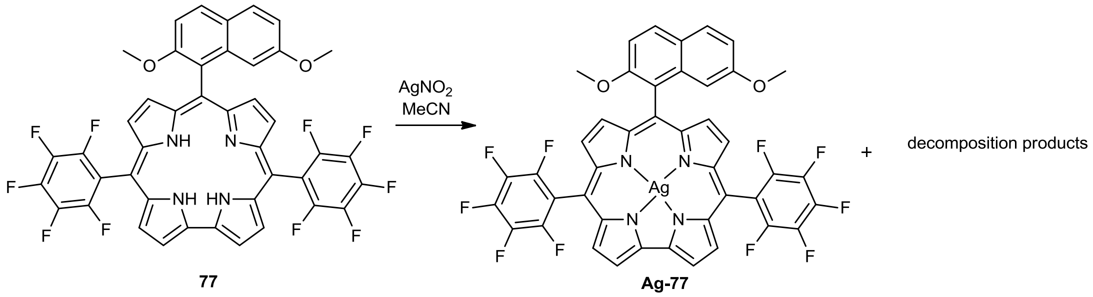
[109] M. Stefanelli, M. Mastroianni, S. Nardis, S. Licoccia, F.R. Fronczek, K.M. Smith, W. Zhu, Z. Ou, K.M. Kadish and P. Paolesse, *Inorg. Chem.,* 2007, **46**, 10791.

Reaction of corrole **77** with silver nitrite in acetonitrile gave green product visible on TLC. Mass spectrometry analysis, showed signal which corresponds to silver complex of corrole **Ag-77** (Scheme 41). Again, no evidence for the formation of *meso-β*-fused complex could be found.



Scheme 41

Undoubtedly, the attempt of obtaining fused corroles *via* radical cations of silver complexes failed. Although the formation of corrole complex occurred but the mechanistic details seem to be more complex than initially described.

3.2.7 5,15-Bis(4-nitrophenyl)corroles

In 2010, Shetti published the synthesis of core-modified 22-thiacorroles. Although the corrole formation had been observed with variety of aromatic aldehydes (including 4-nitrobenzaldehyde), the stable thiacorroles were obtained only from 4- and 3-nitrobenzaldehydes.[110] This could be caused by very strong electron-withdrawing effect of nitro group. In light of published results, I was interested if naphthalene-corroles, will be more stable when subjected to oxidizing conditions if they possess nitrophenyl groups (rather than pentafluorophenyl). Condensation of aldehyde **73** and 5-(4-nitrophenyl)dipyrrane **103**[111] under HCl/H_2O/MeOH conditions for sterically unhindered dipyrranes gave desired 5,15-bis-(4-nitrophenyl)-10-(4,7-dimethoxynaphthalen-1-yl)corrole (**104**) in 3% yield. The same reaction performed in TFA/DCM system turned out to be more efficient, and allowed

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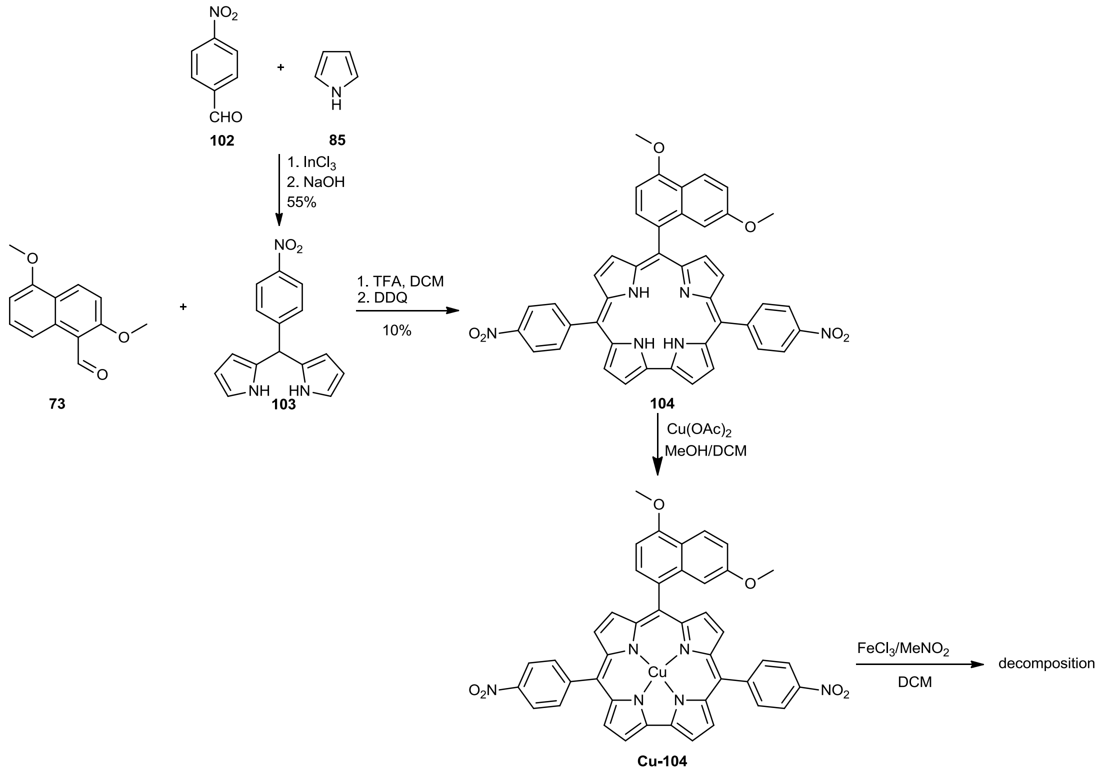
[110] V. S. Shetti, U. R. Prabhu and M. Ravikanth, *J. Org. Chem.*, 2010, **75**, 4172.

[111] W.-S. Cho, H.-J. Kim, B. J. Littler, M. A. Miller, C.Hee Lee and J. S. Lindley, *J. Org. Chem.*, 1999, **64**, 7890.

to obtain **104** in 10% yield (Scheme 37). This corrole was subsequently metalated using copper acetate resulting in the formation of the corresponding complex **Cu-104** in excellent yield (95%).

Nevertheless, complex **Cu-104** turned to be unstable in the presence of $FeCl_3$ and decomposition of the corrole ring was observed, confirmed by ESI-MS (Scheme 42).



Scheme 42

3.2.8 Scope of oxidants

At this point of my research, I came to the conclusion, that perhaps a corrole core could be affected by the $FeCl_3$. As I described in the Chapter 2, numerous oxidants were proved to be useful in the synthesis of *meso-β*-fused porphyrins. It is expected that the first oxidation potential of imaginary meso-*β*-fused corrole would be lower than that of typical corrole. If yes, it would mean that the fused corrole could be decomposed *via* further oxidation, but not necessarily in the presence of all oxidizing agents. Consequently, I decided to investigate variuos oxidants, which proved previously to be useful in porphyrinoid oxidative coupling chemistry (Chapter 2).

As an alternative oxidizing system for oxidative coupling I chose DDQ/Sc(OTf)$_3$.[32] Complexes **Cu-104**, **Ag-77** and **Ag-78** were submitted to these conditions, giving products of decomposition in all cases.

Replacement of DDQ/Sc(OTf)$_3$ by [bis(trifluoroacetoxy)iodo]benzene (PIFA)/BF$_3$·Et$_2$O which is known to promote oxidative dimerization of aromatic compounds[112] resulted in no conversion at the -78 °C. Decomposition occurred again when temperature was increased to 25 °C.

In 2009 Daugulis published results of his investigation af an oxidative C-C bond formation reaction for aromatic compounds. As a specific base for this reaction Daugulis proposed a *i*-PrMgCl·LiCl + tetramethylpiperidine (1:1:1). CuCl$_2$ catalyzed oxidation allowed to form C-C bond between benzofurane molecules.[113]

I decided to check applicability of this method to intramolecular coupling reaction using corrole **Cu-78** as a model. After two hours of heating the reaction mixture at 50 °C without any additional solvent added (*i*-PrMgCl·LiCl/TMP is commercially available as a solution in THF) I observed no conversion, so I added a small amount of dry THF. Since then I observed the progressive consumption of substrate and a few new spots appeared on TLC plate. After prolonged heating (24h) there was still substrate present accompanied by five products. The analysis of this reaction mixture by ESI-MS showed no presence of expected product.

Table 2. Oxidants screening in reaction of corrole Cu-78 oxidation

Entry	**Reactant**	**Conditions**
1	FeCl$_3$	MeNO$_2$, DCM, RT
2	TEMPO	toluene, RT
3	AgNO$_2$	MeCN, RT
4	PIDA	DCM, RT
5	DDQ/Sc(OTf)$_3$	toluene, RT and 50 °C
6	PIFA	BF$_3$·Et$_2$O, -78 °C
7	*i*PrMgCl·LiCl	CuCl$_2$, tetramethylpiperidine, THF, 50 °C

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[112] (a) V. V. Zhdankin and P. Stang, *Chem. Rev*., 2002, **102**, 2523; (b) T. Wirth, *Angew. Chem., Int. Ed.,* 2005, **44**, 3656; (c) R. M. Moriarty, *J. Org. Chem.,* 2005, **70**, 2893.

[113] H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2009, **131**, 17052.

Despite a variety of conditions investigated (Table 2) initially promising concept of oxidative coupling of corrole failed. At this point of my investigation I decided to study other way toward π-extended corroles.

3.2.9 Attempts to perform direct arylation of corroles

One strategy to provide convincing proof of stability of *meso-β*-fused corrole could be the attempt of its synthesis without using oxidative conditions. Out of the several possible ways of forming additional bond between two organic moieties, palladium catalyzed direct arylation is recently the most exhaustively investigated.[114]

Direct arylation is the process of forming the new bond between two carbon atoms: one with proton and second connected with halogen or pseudohalides.

In order to perform planned intramolecular direct arylation reaction it is necessary to start with corrole possessing bromine atom in one of two desired positions: in the *meso*-substituent or at position 8 in the corrole core. As to the second option, the only way to such substrate is bromination reaction. Corroles can be easily brominated because of their high electron density, which facilitates the process. It is not possible, however, to brominate corrole selectively in *β* position 8, which is supposed to participate in formation of an additional bond. Having this in mind, I followed the first option, starting the synthesis from commercially available 5-bromo-3-formylindole (**105**), which possesses bromine in desired position. Moreover, it includes 5-membered pyrrole-ring, which provides more space between second ring and corrole scaffold. It seems that during direct arylation porphyrinoid does not necessarily have to be protected by complexation.

Reaction of 5-(pentafluorophenyl)dipyrrane (**76**) with 5-bromo-3-formylindole (**105**) in the presence of TFA and subsequent oxidation with DDQ afforded the corrole **106** in 15% yield (Scheme 38). On the other hand, the reaction under HCl/H_2O/MeOH conditions failed. For carrying the coupling reaction of **106** I used $PdCl_2(PPh_3)_2$ as a palladium source. An experiment with $PdCl_2(PPh_3)_2$/CuI catalyst and NEt_3 as a base

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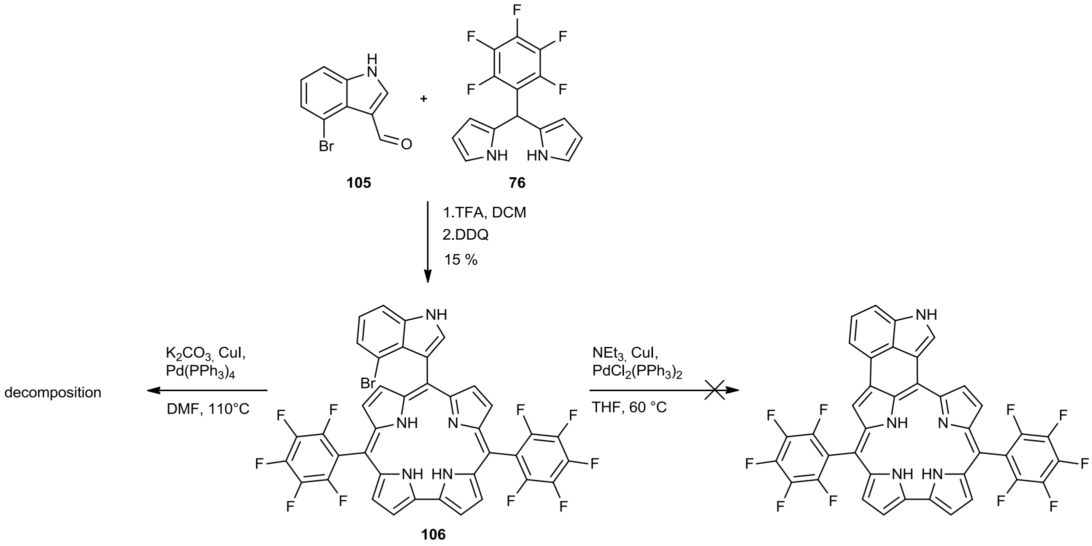
[114] (a) D. Alberico, M. E. Scot and M. Lautens, *Chem. Rev.,* 2007, **107**, 174; (b) D. T. Gryko, O. Vakuliuk, D. Gryko and B. Koszarna, *J. Org. Chem.,* 2009, **74**, 9517.

gave no conversion of starting material despite prolonged refluxing of the reaction mixture.

Alternative conditions, with catalyst $Pd(PPh_3)_4/CuI$[115] in the presence of K_2CO_3 induced decomposition of corrole (Scheme 43).



Scheme 43

I suspected that electron-rich indole moiety was responsible for decomposition of substrate and/or product. This inclined me to carry out direct arylation with substrate bearing another, less electron-rich substituent. I hoped that it would stabilize the product. Moreover, I changed the place of bromoaryl substituent from position 10 to positions 5 and 15 to enable possible reaction to occur at more reactive β positions (3 and 17). Starting from 2-bromobenzaldehyde (**107**), I synthesized 5-(2-bromophenyl)dipyrrane (**108**)[116] in 60% yield, and then reacted it with aldehyde **74** under two sets of conditions: $HCl/H_2O/MeOH$ and TFA/DCM. In both cases, after oxidation with DDQ, two major, unpolar spots on TLC plate appeared, reddish and green with slightly different R_f values. Despite many attempts, further purification of these compounds was impossible because of their low stability. I managed to separate two main components of the mixture and to submit them to MS analysis.

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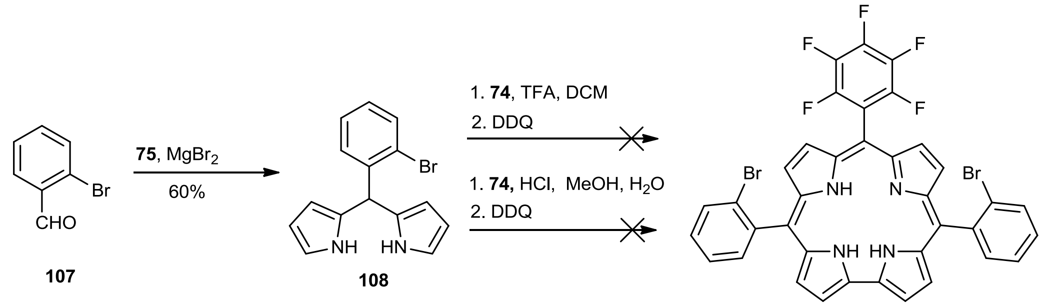
[115] M. Lemhadri, H. Doucet and M. Santelli, *Tetrahedron*, 2005, **61**, 9839.

[116] A. Srinivasan, B. Sridevi, M. Reddy, S. Narayanan and T. K. Chandrashekar, *Tetrahedron Lett.*, 1997, **38**, 4149.

Molecular masses were not in agreement with expected values for desired corrole. As a matter of fact they were several times higher. Moreover, a number of main signals suggested further decomposition. In conclusion, even if desired corrole was formed during this reaction, it was too unstable to purify and handle it (Scheme 44).



Scheme 44

Direct arylation of porphyrinoids is in the very early stage of investigation.[117] In the light of my experiments it seems that this approach failed, at least in the studied cases. I am positive however, that further investigation with the use of electron-poor aryl iodides will eventually end up with success.

3.2.10 Attempts to prepare corroles bearing arylethynyl substituents at *meso* positions

After examining the wide range of concepts, namely:

1) changing of the inserted metal [Cu, Ag]
2) modulating the structure of key substituents at *meso* position
3) changing the position of substituent which supposed to undergo oxidative coupling [5 or 10]
4) applying various oxidants
5) using direct coupling conditions for bromine derivatives

I can definitely claim that extension of corroles' chromophore *via* an oxidative coupling is difficult. I have also made an effort to separate main products of decomposition of corrole complex while using $FeCl_3/MeNO_2$ as an oxidative system. Characterization of appearing violet products was impossible, because reaction was

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[117] Y. Kawamata, S. Tokuji, H. Yorimitsu and A. Osuka, *Angew. Chem. Int. Ed.*, 2011, **50**, 8867.

not repeatable. However, after a lot of effort having been put into described approach, I was still considering π-extending chromophore of corrole.

The literature reveals, that absorption of porphyrins can be batochromically shifted not only by *meso-β* fusion with other aromatic moieties (see Chapter 2). This effect can be achieved by introduction of arylethynyl substituents.[118] This approach has been utilized in the synthesis of porphyrin derivatives displaying strong absorption bands covering the 650-1100 nm region, which makes their properties very interesting. Such porphyrins were utilized in the field of materials chemistry emerging as dye-sensitized solar cells,[119] two-photon absorption (2PA) sensitizers for near-infrared photorefractive composites[120] or optoelectronic devices.[121]

There is, however, no reported example of corrole bearing arylethynyl substituent at *meso* position. Beata Koszarna from our research group managed to synthesize *trans*-A_2B-corrole with TMS-protected ethynyl substituent at position 10, she could not however remove the protecting group.[122] One can expect, that slightly different electron structure of corroles, comparing to porphyrins, will cause that aryl-ethynyl corroles will have different properties. Synthesis of them could be a challenge.

I decided to start my investigation from an attempt of reacting commercially available phenyl propargyl aldehyde (**109**) with 5-(pentafluorophenyl)dipyrrane (**76**) under acidic conditions in order to obtain *meso*-phenylethynyl corrole **110**. The reaction, after rough purification, gave a mixture of the corrole **110** and porphyrin **111** (confirmed by ESI-MS), having similar polarity which makes further purification difficult (Scheme 45) .

Formation of the mixture of porphyrin and corrole is very typical under such conditions.[123] In 2000, our group developed a new methodology, which allowed to diminish the formation of undesired macrocycle. This can be achieved simply by playing with different concentration and ratio of reagents.[124,12] In the majority of

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[118] A. Nowak-Król, B. Koszarna, S. Yeon Yoo, J. Chromiński, M. K. Węcławski, C.-H. Lee and D. T. Gryko, *J. Org. Chem.,* 2011, **76**, 2627.

[119] M. V. Martinez-Diaz, G. de la Torre and T. Torres, *Chem. Commun.,* 2010, **46**, 7090.

[120] K. S. Kim, S. B. Noh, T. Katsuda, S. Ito, A. Osuka and D. Kim, *Chem. Commun.,* 2007, 2479.

[121] V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105.

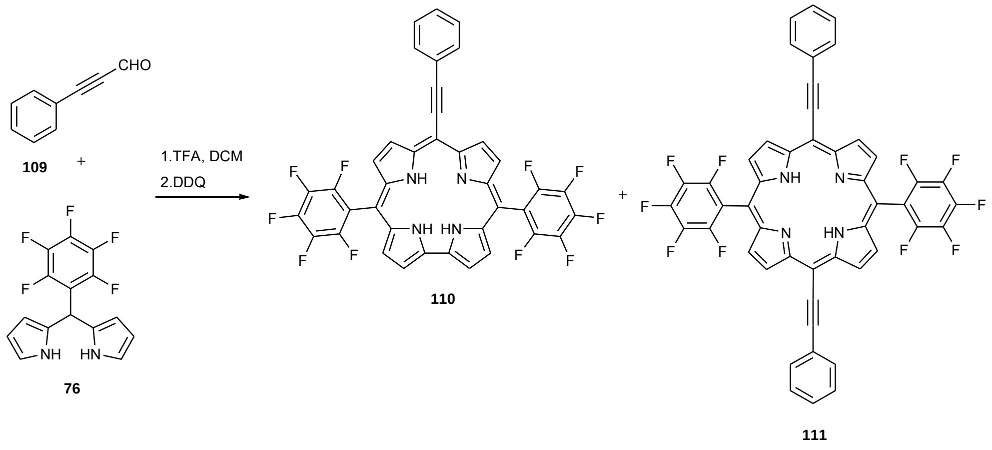
[122] B. Koszarna, *PhD Thesis*, Warsaw, 2006.

[123] R. Paolesse, S. Nardis, F. Sagone and R. G. Khoury, *J. Org. Chem*., 2001, **66**, 550.

[124] D. T. Gryko, *Chem. Commun.*, 2000, **36**, 2243.

cases it is possible to separate the mixture of porphyrin and corrole, on condition that their R_f is differentiated. However, in this particular case, as a result of lack of any functional groups providing the difference in their polarity both corrole **110** and porphyrin **111** have almost identical R_f.

This fact, together with extremely low stability of corrole **110** caused decomposition during each chromatography. Despite illusory pure corrole spot on TLC, there was always small sharp peak observed in the high field of NMR spectrum (around -3 ppm) together with the characteristic, broad signal of corrole protons.



Scheme 45

Consequently, it was necessary to differentiate polarity of both molecules. Literature review reveals, that certain complexes of porphyrins have different polarity comparing to related free bases, and they could easily be separated. This brought the idea to subject the reaction mixture to conditions which selectively transform one of them into complex. It is known, that porphyrins form magnesium complexes rather easily, whereas corroles do not form them at all. I tried then to treat the corrole/porphyrin mixture with magnesium (II) iodide in the presence of ethyldiisopropylamine as a base.[125] I expected that I should obtain a mixture of highly polar magnesium complex of porphyrin and free base corrole, which could help to purify corrole. Surprisingly, during the reaction complete decomposition of corrole occurred while unwanted magnesium complex of porphyrin survived.

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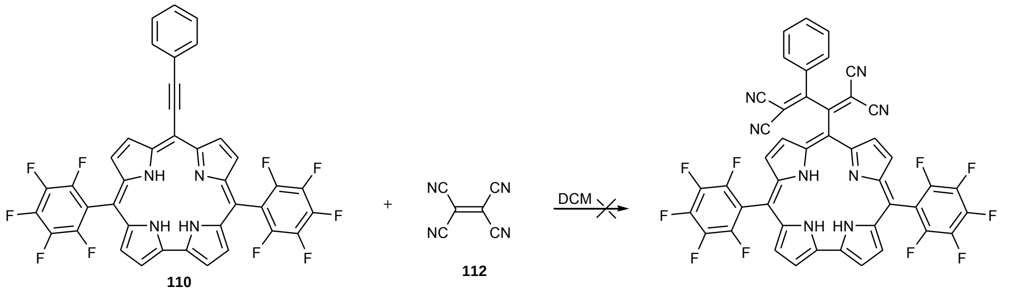
[125] J. S. Lindsey, J. N. Woodford, *Inorg. Chem.*, 1995, **34**, 1063.

Another way of changing the polarity of compounds **110** and **111** is to react them with tetracyanoethylene (TCNE).[126]

Based on literature date, I expected the addition of one molecule of TCNE in case of corrole (Scheme 46) and two in case of porphyrin.



Scheme 46

Setting up the reaction under rather gentle conditions (corrole/porphyrin mixture, tetracyanoethylene, DCM) gave no consumption of any of substrates, even after prolonged time (3 days).

I decided then to redesign the structure of corrole (and porphyrin) by using an aldehyde possessing additional polar group. The *trans*-A_2B_2-porphyrin would contain two such groups versus one group in *trans*-A_2B-corrole, which should influence their R_f. As a key substituent I chose a cyano group. This functional group would not add electrons to the molecule, keeping it stable, and should significantly change the polarity. 4-Cyanophenylpropargylaldehyde (**116**) has never been reported in the literature to that date. Firstly, I reacted 1-bromo-4-cyanobenzene (**113**) with propargyl alcohol (**114**) in the presence of *bis*-(4-cyanophenyl)palladium (II) dichloride/*tris*-(*tert*-butyl)phosphine.[127] Subsequently, I examined several types of potentially suitable oxidants commonly used for oxidation alcohols to aldehydes. Unexpectedly, reaction appeared to be capricious, and searching for a proper oxidizing agent was time-consuming (Scheme 47).

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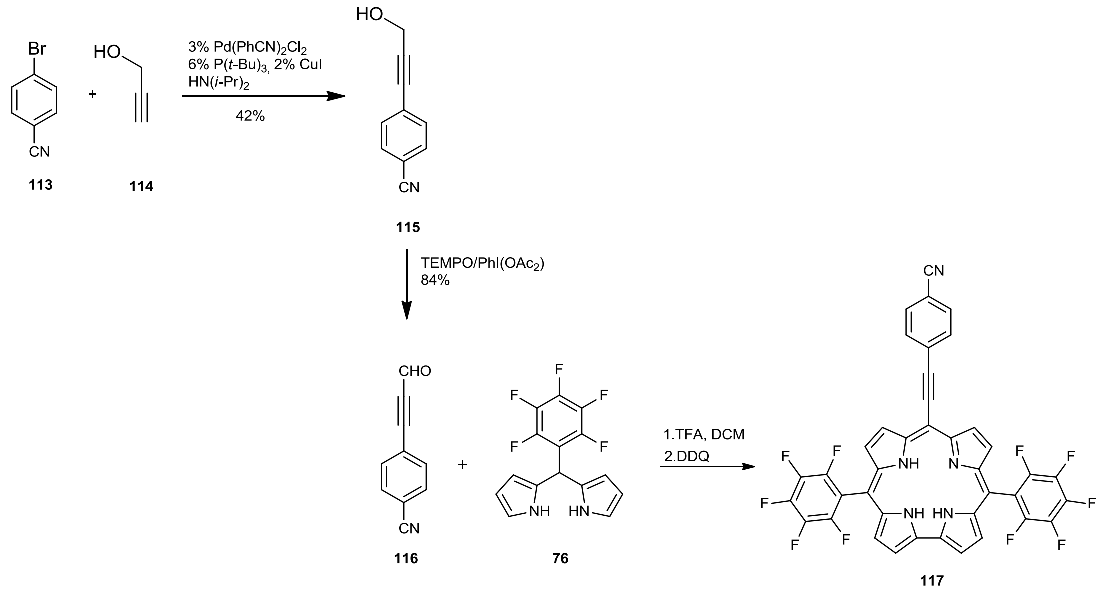
[126] (a) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross and F. Diederich, *Chem. Eur. J.,* 2006, **12**, 1889; (b) D. Koszelewski and D.T. Gryko, *unpublished results*.

[127] T. Hundertmark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.*, 2000, **2**, 1729.



Scheme 47

I observed oxidation of hydroxyl group as well as iodination of triple bond in case of use TEMPO/I$_2$. The use of PCC gave no conversion of alcohol **115**. Temporarily, the most suitable turned out to be titanium tetrachloride, using which I obtained desired aldehyde **116** in 20% yield. This result is far from satisfactory, so farther research was needed. Luckily, at that time my colleague optimized the oxidation step by using system comprised of TEMPO and PhI(OAc)$_2$.[119] Eventually I used this method to obtain desired aldehyde **116** (Table 3).

Table 3. Screening of oxidants used in synthesis of **116**

Entry.	**Oxidizing agent**	**Yield**
1	TEMPO/I$_2$[128]	Iodination of triple bond
2	PCC[129]	No conversion
3	TICl$_4$[130]	20%
4	TEMPO/PhI(OAc$_2$)[118]	84%

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[128] R. A. Miller, R. Hoerrner and R. Scott, *Org. Lett.,* 2003, 285.

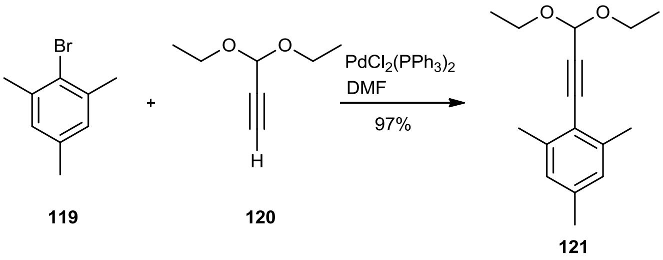
[129] E. Tretyakov, A. Tkachev, T. Rybalova, Y. Gatilov, D. Knight and S. Vasilevsky, *Tetrahedron*, 2000, **51**, 10075.

[130] Z. Han, H. Shinokubo and K. Oshima, *Synlett,* 2001, **9**, 142.

I performed the reaction of 4-cyanophenylpropargylaldehyde (**116**) with dipyrrane **76** under classical conditions (Scheme 47). As expected, the reaction again gave the mixture of corrole **117** and porphyrin **118**. This time the problem with purification was different, though. The difference in R_f was remarkably bigger, but the solubility of the obtained mixture drastically decreased. The compounds smeared during the column chromatography so much, that every collected fraction contained the same ratio of both porphyrinoids.

I tried several methods in order to purify the reaction mixture: crystallization, suspension in cyclohexane, chromatography techniques like: SiO_2 packed, Al_2O_3 packed, size exclusion chromatography (SEC) in THF, preparative TLC. All these attempts failed and I came to conclusion that without enhancing solubility of macrocyclic compounds I would not be able to separate corrole from porphyrin.

I redesigned the structure again. I chose mesityl as a group increasing the solubility. It already proved its usefulness in chemistry of corroles and porphyrins.[108] Particularly, despite having slightly electron-donating character it does not decrease their stability much. Synthesis of mesitylpropargyl aldehyde diethyl acetal was performed following literature procedure.[131] Palladium catalyzed coupling of bromomesitylene (**119**) and propargylaldehyde diethylacetal (**120**) gave desired mesitylpropargylaldehyde diethylacetal (**121**) in excellent 97% yield (improved comparing to original publication by 8%) (Scheme 48).



Scheme 48

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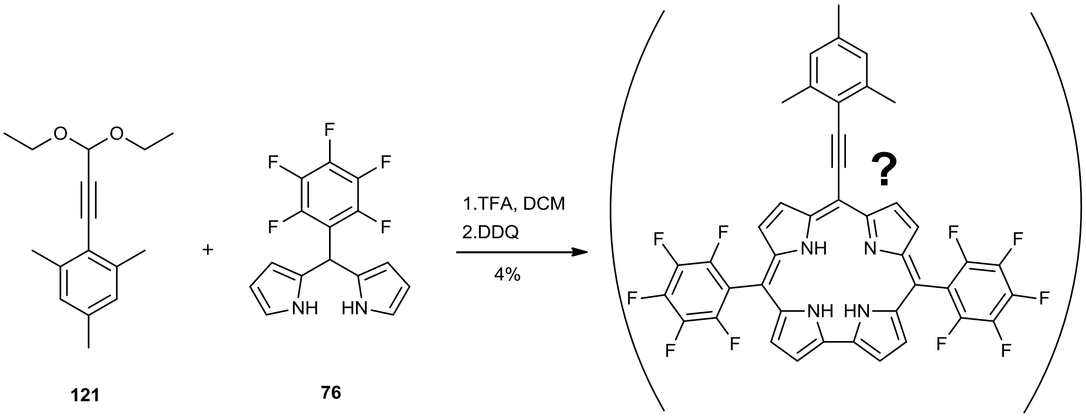
[131] M. Lemhadri, H. Doucet and M. Santelli, *Tetrahedron*, 2005, **61**, 9839.

In this place it is worth to mention, that acetals could be used in the synthesis of corroles as an equivalent of aldehydes. Reaction of **121** with dipyrrane **76** followed by DDQ oxidation gave mixture of few polar products accompanied by one unpolar.



Scheme 49

The latter one was visible as brown-green, non-fluorescent spot on TLC. Purification of the reaction mixture turned to be challenging, because of smearing of compounds. This phenomenon, however, was not caused by poor solubility of substances, which was excellent. The major compound behaved like having basic nitrogen atoms, which can interact with acidic silica during chromatography. Tedious chromatography gave almost pure amorphous product. Typical way for further purification of porphyrinoids is their crystallization. This way turned to be extremely difficult in case of my product because of its very good solubility in the majority of usually used solvents, ranging from hexanes to methanol. Only after dissolving in pentane and gentle solvent evaporation slow forming of tiny crystals occurred, filtered as dark powder. ^{1}H NMR shown, however, no typical signals for corrole's spectrum (e.g. wide signal around -3ppm). Surprisingly, two unexpected singlets appeared at around 14 ppm and the set of β protons of pyrrole part was shifted to higher field. Moreover, every signal of proton in the molecule displayed a different chemical shift, which means that they are not equally surrounded in magnetic field. All these facts suggested different structure then the expected one.

Detailed analysis of 1D and 2D (COSY, HSQC, HMBC, Fig. 6-8) ^{1}H NMR as well as MS and ^{19}F NMR analysis shown clearly, that the following moieties are present in the structure: mesityl, pentafluorophenyl and ‘pyrrole’.

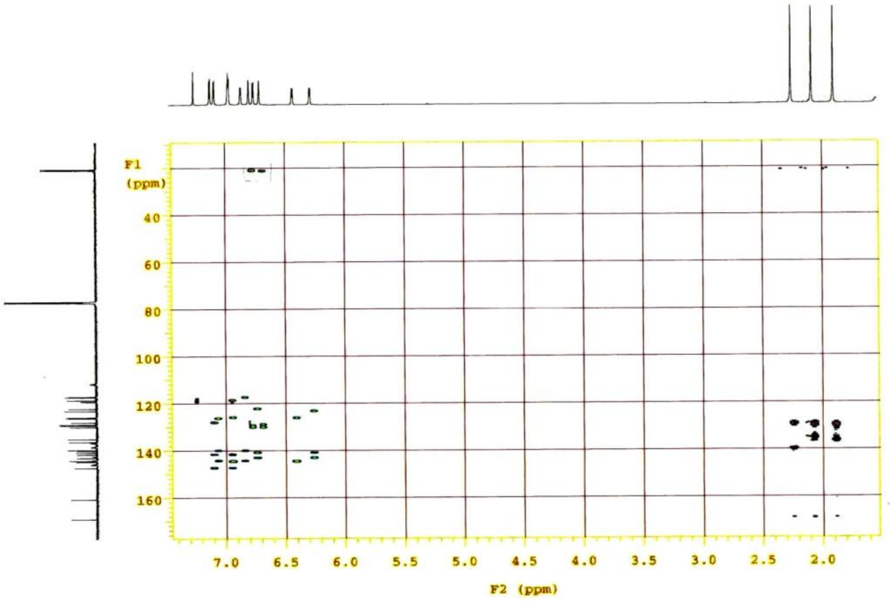


Figure 6

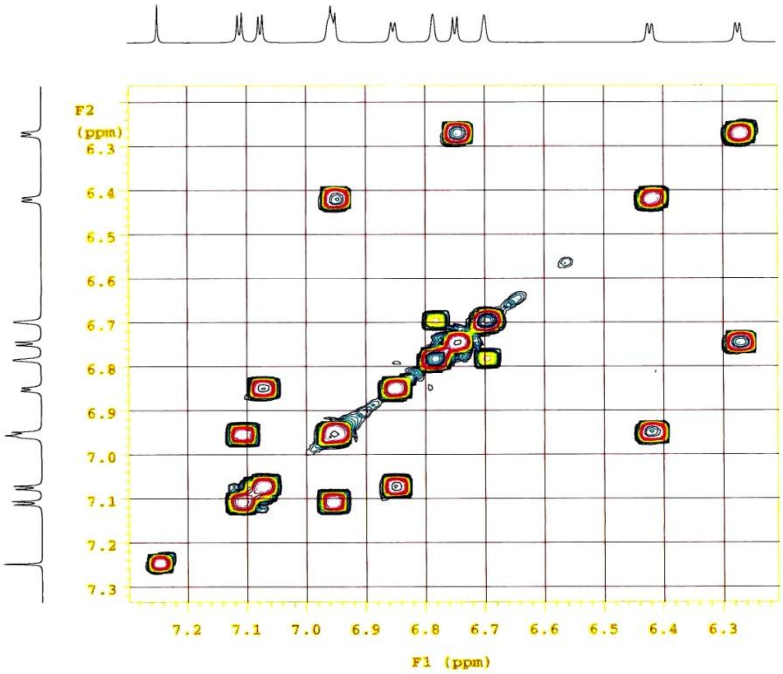


Figure 7

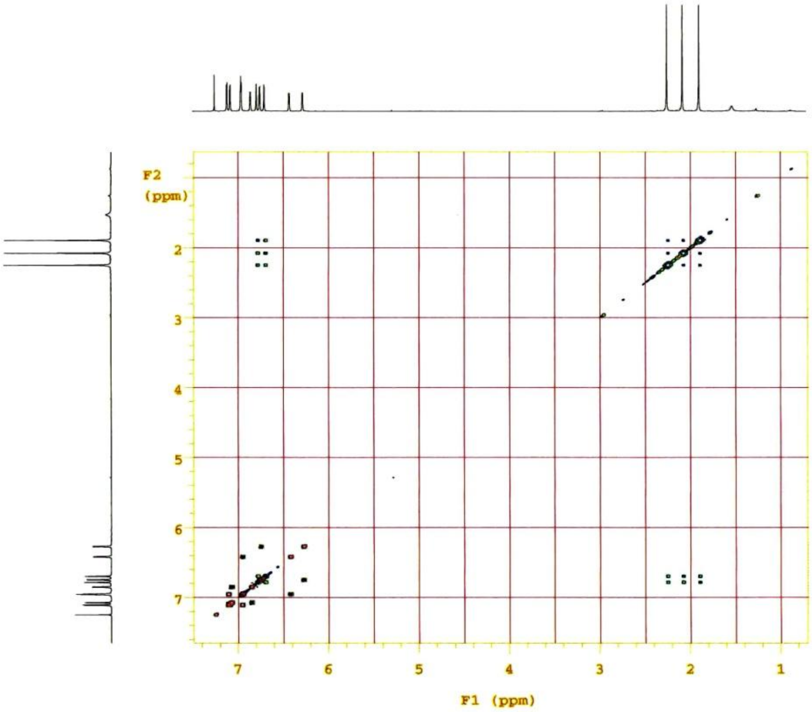


Figure 8

There are two signals on FD-MS spectrum corresponding to producst of [2+1] and [4+2] condensation. Consequently both formulas have to be taken into consideration. Additionally, there are five magnetically different fluorine atoms in the structure. The whole compound is, however, not aromatic. This is supported by fact, that molar absorption coefficient is relatively low. Also, two protons from the cavity are deshielded and signals shifted to around 14ppm. In such conformation planarity probably is not maintained. This led to conclusion, that it is worth to attempt re-aromatization of the structure. There is the reported case of re-aromatization of corrole by complexation.[132] Paolesse and co-workers used cobalt salt to induce the re-aromatization of isocorrole to corrole. Anticipating similar behavior of **122**, I set the reactions under the same conditions. No conversion was observed. After temperature increase to 40 °C, I observed slow decomposition.

At the same time, I decided to synthesize more examples of corrole bearing triple bond in *meso* position. Therefore, I performed reactions of 5-(4-cyanophenyl)dipyrrane, 5-(4-thiomethylphenyl)dipyrrane, 5-(3,5-difluorophenyl)-

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[132] G. Pomarico, X. Xiao, S. Nardis, R. Paolesse, F. R. Fronczek, K. M. Smith, Y. Fang, Z. Ou and K. M. Kadish, *Inorg. Chem.,* 2010, **49**, 5766.

dipyrrane and 5-(2,6-dichlorophenyl)dipyrrane with acetal **121**. In each case only related *trans*-A_2B_2-porphyrin as a product was observed as a green spot on TLC.

The most intriguing part of a structure was triple bond part. Lack of characteristic signals between 2400 and 2800 cm^{-1} in IR spectrum as well as differentiated chemical shifts of mesityl protons proved, that triple bond has been transformed into different arrangement. Insightful analysis of ^{13}C NMR, HSQC and HMBC allowed to certain assignment of signals at 158 and 160 ppm to carbon atoms from former triple bond. As big shifts as 160 ppm are rarely present in chemistry of porphyrinoids and certainly does not fit to triple bond carbons. They may be characteristic for allene configurations. I started to consider the possibility of dimerization during the process of oxidizing porphyrinogens. In order to prove this concept, I measured diffusion index of **122** and two additional species 5,10,15-(*tris*-(pentafluorophenyl)corrole[133] (**123)** and 5,15-(*bis*-(pentafluorophenyl)-10-(4-methoxyphenyl)corrole[86] (**124**)). The index value depends, among the other factors, on the size of molecule. Comparison of three measured values for **122**, **123** and **124**, suggested doubled mass of expected molecule. I proposed then the most possible structure for **122** (Fig. 9).

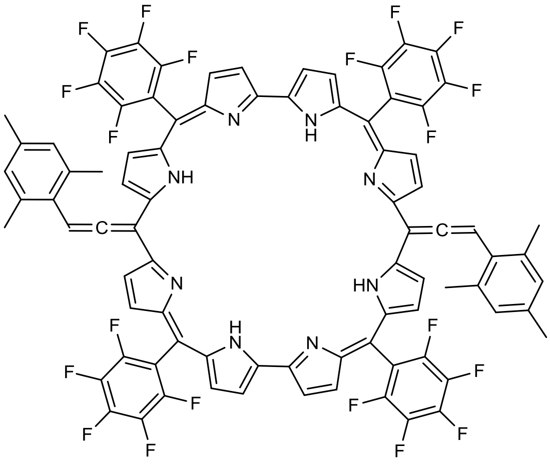

Figure 9

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[133] B. Koszarna and D. T. Gryko, *Org. Biomol. Chem.,* 2003, **2**, 530.

3.2.11 Conclusions

The initial concept of naphthalene corroles oxidative coupling failed due to instability of fused corroles. Direct coupling is not suitable strategy for obtaining fused corroles at least in the studied cases. Synthesis of corrole bearing triple bond gave no desired molecule but has been awarded new interesting structure.

3.3 Oxidative coupling of *meso*-substituted porphyrins

3.3.1 Introduction

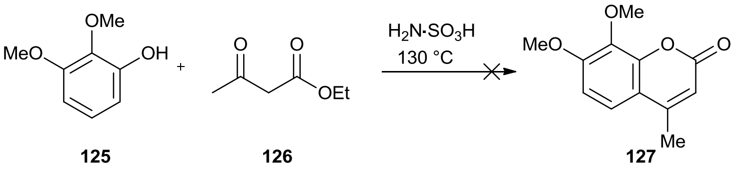
The survey of the literature related to *meso-β*-fused porphyrin chemistry (Chapter 2) shows growing interest in investigation of oxidative coupling reaction of these macrocycles. Understanding the relationship between the structure of porphyrinoids and their spectroscopic and photophysical properties is a complex and deeply intriguing issue.[16] The subtle nature of this relationship can be exemplified by Osuka's π-extended porphyrin which, in spite of possessing an extra double bond, displays hipsochromic shift.[17] In-depth analysis leads to the conclusion that the magnitude of HOMO-LUMO alteration depends more on the type of conjugation than on the actual number of double or triple bonds added. The vast diversity of π-expanded and π-extended porphyrinoids attracts attention not only because of the theoretical issues involved, but also because of the opportunities to explore their linear and non-linear optical properties in technology and medicine.[19] In principle, any aromatic unit located at the *meso*-position of a porphyrin and possessing high electron density should be able to form fused products *via* oxidative aromatic coupling. In parallel to unsuccessful attempts towards obtaining *meso-β*-fused corroles, discussed in Chapter 3.2, I started second part of my investigation focused on *meso-β*-fused porphyrins. At the moment when my research started (2007) only limited number of papers were published concerning oxidative coupling of porphyrins with other aromatic units. The outcome of last 5 years is significant and needless to say it influenced my research to certain degree. I was particularly interested in the following directions:

- attachment of relatively simple units like naphthalene in order to investigate structure-optical properties relationship
- oxidative coupling with heterocyclic units such as: coumarin, indole and quinoline
- chance for regioselectivity in oxidative coupling of *trans*-A_2B_2-porphyrins bearing two electron-rich units
- new reagents and new, optimized conditions for this reaction

3.3.2 Studies on *meso*-coumarin porphyrins

I chose coumarins as one of the aromatic components for investigation of porphyrin intramolecular oxidative aromatic coupling due to their excellent and well documented photochemical and photophysical behavior.[134] Owing to their intense fluorescence, coumarin dyes have attracted considerable interest as laser dyes,[135] emitter layers in OLEDs[136] and as optical brighteners.[137] It was interesting therefore, what kind of optical properties fused coumarin-porphyrins may possess. In this context I designed two coumarin-derived aldehydes with the goal of transforming them into the corresponding A_3B-porphyrins. Macrocycles of this type can be in principle synthesized either *via* Suzuki coupling starting from porphyrins bearing at one *meso* position bromine or boronic acid/ester functionality or from the corresponding aldehydes *via* mixed condensation. The second route is more straightforward for the preparation of A_3B-porphyrins. I designed aldehyde **129** in such a way as to possess high electron-density at position 5, which is induced by the electron-donating substituents at positions 7 and 8. A literature search revealed that coumarins that are unsubstituted at position 3 react with $FeCl_3$ to form 3,3'-dimeric structures.[138]

I attempted von Pechmann reaction of 2,3-dimethoxyphenol (**125**) with ethyl acetylacetate (**126**) in the presence of sulphamic acid, but only small conversion of substrates was observed.



Scheme 50

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[134] (a) *The Chemistry of Heterocyclic Compounds, vol. 31, Chromenes, Chromanones, and Chromones*, G. P. Ellis, Ed., (b) K. H. Drexhage in *Dye Lasers,* F. P.Schafer, Ed., *Springer*, New York, 1977.

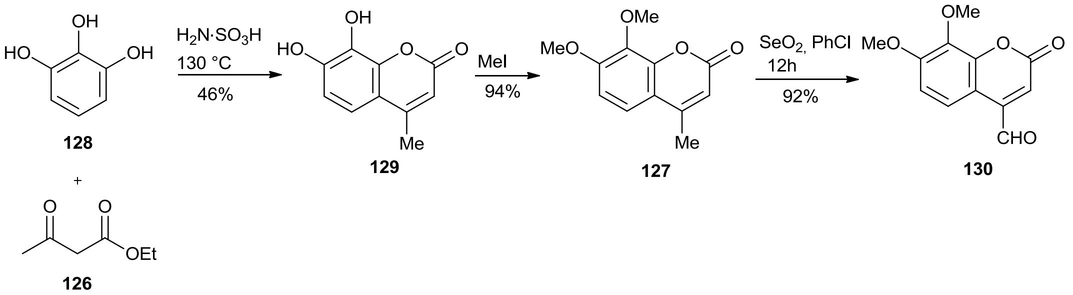
[135] L. Chen, T.-S. Hu and Z.-J. Yao, *Eur. J. Org. Chem.*, 2008, **73**, 6175.

[136] (a) A. R. S. Koefod and K. R. Mann, *Inorg. Chem.*,1989, **28**, 2285; (b) B. S. Tasch, C. Brandstatter, F. Meghdadi, G. Leising, G. Froyer and L. Athouel, *Adv. Mater.*, 1997, **9**, 33.

[137] C. A. E. Siegrist, H. Hefti, H. R. Mayer and E. Schmidt, *Rev. Prog. Coloration,* 1987, **17,** 39.

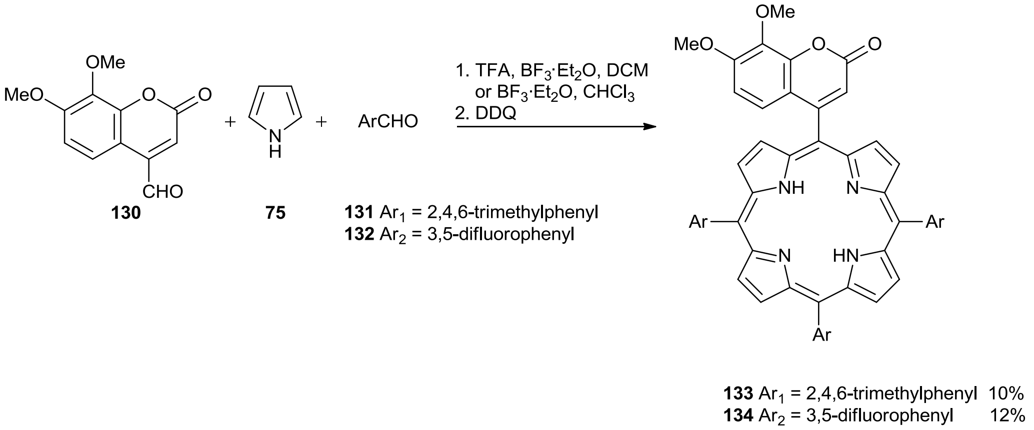
[138] J. Reisch and J. Zappel, *J. Het. Chem*., 1992, **29**, 1035.

Slightly altering the initial synthetic plan, I transformed more reactive pyrogallol (**128**) into coumarin **129** using a modern version of standard Pechmann's condensation[139] followed by a Williamson etherification.[140] Oxidation of the resulting heterocyclic product **127** using SeO_2[141] gave the desired aldehyde **130** in 92% yield (Scheme 51).



Scheme 51

A mixed condensation of pyrrole (**75**), aldehydes **131** or **132,** and coumarinaldehyde **130** followed by oxidation of the porphyrinogens with DDQ yielded a mixture of six possible porphyrins, from which A_3B-type porphyrins **133** and **134** were separated in 10 and 12% yield, respectively (Scheme 52). Porphyrin synthesis was performed using Lindsey's procedures for sterically hindered aldehydes[142] (for mesitaldehyde **131**) or for non-hindered aldehydes[143] (3,5-difluorobenzaldehyde **132**).



Scheme 52

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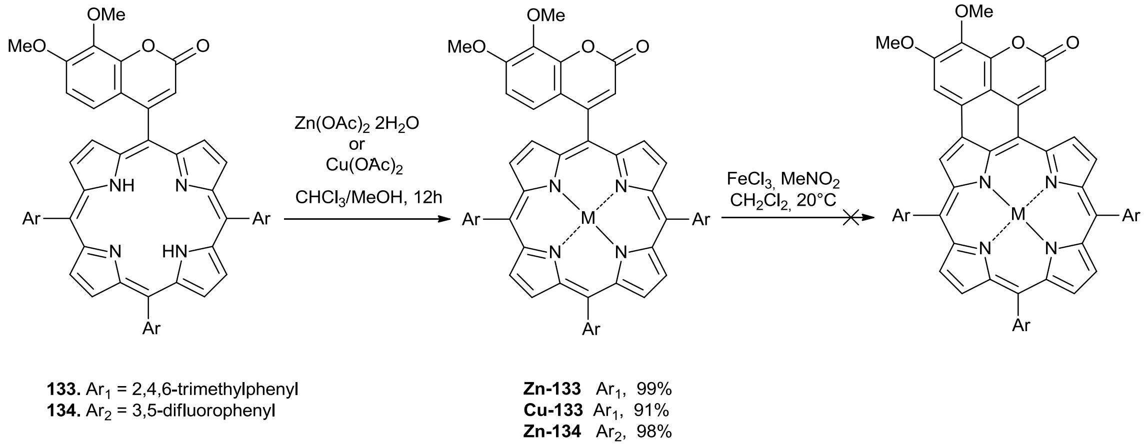
[139] S. R. Pankajkumar, S. U. Devendrapratap and S. D. Amant, *Synlett*, 2004, 1909.
[140] V. S. Parmar and S. Singh, *J. Ind. Chem. Soc.,* 1987, **64**, 745.
[141] T. Matsui, S. Tahara and M. Nakayama, *Bull. Chem. Soc. Jpn*., 1984, **57**, 3355.
[142] R. W. Wagner, F. Li, H. Du and J. S. Lindsey, *Org. Process Res. Dev.*, 1999, **3**, 28.
[143] G. R. III Geier, J. A. Riggs and J. S. Lindsey, *J. Porphyrins Phthalocyanines*, 2001, **5**, 681.



Scheme 53

Their subsequent metalation using zinc acetate gave complexes **Zn-133** and **Zn-134** in excellent yields (Scheme 53). Oxidative coupling of complexes **Zn-133** and **Zn-134** was attempted with $FeCl_3$ but no reactions took place. Treatment of **Zn-133** and **Zn-134** with $Sc(OTf)_3$/DDQ in toluene led to the formation of dozens of products, which were unstable on silica gel. Unfortunately, treatment of the copper analog **Cu-133** with $FeCl_3$ again led to a mixture of very polar products (as evidenced by TLC), suggesting multiple reaction pathways. I hoped that placing electron-donating methoxy- substituents at suitable positions of the coumarin moiety will alter their reactivity. My results showed however, that coumarins with such substitution pattern have similar electron density at position 3 and 5. As a consequence reactions occur at various positions of coumarin skeleton.

In the light of this results, the obvious idea was to block the position 3. In order to perform Pechmann condensation reaction with pyrogallol (**128**), I decided to use 2-acetyl-succinic acid dimethyl ester (**135**) under reaction conditions (p-TsOH) reported by Tanaka.[144] Despite prolonged heating, I observed no consumption of substrates (Scheme 54).

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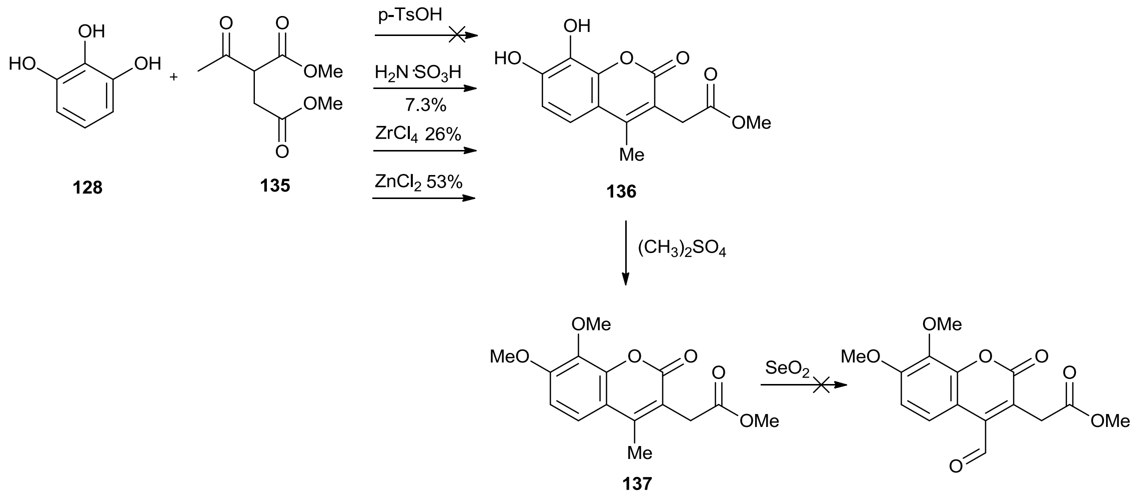
[144] T. Sugino and K. Tanaka, *Chem. Lett.*, 2001, **2**, 110.



Scheme 54

After changing catalyst to $H_2N{\cdot}SO_3H$[139] I obtained desired product in low yield (1.1%) due to incomplete conversion. Modifications of reaction conditions allowed to a complete consumption of substrates, but yield was increased up to 7.3% only. Further literature search revealed another method with the use of zirconium tetrachloride.[145] After three days of heating I obtained pure 3-carbomethoxymethylene-8,9-dihydroxy-4-methylcoumarin (**136**) in 26% yield. The use of another method, with $ZnCl_2$ as catalyst combining with the change of substrates ratio from 1:1 to 1:1.2 (in favor of ester) allowed to increase yield of **136** to 53%. Subsequent methylation with $(CH_3)_2SO_4$ gave coumarin **137** in 91% yield. Oxidation of **137** using SeO_2 failed despite numerous attempts in different solvents and temperatures (chlorobenzene, trichlorobenzene). The most probable explanation of its lack of reactivity is the steric hindrance imparted by methoxycarbonylmethylene group which decreases the reactivity of the methyl group (supposed to be oxidized).

Since oxidation of coumarin **137** failed, I decided to obtain similar, less sterically hindered coumarin having another substituent in position 3, so it could react yielding desired aldehyde. In order to obtain 3-carboethoxy-8,9-dimethoxy-4-methyl-coumarin, I performed reaction of 2,3-dimethoxyphenol (**125**) with dimethyl acetyl malonate (**138**) under classical conditions. Surprisingly, during the reaction

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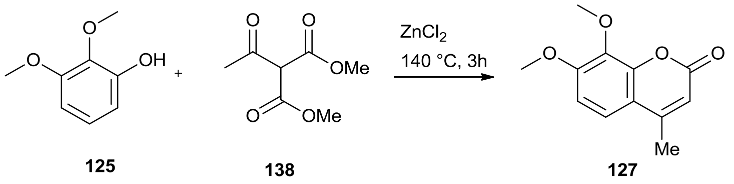
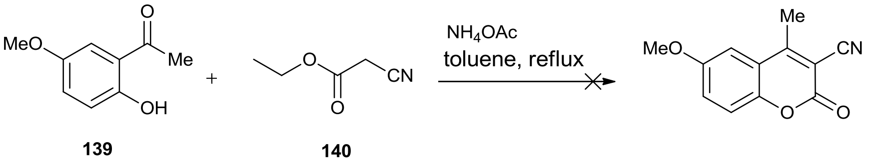
[145] G. Smitha and C. S. Reddy, *Synth. Commun.*, 2004, **34**, 3997.

spontaneous removal of CH_3CO occurred, and I obtained 8,9-dimethoxy-4-methylcoumarin (**127**) only (Scheme 55).



Scheme 55

An another idea was to obtain 3-cyano-4-methyl-6-methoxycoumarin as the building block.[146] It should not interfere with oxidation reaction, comparing to **137**, because of smaller size of cyano group. Therefore, I reacted 2-hydroxy-5-methoxyacetophenone (**139**) with ethyl cyanoacetate (**140**) in the presence of ammonium acetate. No conversion was observed despite of conditions' modification (Scheme 56).



Scheme 56

Finally, I decided to change the structure of key coumarin by adding to its skeleton benzene ring in angular fashion. Benzo[*h*]coumarins possess slightly different electron density comparing to coumarins. I hoped, that this will favor oxidative aromatic coupling at desired position. I synthesized an aldehyde **141**, benzo[*h*]coumarin derivative, using known procedures.[147] A mixed condensation of aldehyde **141** with pyrrole (**75**) and mesitaldehyde (**131**) gave porphyrin **142** in 16% yield. Subsequent metalation with $Ni(acac)_2$ gave the complex **Ni-142** quantitatively, however the latter one was unreactive under the aforementioned conditions

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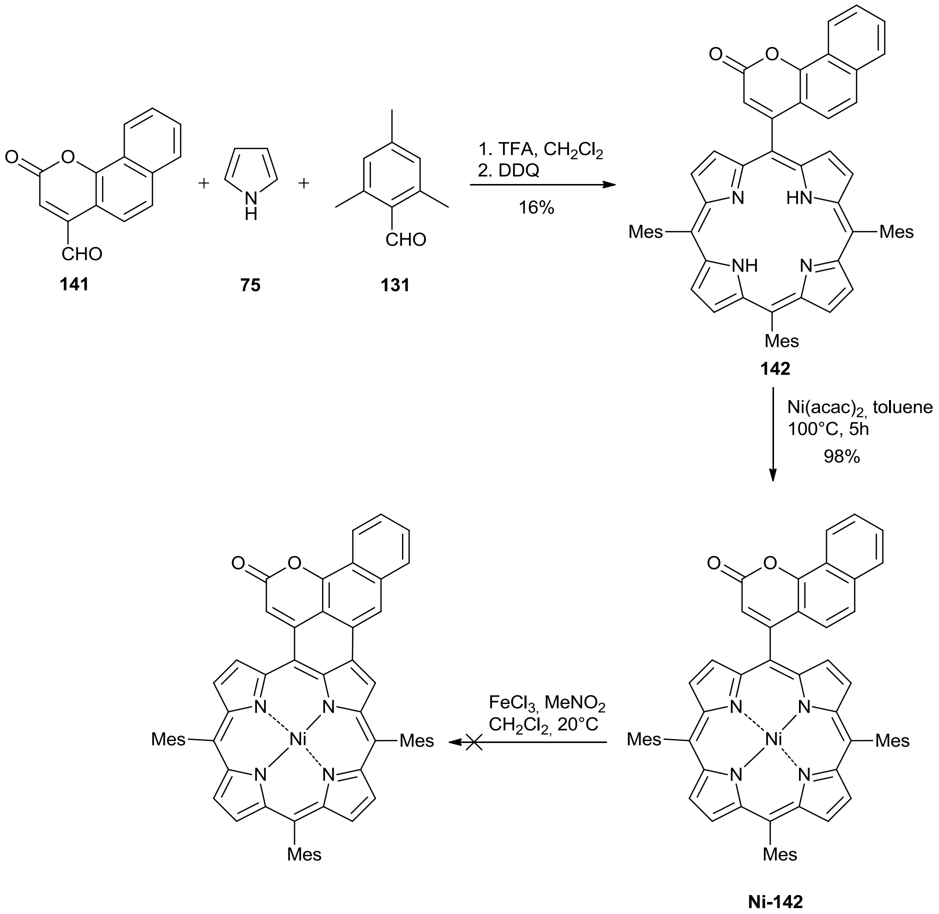
[146] H. M. F. Madkour, *Heterocycles*, 1993, **36**, 947.
[147] M. Ilyas and M. Parveen, *Tetrahedron*, 1996, **52**, 3991.

($FeCl_3/MeNO_2$). The use of other oxidizing reagents such as PIFA/$BF_3(OEt)_2$[39] or DDQ/$Sc(OTf)_3$[32] did not change the output of this reaction (Scheme 57). This is quite surprising in light of the positive results obtained by Imahori[49] with an electron-poor naphthalene-based substituent. Apparently the electron density in the corresponding position of the benzo[*h*]coumarin skeleton is too low to favor the formation of a radical cation, which is a prerequisite for this reaction to occur.



Scheme 57

3.3.3 Studies on naphthalene porphyrins

I was intrigued by the following question: what kind of changes can be introduced by fusion of the porphyrin core with the most fundamental two-ring aromatic unit – naphthalene. Naphthalene-fused porphyrins have been prepared only three times in the past (see Chapter **2.4**).

Naphthalene-fused porphyrinoids are simple systems that allow us to study chemical, spectroscopic, and photophysical effects of this type of π-expansion. I was also intrigued by the relation between the output of oxidative aromatic coupling reactions, the nature of the oxidizing agent and the central metal cation.

3.3.3.1 Synthesis of A_3B-type naphthalene-porphyrins

In analogy to corroles' synthesis I have chosen 4,7-dimethoxy-1-naphthaldehyde (**73**) as a precursor of A_3B-porphyrins, which possesses high electron density at the required position 8 due to the suitably positioned methoxy groups. The protocol describing its synthesis has been mentioned in Chapter 3.2.1 (p. 42). I chose mesitaldehyde (**131**) as the second coupling partner since its presence in porphyrin molecules ensures their high solubility. This aspect is of paramount importance as the products are expected to possess a larger π-electron system, which usually substantially decreases solubility. In addition, aldehyde **131** has a slightly donating character, which may affect the results of oxidative coupling. Moreover, I chose 3,5-difluorobenzaldehyde (**132**) as a second, less sterically hindered aldehyde to investigate. I attempted the synthesis of two porphyrins in parallel using two different methods, depending on steric hinderence of aldehyde.

Literature shows, that porphyrin skeleton can be built *via* acid catalyzed condensation of a dipyrrane-dicarbinol with a dipyrrane followed by oxidation with DDQ.[148] Dicarbinol is obtained by diacylation of the dipyrrane and subsequent reduction. This approach offers good yields, employs minimal chromatography and affords up to gram quantities pure porphyrins.[148] I planned retrosynthesis of 5-(4,7-dimethoxynaphth-1-yl)-10,15,20-tris(3,5-difluorophenyl)porphyrin (Scheme 58).

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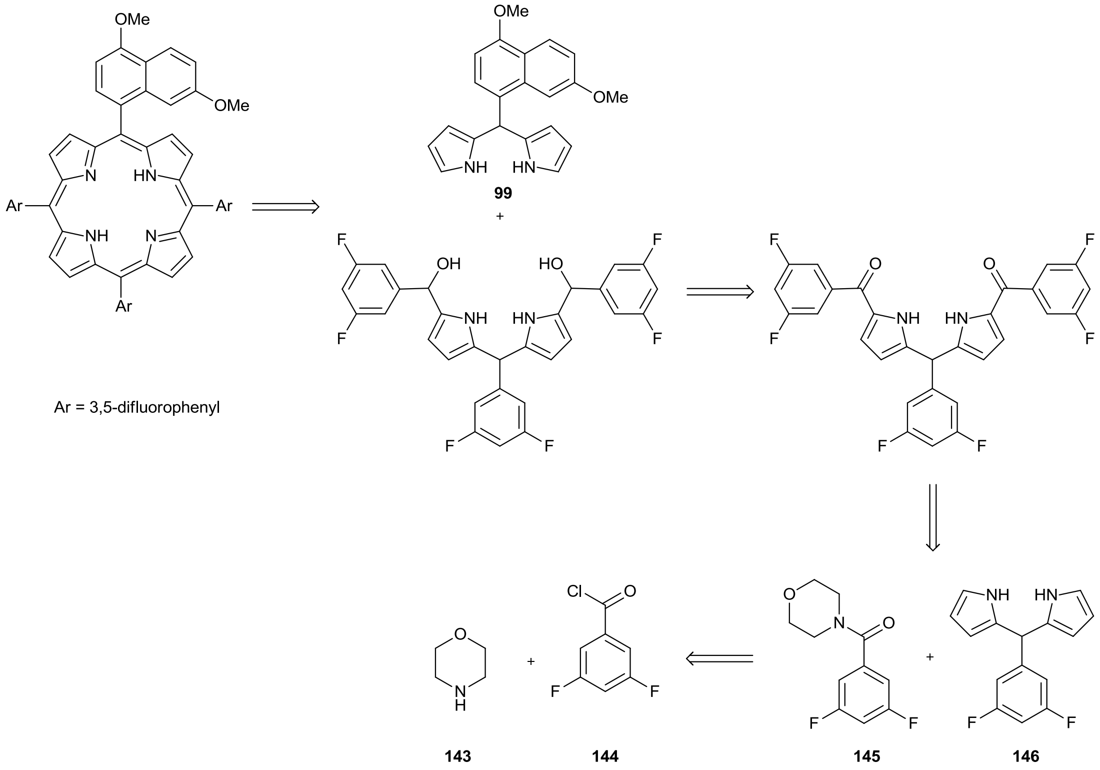
[148] P. D. Rao, S. Dhanalekshmi, B. J. Littler and J. S. Lindsey, *J. Org. Chem.,* 2000, **65**, 7323.



Scheme 58

In the reaction of morpholine (**143**) with 3,5-difluorobenzoyl chloride (**144**) I obtained **145** in 97% yield.[149] 5-(3,5-Difluoro)dipyrrane (**146**) was obtained in 81% yield. I attempted acylation of **146** using literature conditions.[150] Despite several attempts I did not observe the formation of required diketone.

In parallel, I tried to perform a mixed condensation of aldehyde **73**, pyrrole (**75**) and 3,5-mesitaldehyde (**131)** *via* mixed condensation under Lindsey's[142] conditions, catalyzed by trifluoroboron etherate. I obtained the porphyrin **148** in 20% yield (Scheme 59). This porphyrin was subsequently metalated under standard conditions resulting in zinc, copper and nickel complexes in excellent yields. An attempt of zinc porphyrin **Zn-148** oxidation, subjecting to standard conditions ($FeCl_3/CH_3NO_2$, substrate/CH_2Cl_2), gave a distinct green spot on TLC representing probably fused complex **Zn-150**.

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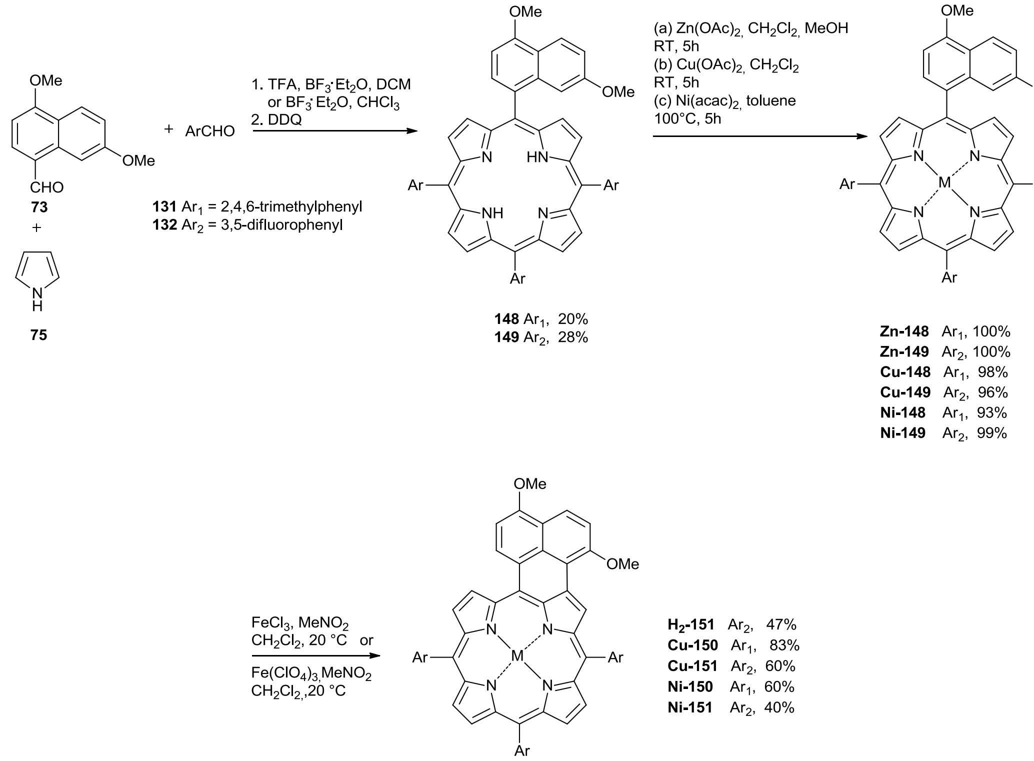
[149] G. R. Pettit, B. Toki, D. L. Herald, P. Verdier-Pinard, M. R. Boyd, E. Hamel and R. K. Pettit, *J. Med. Chem.*, 1998, **41**, 1688.

[150] M. Tasior, B. Koszarna, D. T. Gryko, *J. Porphyrins Phthalocyanines*, 2003, **7**, 239.

Chromatography of that porphyrin revealed its instability, and in spite of many attempts I could not achieve its purification. In light of this result I decided to replace the moderately electron-rich mesityl unit with an electron-neutral 3,5-difluorophenyl. Since previously used method (Scheme 58) did not give positive result, I used a mixed condensation performed under Lindsey's[143] conditions, which gave A_3B-porphyrin **149** in 28% yield (Scheme 59). After transformation into the zinc complex **Zn-149** and subsequent treatment under $FeCl_3/CH_3NO_2$ conditions free-base porphyrin **H$_2$-151** was obtained in 47% yield as green solid, which turned out to be the product of oxidative aromatic coupling followed by demetalation.



Scheme 59

Since zinc complexes proved to be unstable in the presence of a Lewis acid ($FeCl_3$), I focused on copper(II) and nickel(II) complexes, which are significantly more robust. Complexes **Cu-148**, **Cu-149**, **Ni-148**, and **Ni-149** were synthesized using the standard procedure (Scheme 9). I was delighted to see that all four compounds underwent intramolecular oxidative ring closure in the presence of $FeCl_3$ to give **Cu-150**, **Cu-151**, **Ni-150**, and **Ni-151** in 50%, 77%, 86%, 72% yields, respectively, and I observed no demetalation. Unfortunately, fused products were contaminated with mono-chlorinated by-products, which were clearly visible by FD/MS as well as by elemental analysis. This serious problem was mentioned before by Osuka[57] and Anderson.[54] Since separation of these side-products from the desired fused porphyrins is basically impossible, my efforts were directed toward suppressing chlorination. I have chosen porphyrin **Ni-148** as a model, and oxidative aromatic coupling was performed on this compound using various conditions (Table 4).

Replacement of $FeCl_3$ with the standard procedure for preparation of *meso-meso*, *β-β, β-β* triple-fused porphyrins (i.e. DDQ/$Sc(OTf)_3$) led to drastically lower yields (Table 4, entries 4-6). Use of copper (II)[151] or molybdenum (V) salts did not give desired product.

Table 4. Oxidation of porphyrin **Ni-148** into **Ni-150**

Entry	Oxidizing reagent	Solvent	Temp.(°C)	Time(h)	Yield (%)
1	$FeCl_3$	$MeNO_2$/DCM	RT	0.5	86[a]
2	$FeCl_3$/AgOTf	$MeNO_2$/DCM	RT	0.5	80[a]
3	PIFA/$BF_3{\cdot}OEt_2$	toluene	110	5	46
4	DDQ, $Sc(OTf)_3$	toluene	110	72	12.5
5	DDQ, $Sc(OTf)_3$	xylenes	140	72	20
6	DDQ, $Sc(OTf)_3$	1,2-dichlorobenzene	170	72	decomp.
7	$CuCl_2,O_2$/ [*i*PrMgCl·LiCl+TMP]	THF	50	48	0
8	$Mo[O_2CCH(Et)Bu]_x$	DCM	RT	48	0
9	$Fe(acac)_3$	DCM	RT	48	0
10	$K_3[Fe(CN)_6]$	THF/18-crown-6	RT	48	0
11	$Cu(ClO_4)_2$	DCM	RT	48	0
12	$Mn(CH_3COO)_3{\cdot}2H_2O$	DCM	RT	48	14
13	$Fe(ClO_4)_3{\cdot}2H_2O$	$MeNO_2$/DCM	RT	0.33	60

[a] product contaminated with chlorinated impurities

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[151] S. Buscemi and M. Gruttadauria, *Tetrahedron*, 2000, **56**, 999.

Osuka et al. reported that addition of silver triflate suppresses formation of chlorinated fused porphyrins.[37] When applied to my compound, this procedure still resulted in formation of chlorinated impurities (Table 4, entry 2). Testing other oxidation methods suggested that iron perchlorate dihydrate may offer a solution to this problem - indeed, I obtained pure **Ni-150** in 60% yield. The detailed analysis revealed that this time complex Ni-150 is free of any chlorinated side-products. Subsequently I used these conditions for other porphyrins. The reaction with $Fe(ClO_4)_3 \cdot 2H_2O$ gave compounds **Cu-150**, **Cu-151** and **Ni-151** in 83%, 60% and 40% yields, respectively (Scheme 59).

Replacing the typically used $FeCl_3$ with readily available $Fe(ClO_4)_3$ as an oxidizing reagent was an effective strategy for preventing chlorinated by-products.

Purification and characterization of **Cu-150**, **Cu-151**, **Ni-150**, and **Ni-151** proved to be challenging due to their low solubility and tendency to aggregate, but I managed to purify them and obtain satisfying ^{1}H NMR (Ni) or HPLC (Cu) analysis.

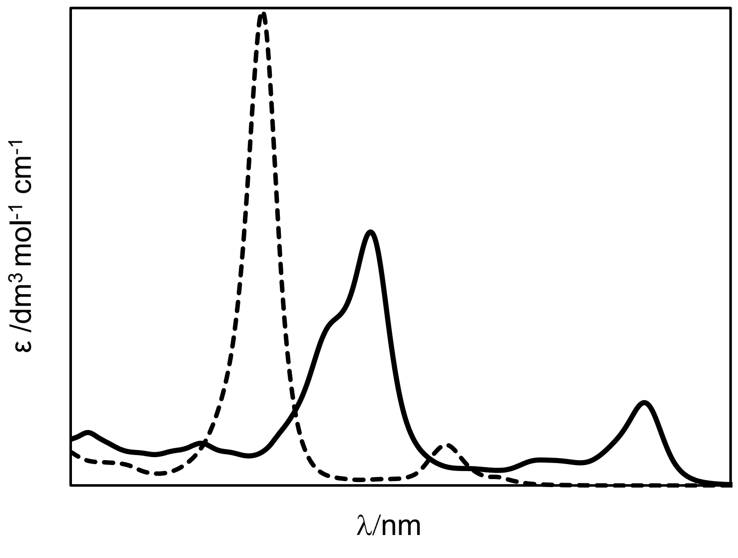


Figure 10. Absorption of **Ni-148** (dotted line) and **Ni-150** (solid line).

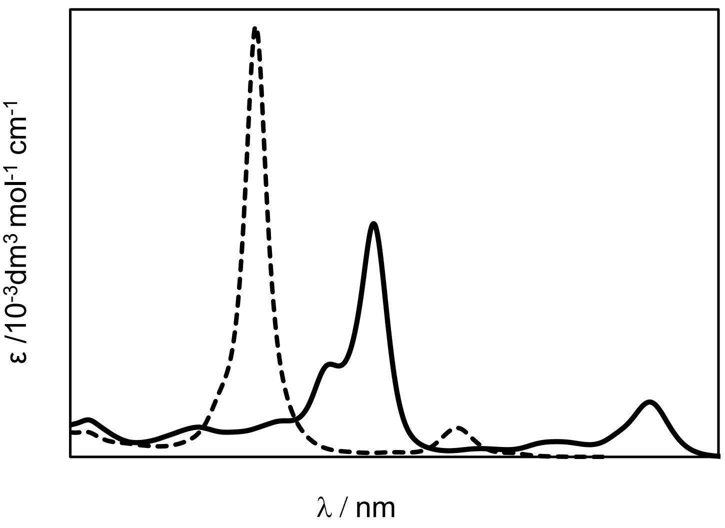


Figure 11**.** Absorption of **Cu-149** (dotted line) and **Cu-151** (solid line)

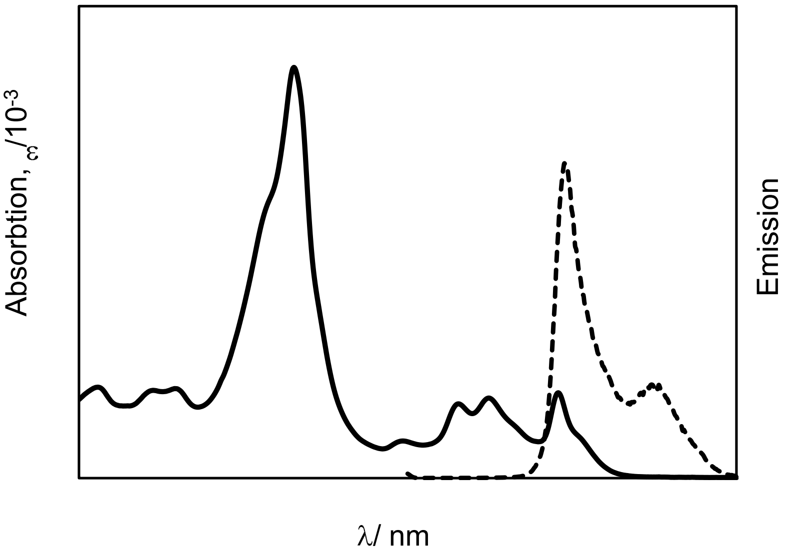


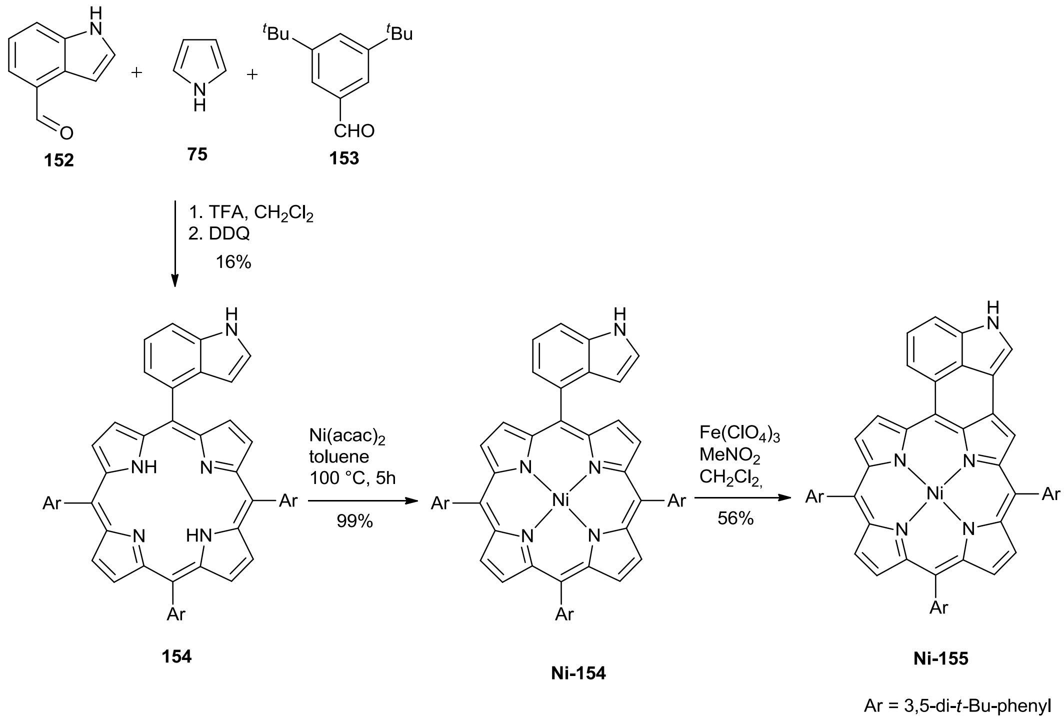
Figure 12. Absorption (solid line) and normalized fluorescence (dotted line) of porphyrin **H_2-151** in CH_2Cl_2.

The striking deep green color of the fused porphyrins has its origin in absorption spectra (Fig. 10-12). The bathochromic shift that resulted from attaching the dimethoxynaphthalene unit at positions 1 and 3 is ~ 60-70 nm for the Soret bands and ~100-130 nm for the Q-bands, depending on the type of complex. For nickel complexes red-shift of Q-bands is higher than for corresponding copper complexes. For both copper and nickel fused-complexes the lowest energy Q-bands are significantly more intense than in case of their non-fused counterparts. In accord with previous findings of Imahori et al. I observed that molar absorptivity at the Soret band of fused porphyrins is lower than that of non-fused porphyrin complexes. At the same time I observed broadening of both Soret and Q-bands. The free-base fused-porphyrin **H_2-151** produces the most complex absorption spectrum (Fig. 12): not only does it possess five well resolved peaks (with additional shoulders), but the lowest energy Q-band has intense ($\varepsilon = 27000$) absorption at 701 nm with a shoulder up to 750 nm. Free base π-expanded porphyrin **H_2-151** displays also fluorescence in the near-infrared region ($\lambda_{max} = 710$ and 760 nm, $\Phi_{fl} = 10\%$).

3.3.4 Studies on A_3B-indoleporphyrin

In parallel, I decided to investigate oxidative coupling of porphyrin bearing one heterocycle moiety at *meso* position. It is rather obvious that aromatic hydrocarbons can be replaced with electron-rich heterocycles in general scheme leading to *meso-β* linked π-extended porphyrins. I have chosen indole as suitable aromatic heterocyclic system which possesses the highest electron density at desired positions. Starting from commercially available indole-4-carboxaldehyde **152** I obtained porphyrin **154**, which was subsequently metalated affording **Ni-154**. The latter one was subsequently oxidized with $Fe(ClO_4)_3 \cdot 2H_2O$ to give porphyrin **Ni-155** in 56% yield (Scheme 60).

Absorption spectrum of fused porphyrin **Ni-155** is similar to that of naphthalene fused porphyrin **Ni-150**.



Scheme 60

3.4 *Trans*-A_2B_2-porphyrins

3.4.1 *Trans*-A_2B_2-porphyrins fused with perylene and fluoranthene

In 2010 Thompson and co-workers presented results of thermal coupling on *trans*-A_2B_2 porphyrin bearing pyrenyl units.[152] It is worth to mention, that the reaction regioselectively provided only the *anti* isomer. This encouraged me to investigate if *trans*-A_2B_2-type peryleneporphyrin also undergoes such type of reaction. I decided to use unfunctionalized perylene in order to maintain porphyrin framework not damaged; the process of heating electron enriched porphyrin up to 500 °C could affect it. The chosen moiety possesses relatively large π-electrons system, which could possibly cause large chromophore extension if fused to porphyrin.

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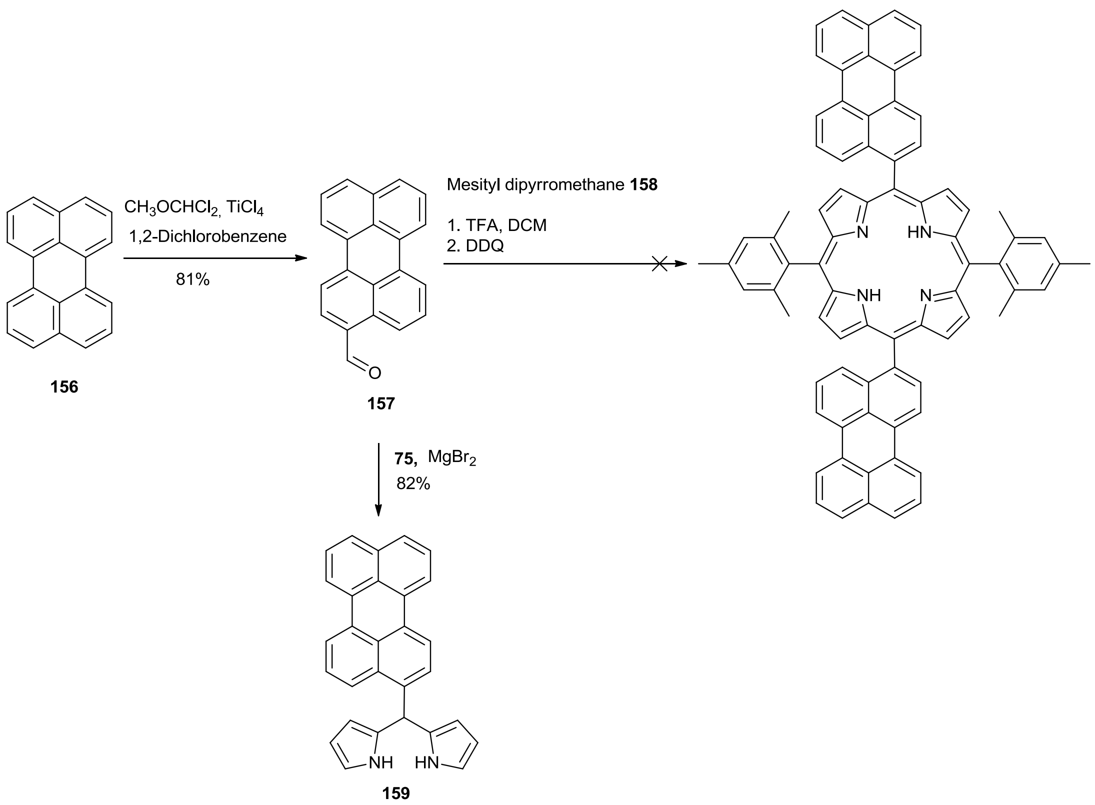
[152] V. Diev and M. Thompson, *6th International Conference on Porphyrins and Phthalocyanines*, USA, poster, 2010.

Firstly, I converted perylene (**156**) into an aldehyde **157**. The starting hydrocarbon was selectively formylated in the position 3 in 81% yield.[153] An attempt to synthesize *trans*-A_2B_2-porphyrin in reaction of aldehyde **156** with mesityl dipyrrane **158** gave no positive results – unreacted aldehyde remained in the mixture and has been recovered (Scheme 61).



Scheme 61

Since perylene-3-carboxyaldehyde turned out to be rather unreactive in porphyrin synthesis, I decided to react mesitaldehyde (**131**) with perylenedipyrrane **159**. Although both aldehydes are sterically-hindered, hence less-reactive, I hoped to achieve better results than in the previous attempts. I prepared **159** in 82% yield (Scheme 61).

Subsequent reaction of dipyrrane **159** with mesitaldehyde (**131**) gave no positive results. Decomposition of perylenedipyrrane occurred while aldehyde **131** remained unreacted. These negative results prompted me to change perylene unit to

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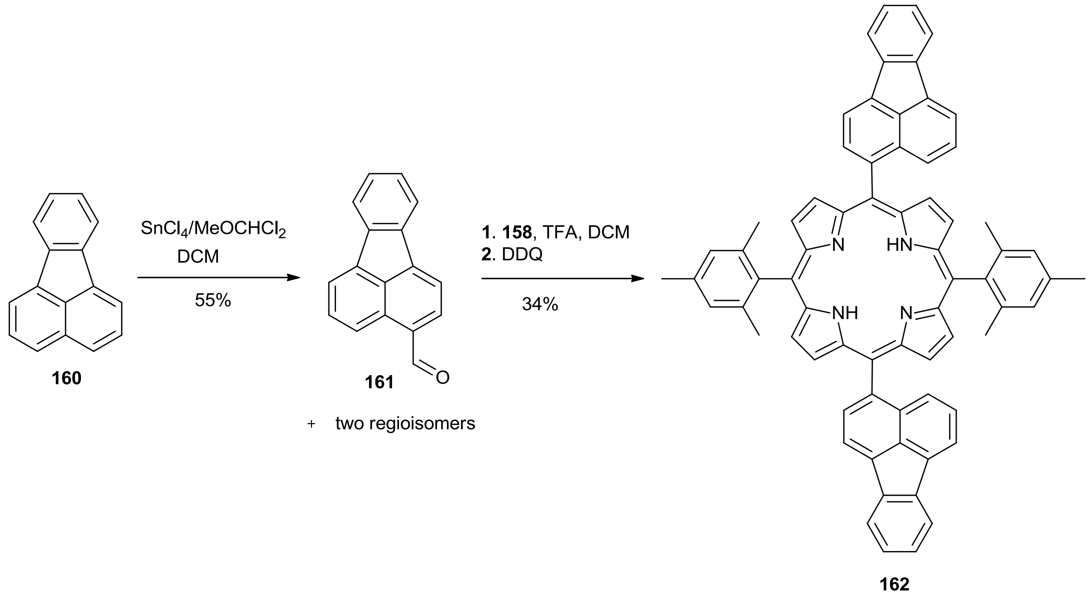
[153] M. V. Skorobogatyi, A. A. Pchelintseva, A. L. Petrunina, I. A. Stepanova, V. L. Andronova, G. A. Galegov, A. D. Malakhov and V. A. Korshun, *Tetrahedron*, 2006, **62**, 1279.

fluoranthene. Fluoranthene moiety also possesses relatively large π-electron system, containing five-membered ring.

I prepared 3-formylfluoranthene **161** according to literature procedure.[154] Purification of the reaction mixture containing three regioisomers can be achieved by crystallization. It gave 3-fluoranthenecarbaldehyde (**161**) in 55% yield, which I used in the synthesis of porphyrin **162** (Scheme 62). Heating the sample of porphyrin **162** in a sealed tube filled with Ar to 500 °C[50] resulted in decomposition. Analysis of black residue showed the presence of fluoranthene.



Scheme 62

Due to the unsuccessful synthesis of *trans*-A_2B_2-peryleneporphyrin and decomposition of **162** during heating I stopped investigation of the thermal approach.

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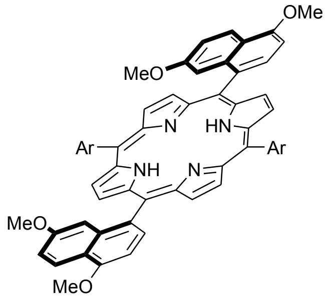
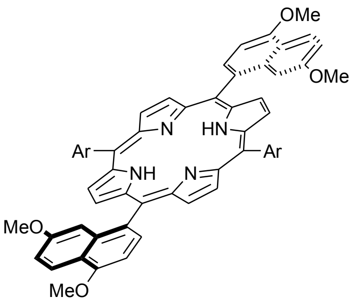
[154] F. I. Carroll, *Org. Prep Proc. Int.*, 1978, **10**, 201.

3.4.2 *Trans*-A_2B_2-naphthalene porphyrin

In the subsequent phase of my research I decided to investigate oxidative coupling of exemplary *trans*-A_2B_2-porphyrin. This approach promises larger bathochromic shift in comparison with porphyrins described in previous Chapter (**3.3**). In order to fuse two aromatic segments directly onto the periphery of the porphyrin unit, I introduced two electron rich 4,7-dimethoxynaphthalene units at positions 10 and 20. The required *trans*-A_2B_2-porphyrin can be obtained in the reaction of mixed condensation of aldehyde **73**, pyrrole and aldehyde **131**, however, the yield is statistically limited. In order to increase the yield, I used an approach reported by Lindsey[155] for synthesis of A_2B_2 porphyrins. Reaction of aldehyde **73** with mesityldipyrrane (**158**) gave porphyrin **163 a/b** as a mixture of two atropisomers in 21% yield. Two main spots were observed on TLC (Fig. 13).



162a



162b

Ar = 2,4,6-trimethylphenyl

Figure 13

Subsequent metalation of mixture **163a** and **163b** gave nickel complex **Ni-163**. The difference on TLC between two atropisomers after metalation occurred even more distinct comparing to free base. I did not attempt their separation because it was obvious that both can give rise to the same two fused π-extended porphyrins. During the oxidation of **Ni-163** using $Fe(ClO_4)_3$ I observed a change of mixture color from purple to green.

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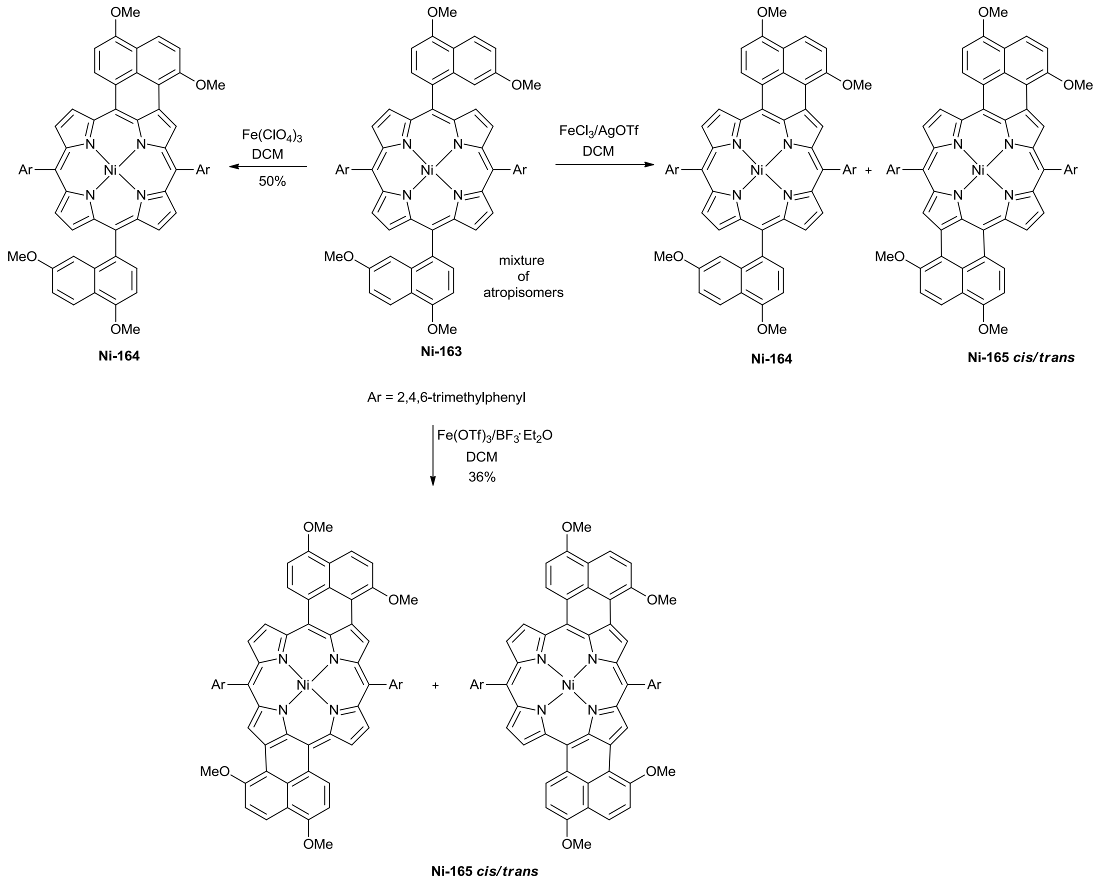
[155] B. J. Littler, Y. Ciringh and J. S. Lindsey *J. Org. Chem.*, 1999, **64**, 2864.

Analysis revealed, that the product, separated in 50% yield, is mono-*meso-β*-fused porphyrin **Ni-164**. It is obvious, but complex Ni-164 is chiral. The lack of free rotation of naphthyl substituent differentiates two sides of the π-conjugated macrocycle. Neither prolonged time of reaction nor increasing amount of oxidant induced second oxidation. The problem with double oxidative coupling of *trans*-A_2B_2-porphyrin has been mentioned already by Anderson.[55] I decided to use the proposed method ($FeCl_3$/$MeNO_2$) to check if double fusion of **Ni-163** is possible. $FeCl_3$ has a great capability to oxidize porphyrins, but side chlorination is unacceptable. In order to avoid this side effect, I added AgOTf to the reaction mixture. This method of suppressing chlorination was published by Osuka[57] while using $AuCl_3$ in oxidation of porphyrin dimers. This approach applied to porphyrin **Ni-163** yielded a mixture of two porphyrins: mono- and bis- fused. Encouraged by this result, I came to conclusion that the effective oxidant in the system $FeCl_3$/AgOTf is actually $Fe(OTf)_3$, formed *in situ*. Therefore, $Fe(OTf)_3$ used directly could serve as a powerful oxidant at the same time this ensures 100% suppressing chlorination. Indeed, the use of it gave fully oxidized porphyrin **Ni-165** *cis/trans* in 36% yield. Further modification was addition of $BF_3{\cdot}Et_2O$, which increases the yield (Scheme 63).



Scheme 63

^{1}H NMR analysis clearly showed the presence of two regioisomers, in contrary to what I expected from literature search, where Osuka claimed regioselectivity of *trans*-A_2B_2 azulenylporphyrin oxidative coupling.[52] Solubility of product was drastically decreased, hence purification proved to be difficult and caused significant lose of product. I could not clearly establish the yield for each regioisomer, because of fruitless separation. TLC, however, showed the minimal difference in R_f values, so I attempted to separate them by HPLC, which also failed.

The color of bis-fused porphyrins **Ni-165** is intensively purple. It is a result of broadened UV-vis spectrum, in which Q band reaches 800nm.

3.4.3. *Trans*-A_2B_2-porphyrin fused with naphthalene and possessing carbon-carbon triple bonds

The next step in extending porphyrin's chromophore was compilation of two approaches: oxidative coupling and carbon – carbon triple bonds introduction into *meso* positions. The latter way has been recently widely investigated.[156] Porphyrin bearing one triple bond possesses ca 20 – 30 nm batochromically shifted spectrum comparing to its analog with no triple bond. I designed new target structure by replacing mesityl groups in porphyrin **163** with TIPS-acetylene moieties. Not only do they participate in extension of chromophore, but also provide sufficient solubility, which matters in case of large plain structures tending to aggregate.

I obtained aldehyde **166** according to literature procedure in 99% yield.[157] Reaction of **166** with dipyrrane **99** under previously used conditions for synthesis **163** gave porphyrin **167** in 5% yield. Modification of another literature procedure[158] allowed to increase the yield up to 43% (Scheme 64).

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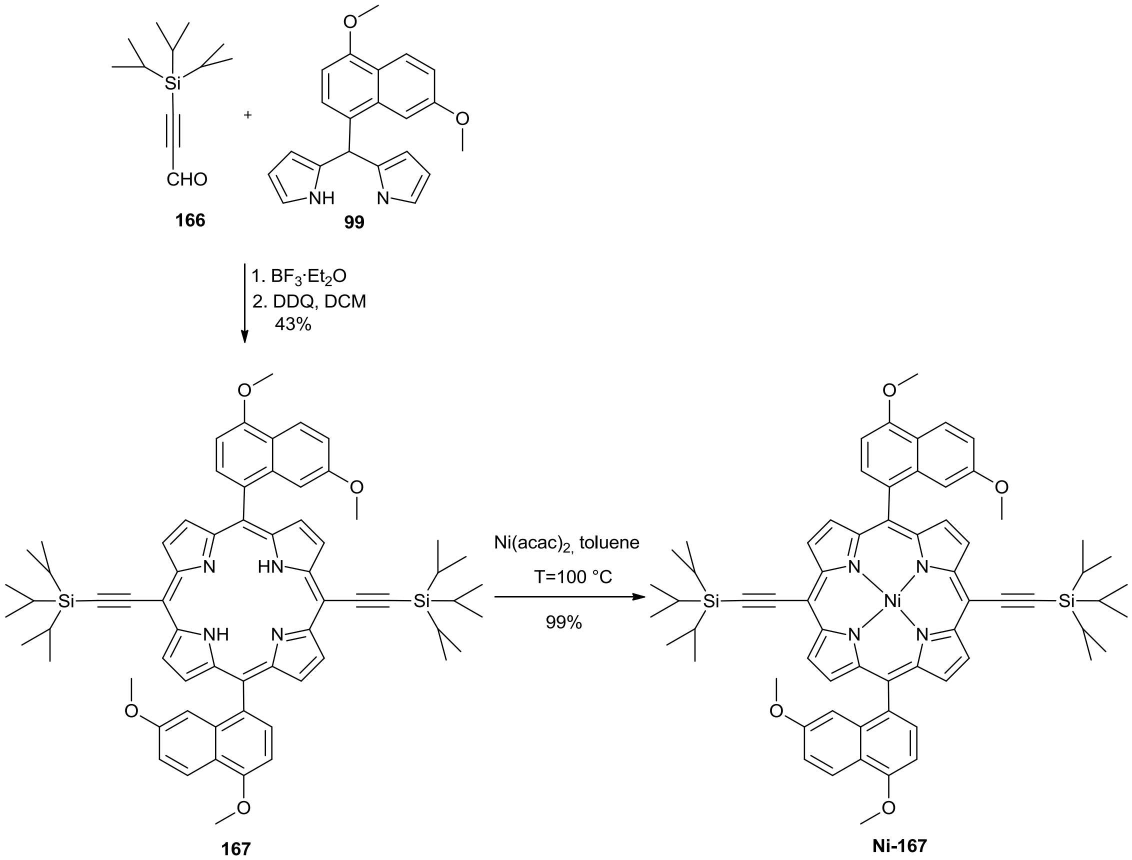
[156] (a) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, 1996, **118**, 1497; (b) M. J. Plater, S. Alken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405; (c) H. L. Anderson, A. P.Wylie and K. Prout, *J. Chem. Soc., Perkin Trans. 1,* 1998, 1607; (d) M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2415.

[157] G. B. Jones, J. M. Wright, G. W. Plourde, G. Hynd, R. S. Huber and J. E. Mathews, *J. Am. Chem. Soc.*, 2000, **122**, 1937.

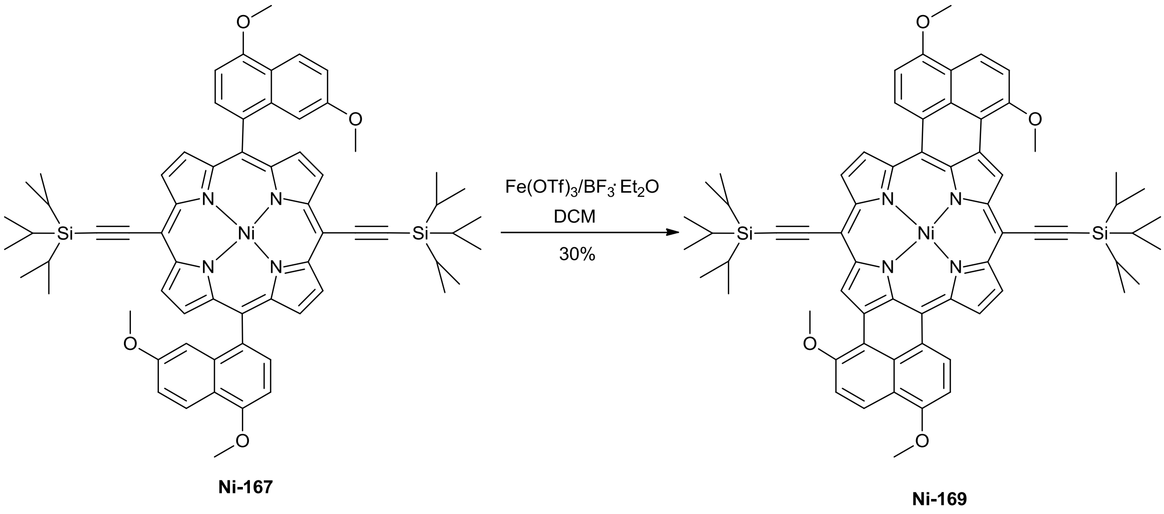
[158] H. L. Anderson, *J. Mater. Chem.*, 2001, **11**, 312.



Scheme 64

Metalation of *trans*-A_2B_2-porphyrin **167** gave nickel complex **Ni-167** in excellent yield. Attempted oxidation with $Fe(ClO_4)_3$ caused change of color from green (which is typical for triple bond extended porphyrin) into violet. This suggested the formation of new bond. Mass spectrum analysis revealed that obtained product was mono-fused **Ni-168**. Replacing the solvent with $C_6H_5CF_3$ and increasing temperature caused no further oxidation.

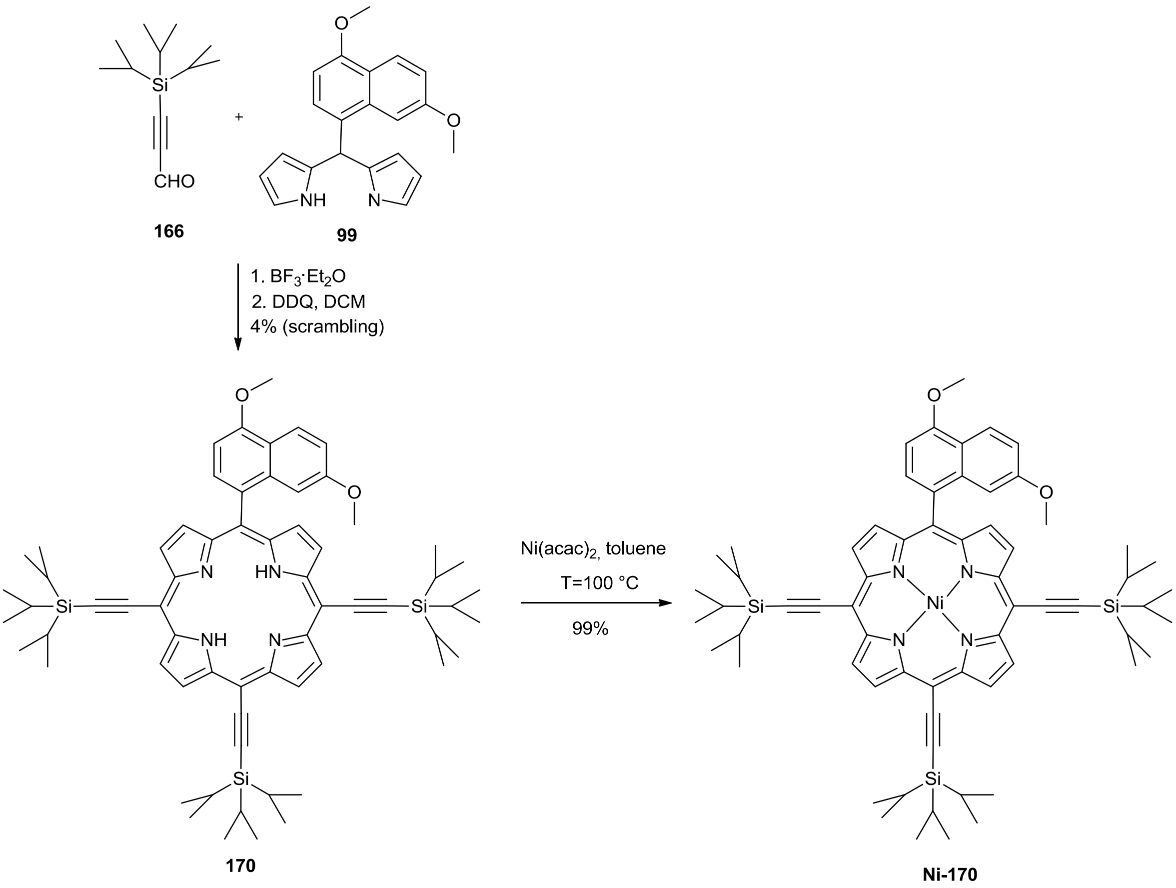
I solved this problem using the same method as described in Chapter 3.4.2. Reaction of porphyrin **Ni-167** with $Fe(OTf)_3$ in the presence of $BF_3{\cdot}Et_2O$ gave bis-fused, pink porphyrin **Ni-169** in 30% yield (Scheme 65). The formation of porphyrin **Ni-169** was proved by mass analysis. ^{1}H NMR spectrum of **Ni-169**, however, showed no sharp but broadened signals with low intensity, which couldn't be assigned. This may be due to radical character of porphyrin **Ni-169**.



Scheme 65

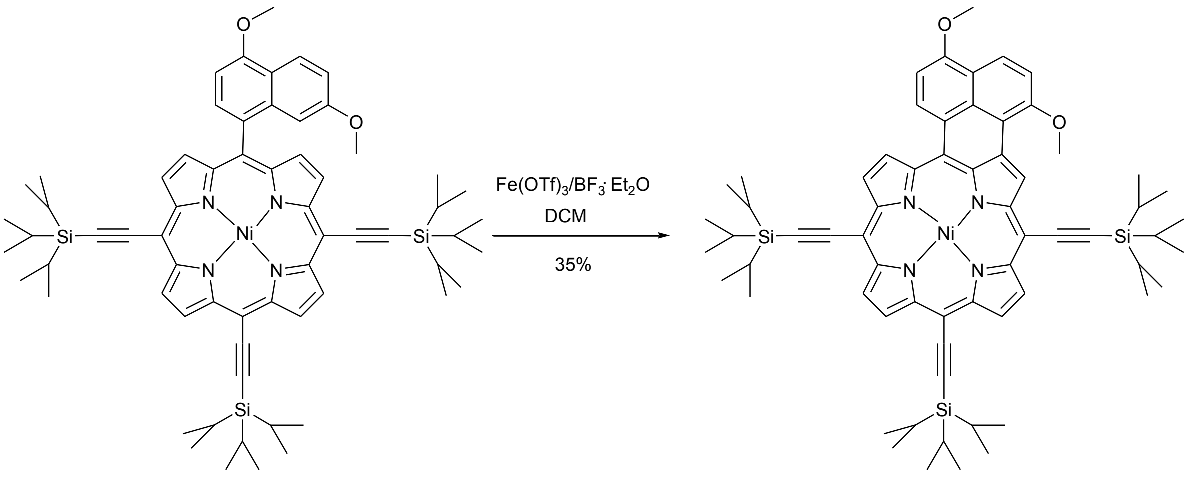
3.4.4 A_3B-Porphyrin fused with naphthalene and TIPS-acetylene

At the same time, I wanted to obtain 5-(4,7-dimethoxynaphthalene)-tris-10,15,20-(triisopropylsillylacetylene)porphyrin (**170**) as a simpler model system. Surprisingly, the separated main side-product of synthesis of **167** turned to be A_3B-porphyrin **170**. This unexpected formation can be explained only by occurrence of scrambling during the reaction. I also approached synthesis of **170** using mixed condensation. Despite few attempts it gave desired porphyrin in 1.1% yield only (Scheme 66).



Scheme 66

After metalation, I subjected nickel complex **Ni-170** to Fe(OTf)$_3$/DCM conditions (Scheme 67). After the entire consumption of substrate, I observed one main product on TLC as a violet spot. TOF MS FD shown weak signal of a fused porphyrin **Ni-171**. ^{1}H NMR analysis, similarly to **Ni-169**, was not readable.



Ni-170 **Ni-171**

Scheme 67

The oxidative aromatic coupling of *trans*–A_2B_2- and A_3B–porphyrins bearing trisopropylsilylethynyl substituents can be performed using $Fe(OTf)_3/BF_3{\cdot}Et_2O$ system. Although the identity of *meso-β*-fused products can be proved using mass spectrometry, their broad NMR spectra suggest that they exist in the form of radical cation or radical. At present state of research the difference in behaviour of **Ni–169** and **Ni–171** versus previously synthesized meso-*β*-fused porphyrins (Chapters **3.3.3**, **3.3.4**) is difficult to understand.

4 Summary and conclusions

Taking into consideration the results presented in this Thesis, I can affirm that all main objectives of my investigation were achieved.

In the first stage of my research, I tried to perform intramolecular oxidative coupling starting from *trans*- and *cis*-A_2B-corroles bearing various two-rings aromatic substituents at *meso*-positions. Numerous compounds composed of corrole moiety and smaller aromatic units such as naphthalene and quinolines were synthesized. These aromatic units were carefully chosen to possess electron-rich or moderately electron-rich character. Although this approach did not led to the final success, the substantial knowledge has been accumulated related to the synthesis of *meso*-substituted corroles from more demanding substrates. I have also proved that structural similarity between corroles and porphyrins is often misleading and that attempts to apply strategies, which proved to be successful in porphyrin chemistry can lead to strikingly different results. This holds true also for condensation of dipyrranes with arylpropargyl aldehydes. I presented that although expected *trans*-A_2B-corroles bearing one arylethynyl substituent at *meso*-position are formed under typical conditions, they are too unstable to be purified. This approach, when applied to the reaction of mestitylpropargylaldehyde diethyl acetal with 5-(pentafluorophenyl)dipyrrane resulted in the formation of unique product probably possessing octaphyrin(1.1.1.0.1.1.1.0) core.

Subsequently, I proved that intramolecular oxidative aromatic coupling can be performed on *meso*-substituted A_3B-porphyrins possessing one electron-rich naphthalenyl substituent. For one of my key achievements I consider the development of $Fe(ClO_4)_3$-mediated protocol for oxidative aromatic coupling, which enables to obtain final *meso*-*β*-fused porphyrins (as copper or nickel complexes) free of contamination with chlorinated side-products. The advantage of $Fe(ClO_4)_3$ over DDQ/$Sc(OTf)_3$ system are consistently high yields. This reagent was, to the best of my knowledge, never used before in oxidative coupling. Among other successes, I synthesized *meso*-*β*-linked indole-porphyrin, which was never done before.

I showed that an analogous approach applied to *trans*-A_2B_2-porphyrins, leads to the formation of singly-fused, chiral naphthalene-porphyrin. During the attempts to force the second oxidative coupling I discovered that iron (III) triflate is another excellent reagent to perform this type of reaction. The use of $Fe(OTf)_3$ allowed me to obtain bis-fused porphyrin as a mixture of regioisomers.

Finally, I focused on *trans*-A_2B_2-porphyrins possessing both suitable naphthalene moieties and ethynyl substituents. These compounds also proved to be prone to oxidative aromatic coupling, although the products displayed different behavior than analogous porphyrins lacking carbon-carbon triple bonds.

In conclusion, the chemistry described in this Dissertation demonstrates that oxidative aromatic coupling of various porphyrinoids is still a developing field, which holds many questions and surprises. It will surely attract interest of chemists for many years to come.

5 Experimental part

5.1 General notes

All chemicals were used as received unless otherwise noted. Reagent grade solvents (DCM, hexanes) were distilled prior use.[159]

Reactions involving air or moisture sensitive reagents were performed under inert atmosphere (Ar).

Reactions progress was controlled by thin layer chromatography (TLC), performed on commercially available aluminum plates covered with silica gel or neutral aluminum oxide (60 F_{254}, Merck). All R_f values are referred to SiO_2.

Chromatography was performed on silica (Kieselgel 60, 200 - 400 mesh, Merck). Dry column vacuum chromatography (DCVC)[160] was performed on preparative thin-layer chromatography silica. Size exclusion chromatography (SEC) was filled with BioRad Bio-Beads SX-1 and eluted with either THF or toluene.

Melting points were measured on Automatic Melting Point Apparatus (EZ-Melt, Stanford Research Systems) and are presented without correction.

All reported NMR spectra were recorded on Varian Mercury 400 MHz, Bruker DRX 500, Varian VNMRS 500 or 600 MHz spectrometers unless otherwise reported. Reported chemical shifts (δ, ppm) were determined relatively to TMS as the internal reference.

UV-vis absorption and fluorescent spectra were recorded on Lambda 25 Spectrometer in THF or DCM.

Mass spectra were obtained on AMD-604, Mariner, 4000 Q-TRAP or GCT Premier via FD-MS or ESI-MS.

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[159] W. L. F. Armarego and C. L. L. Chai , *Purification of laboratory Chemicals*, 4th ed.; Elsevier Science, 2003.

[160] D. S. Pedersen and C. Rosenbohm, *Synthesis*, 2001, 2431.

HPLC was equipped with detector DD UV-VIS and dynamic mixing chamber. The HPLC method for measurement of reaction outcome was as follows: hexanes:AcOEt, 90:10, flow rate 0.5 mL/min., 30 min., λ = 487nm.

5.2 Starting materials for syntheses

Some compounds were synthesized following literature procedures: **69**,[89] **70**,[89] **72**,[89] **73**,[89] **76**,[90] **88**,[96] **89**,[96] **94**,[96] **95**,[96] **97**,[105] **103**,[111] **108**,[116] **115**,[127] **116**,[118] **121,**[131] **123**,[134] **124**,[86] **127**,[140] **129**,[139] **141**,[147] **145**,[149] **157**,[153] and **166**.[157]

Compounds **68**, **70,** **71**, **74**, **75**, **80**, **81**, **82**, **86**, **87**, **91**, **92**, **102**, **105**, **107**, **109**, **112**, **113**, **114**, **119**, **120**, **125**, **126**, **128**, **131**, **132**, **143**, **144**, **152**, **153** were commercially available and used without further purification.

5.3 Syntheses and characterization of obtained compounds

4,7-Dimethoxy-1-naphthaldehyde (73).

1,6-Dihydroxynaphthalene (**71,** 10 g, 62.4 mmol), was added to an aqueous solution (50 ml) of NaOH (5.6 g, 0.14 mmol). The mixture was then cooled to 10 °C and CH_3I (28.56 mL, 0.31 mmol) was added dropwise while stirring. The reaction was heated at reflux for 5 h, then was cooled, water (100 mL) was added and the product was extracted with ether (3x100 mL). The organic layer was washed subsequently with water and saturated aqueous NaCl, dried over K_2CO_3, filtered through a pad of silica to eliminate colored impurities, and evaporated to dryness. The residue was dried in vacuum to give 10.5g of 1,6-dimethoxynaphtalene (**72**) (90%)**.**

To a solution of **72** (7.81 g, 41.5 mmol) in 1,2-dichloroethane (155 mL), *N*-methylformanilide (6.8 mL, 54.75 mmol) and $POCl_3$ (5.00 mL, 54.75 mmol) were added.

The solution was heated at 100 °C for 10 h. After cooling, the mixture was poured into an ice-water mixture. The product was extracted with ether (3x100 mL), and the organic layer was washed with 2 M aqueous HCl (50 mL), dried over Na_2SO_4, filtered, and evaporated. The oily residue after drying in vacuum overnight became solid. Suspending it in small amount of Et_2O, subsequent ultrasonification and filtration gave 3.5 g of pure **73**; combining it with second crop (0.55 g) gave 45% total yield.

10-(2,7-Dimethoxynaphthalen-1-yl)-5,15-bis(pentafluorophenyl)corrole (77).

Method A.

Aldehyde **70** (108 mg, 0.5 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 312 mg, 1 mmol) were dissolved in MeOH (50 mL). Subsequently, a solution of HCl_{aq} (36%, 2.5 mL) in H_2O (50 mL) was added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$ (2x50 mL), and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. DDQ (300 mg, 1.3 mmol) was added, and the mixture was stirred overnight at room temperature. The reaction mixture was concentrated to half the volume and was passed through a column (silica, DCM/hexanes, 1:3). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes, 1:9 → 1:4) afforded title compound as a dark solid. The resulting solid was suspended in hot MeOH, cooled, and filtered to give pure corrole **77** (19 mg, 4.7%).

Method B.

Aldehyde **70** (108 mg, 0.5 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 312 mg, 1 mmol) were dissolved in a pre-prepared solution (8.4 mL) of TFA (10 μL) in DCM (10 mL). After 1h at room temperature the reaction mixture was dissolved in DCM (800 mL) and a solution of DDQ (300 mg, 1.3 mmol) in toluene (3 mL) was added, and the reaction was stirred at room temperature for an additional 0.5h. The reaction mixture was passed through a silica column (silica, DCM/hexanes, 1:3). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes, 1:9 → 1:4) afforded title compound as a dark solid. The resulting solid was suspended in hot MeOH, cooled, and filtered to give pure corrole **77** (73 mg, 18%).

R_f (DCM/hexanes, 1:1) = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ (-3) – (-1) (br s, 3H, NH), 2.87 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.20 (d, 1H, J = 2.5 Hz, naphth.), 7.03 (dd, 1H, J_1 = 2.5, J_2 = 9 Hz, naphth.), 7.54 (d, 1H, J = 9.1 Hz, naphth.), 7.94 (d, 1H, J = 9.1 Hz, naphth.), 8.20 (d, 1H, J = 9.0 Hz, naphth.), 8.41 (d, 2H, J = 4.6 Hz, β-H), 8.53 (d, 2H, J = 3.2 Hz, β-H), 8.58 (d, 2H, J = 4.8 Hz, β-H), 9.07 (d, 2H, J = 4.3 Hz, β-H); HRMS (FD): [M^+] 816.1606 $C_{43}H_{22}F_{10}N_4O_2$ requires: 816.1583. Anal. Calcd. for $C_{43}H_{22}F_{10}N_4O_2$: C, 63.24; H, 2.72; F, 23.26, N, 6.86. Found: 63.01; H, 2.78; F, 23.18, N, 6.97.

10-(4,7-Dimethoxynaphthalen-1-yl)-5,15-bis(pentafluorophenyl)corrole (78).

Method A.

Aldehyde **73** (108 mg, 0.5 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 312 mg, 1 mmol) were dissolved in MeOH (50 mL). Subsequently, a solution of HCl_{aq} (36%, 2.5 mL) in H_2O (50 mL) was added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$ (2x50mL), and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. DDQ (300 mg, 1.3 mmol) was added, and the mixture was stirred for 0.5h at room temperature. The reaction mixture was concentrated to half the volume and was passed through a silica column (silica, DCM/hexanes, 1:1). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes, 1:4) afforded title compound as a dark solid. The resulting solid was precipitated from hot DCM by adding cyclohexane. Crystals were filtered off and dried in vacuum to give 115 mg of pure corrole **78** (28%).

Method B. Aldehyde **73** (108 mg, 0.5 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 312 mg, 1 mmol) were dissolved in a pre-prepared solution (8.4 mL) of TFA (10 μL) in DCM (10 mL). After 1h at room temperature the reaction mixture was dissolved in DCM (800 mL) and a solution of DDQ (300 mg, 1.3 mmol) in toluene (3 mL) was added, and the reaction was stirred at room temperature for an additional

0.5 h. The reaction mixture was passed through a silica column (silica, DCM/hexanes 1:1). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes 1:4) afforded title compound as a dark solid. The resulting solid was precipitated from hot DCM by adding cyclohexane. Crystals were filtered off and dried in vacuum to give 41 mg of pure corrole **78** (10%).

R_f (DCM/hexanes, 1:1) = 0.57; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ (-2.5) – (-1) (br s, 3H, NH), 2.94 (s, 3H, OCH_3), 4.24 (s, 3H, OCH_3), 6.47 (d, 1H, J = 2.3 Hz, naphth.), 7.08 (d, 1H, J = 7.9 Hz, naphth.), 7.15 (dd, 1H, J_1 = 2.5, J_2 = 9.3 Hz, naphth.), 8.02 (d, 1H, J = 7.9 Hz, naphth.), 8.46 (d, 1H, J = 9.3 Hz, naphth.), 8.50 (d, 2H, J = 4.6 Hz, β-H), 8.56 (br s, 2H, β-H), 8.60 (d, 2H, J = 4.4 Hz, β-H), 9.10 (d, 2H, J = 4.0 Hz, β-H); HRMS (ESI): [MH^+] 817.1678 $C_{43}H_{23}F_{10}N_4O_2$ requires: 817.1655. Anal. Calcd. for $C_{43}H_{22}F_{10}N_4O_2$: C, 63.24; H, 2.72; N, 6.86. Found: 63.33; H, 2.70; N, 6.71.

[10-(4,7-Dimethoxynaphthalen-1-yl)-5,10-bis(pentafluorophenyl)corrolato] copper (Cu-78).

Corrole **78** (50 mg, 61 μmol) was dissolved in 10 mL of DCM/MeOH = 1:1 mixture and $Cu(OAc)_2$ (240 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature overnight. The crude product was passed through a short silica gel column with dichloromethane as eluent. The resulting solution was rotary evaporated to dryness and the resulting solid was crystallized from hot DCM by adding hexanes affording 53 mg of complex **Cu-78** (99%).

R_f (DCM/hexanes, 1:1) = 0.71; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.59 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3), 6.79 (d, 1H, J = 8 Hz, naphth.), 6.87 (d, 1H, J = 2.4 Hz, naphth.), 7.01 (d, 2H, J = 4.6 Hz, β-H), 7.10-7.12 (m, 3H, 2 β-H, 1 naphth.), 7.42 (d, 2H, J = 3.8 Hz, β-H), 7.52 (d, 1H, J = 8 Hz, naphth.), 7.96 (d, 2H, J = 4.4 Hz, β-H), 8.25 (d, 1H, J = 9.2 Hz, naphth.), HRMS (TOF MS FD): [M^+] 876.0599 $C_{43}H_{19}CuF_{10}N_4O_2$ requires: 876.0644; Anal. Calcd. for $C_{43}H_{19}CuF_{10}N_4O_2$: C, 58.88; H, 2.18; N, 6.39. Found: C, 58.43; H, 2.42; N, 6.36. UV-vis (DCM) λ 401, 558 nm.

Fused corrole Cu-79.

Complex **Cu-78** (8.8 mg, 0.01 mmol) was dissolved in dry DCM (4 mL) and $FeCl_3$ (16 mg, 0.1 mmol) in $MeNO_2$ (2 mL) was added via syringe within 5 min. After 20 min. additional portion of $FeCl_3$ (16 mg, 0.1 mmol) in $MeNO_2$ (2 mL) was added. The reaction was filtrated directly through a pad of silica. Collected green fraction was evaporated and subsequently submitted to analysis. Further purification turned to be impossible due to complete decomposition under air and light exposition. R_f (DCM/hexanes, 1:1) = 0.65; LRMS (ESI): [M^+] 874.1 $C_{43}H_{19}CuF_{10}N_4O_2$ requires: 874.3; UV-vis (DCM) λ 504, 626, 670, 800 nm.

(6,8-Dimethoxy-2-(*p*-tolyl)quinolin-4-yl)carboxylic acid (83).

p-Toulaldehyde (**81**, 1.2 g, 10 mmol), pyruvic acid, (**82**, 880 mg, 10 mmol) were dissolved in EtOH (99.9%, 6 mL) The mixture was heated at 80 °C for 20 min. Solution of 2,4–dimethoxy-aniline (**80**, 1.53 g, 10 mmol) in EtOH (4 mL) was added over 30 min. in four portions. Heating continued for the next 3 h and the mixture was left stirring for the night. The reaction mixture was poured on NaOH (1 g) in H_2O (50 mL) solution and extracted exhaustively with Et_2O (3x100 mL). Water layer was mixed with glacial acetic acid (10 mL) and stirred for 2 h. The resulting precipitate was filtered off and dried in vacuum to give 865 mg of pure acid **83** (27%). R_f (DCM/acetone, 9:1) = 0.30; ^{1}H NMR (400 MHz, DMSO-d_6, Me_4Si, ppm) δ 2.39 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 6.91 (d, 1H, J = 2.5 Hz, quin.), 7.35 (d, 2H, J = 8.1 Hz, tolyl), 7.67 (d, 1H, J = 2.5 Hz, quin.), 8.14 (d, 2H, J = 8.3 Hz, tolyl), 8.43 (s, 1H, quin.), 13.78 (br s, 1H, COOH); ^{13}C NMR (100 MHz, DMSO-d_6, Me_4Si, ppm) 20.9, 55.4, 56.0, 95.1, 101.8, 119.7, 125.5, 126.7, 129.5, 133.4, 135.5, 137.3, 138.9, 151.4, 156.4, 158.8, 167.9. HRMS (EI): [$M^{\cdot +}$] 323.1168 $C_{19}H_{17}NO_4$ requires: 323.1157. Anal. Calcd. for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.37; H, 5.37; N, 4.40.

(6,8-Dimethoxy-2-(*p*-tolyl)-quinolin-4-yl)-methanol (83a).

To a solution of acid (**83**, 840 mg, 2.6 mmol) in a freshly distilled THF (20 mL), LAH (148 mg, 3.9 mmol) was added in ten portions while stirring. After 3 h, reaction was quenched by NH_4Cl (saturated solution, 30 mL), filtrated and washed with EtOAc. Combined filtrates were dried over $MgSO_4$. Evaporation gave crude **83a**, which was then recrystallized from hot EtOH to give 637 mg of **83a** (79%). R_f (DCM/acetone, 95:5) = 0.50; ^1H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.38 (s, 3H, CH_3), 3.09 (br s, 1H, OH), 3.81 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.90 (s, 2H, CH_2), 6.51 (d, 1H, $J = 2.3$ Hz, quin.), 6.66 (d, 1H, $J = 2.3$ Hz, quin.), 7.22 (d, 2H, $J = 8.0$ Hz, tolyl), 7.66 (s, 1H, quin.), 7.91 (d, 2H, $J = 8.0$ Hz, tolyl); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.3, 55.3, 56.1, 62.35, 92.8, 101.1, 116.5, 126.3, 127.0, 129.3, 135.9, 136.3, 138.9, 145.4, 153.1, 156.4, 158.0. HRMS (EI): $[M^{\cdot +}]$ 309.1359 $C_{19}H_{19}NO_3$ requires: 309.1365. Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.67; H, 6.21; N, 4.37**.**

6,8-Dimethoxy-2-(*p*-tolyl)-quinoline-4-carbaldehyde (84).

To a solution of alcohol **83a** (618 mg, 2 mmol) in dioxane (15 mL), SeO_2 (550 mg, 5 mmol) was added. The reaction mixture was heated for 4 h at 70 °C. Filtration, evaporation and drying in vacuum afforded 450 mg of **84** (73%). ^1H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.43 (s, 3H, CH_3), 3.99 (s, 3H, OCH_3), 4.08 (s, 3H, OCH_3), 6.80 (d, 1H, $J = 2.5$ Hz, quin.), 7.33 (d, 2H, $J = 8.0$ Hz, tolyl), 8.03 (d, 1H, $J = 2.5$ Hz, quin.), 8.10 (d, 2H, $J = 8.0$ Hz, tolyl), 8.22 (s, 1H, quin.), 10.5 (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.3, 55.7, 56.3, 94.2, 102.2, 125.0, 125.9, 127.0, 129.7, 135.7, 136.1, 138.4, 139.5, 153.4, 156.5, 161.1, 193.6. HRMS (EI): $[M^{\cdot +}]$ 307.1218 $C_{19}H_{17}NO_3$ requires: 307.1208.

10-(6,8-Dimethoxy-2-(*p*-tolyl)-quinolin-4-yl)-5,15-bis(pentafluorophenyl)corrole (85).

Aldehyde **84** (87 mg, 0.285 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 178 mg, 0.57 mmol) were dissolved in DCM (18 mL). To the resulting mixture TFA (66 μL, 0.85 mmol) was added and the reaction mixture was stirred for 25 min. Subsequently NEt_3 (135 μL) was added and, after diluting with DCM to 300 mL, solution of DDQ (180 mg, 0.8 mmol) in toluene (4 mL) was added, and the reaction was stirred at room temperature for a further 0.5 h. The reaction mixture was passed through a silica pad (silica, DCM/hexanes, 1:1). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, toluene/EtOAc, 95:5) afforded title compound as a purple solid. The resulting solid was precipitated from hot DCM by adding cyclohexane. Crystals were filtered off and dried in vacuum to give 29 mg of pure corrole **85** (11%). R_f (toluene/EtOAc, 95:5) = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.42 (s, 3H, CH_3), 2.95 (s, 3H, OCH_3), 4.22 (s, 3H, OCH_3), 6.77 (d, 1H, J = 2.0, quin.), 7.32 (d, 2H, J = 8.1 Hz, tolyl), 8.23 (d, 2H, J = 7.3 Hz, tolyl), 8.51 (br s, 2H, β-H), 8.56 – 8.58 (br s, 4H, 2 β-H, 2 quin.), 8.67 (br s, 2H, β-H), 9.13 (br s, 2H, β-H). Despite a few attempts it turned to be not possible to obtain MS analysis; corrole **85** decomposes during measurement.

10-(6-Methoxyquinolin-4-yl)-5,15-bis(pentafluorophenyl)corrole (90).

Aldehyde **89** (160 mg, 0.85 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 530 mg, 1.7 mmol) were dissolved in DCM (55 mL). To the resulting mixture TFA (200 μL, 2.55 mmol) was added and the reaction mixture was stirred for 30 min. Subsequently NEt_3 (400 μL) was added and, after diluting with DCM to 300 mL of volume, solution of DDQ (550 mg, 2.38 mmol) in toluene (10 mL) was added, and the reaction was stirred at room temperature for a further 0.5 h. The reaction mixture was passed through a silica pad (silica, DCM/acetone, 9:1). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/acetone, 9:1) afforded title compound as a dark solid. The resulting solid was precipitated from hot DCM by adding hexanes. Crystals were filtered off and dried in vacuum to give 75 mg of pure corrole **90** (11.2%). R$_f$ (DCM/acetone, 95:5) = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ (-2.5) – (-1) (br s, 3H, NH), 3.01 (s, 3H, OCH_3), 6.54 (s, 1H, quin.), 7.45 (dd, 1H, J_1 = 2.5, J_2 = 9.5 Hz, quin.), 8.10 (d, 1H, J = 4.0 Hz, quin.), 8.36 (br s, 1H, quin.), 8.39 (d, 2H, J = 5 Hz, β-H), 8.59 (d, 2H, J = 3.0 Hz, β-H), 8.66 (d, 2H, J = 4.5 Hz, β-H), 9.08 (d, 1H, J = 4.5 Hz, quin.), 9.14 (d, 2H, J = 4.0 Hz, β-H); HRMS (TOF MS FD): [M$^+$]: 787.1420 $C_{41}H_{19}N_5OF_{10}$ requires: 787.1430. Anal. Calcd. for $C_{41}H_{19}N_5OF_{10}$: C, 62.52; H, 2.43; F, 24.12; N, 8.89. Found: C, 62.35; H, 2.68; F, 24.09; N, 8.77.

[10-(6-Methoxyquinolin-4-yl)-5,15-bis(pentafluorophenyl)corrolato]copper (Cu-90).

Corrole **90** (55 mg, 70 μmol) was dissolved in 12 mL of $CHCl_3$/MeOH = 1:1 mixture and $Cu(OAc)_2$ (250 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature overnight. The crude product was passed through a short silica gel column with dichloromethane as eluent. The resulting solution was rotary evaporated to dryness and the resulting solid was crystallized from hot DCM by adding hexanes afforcing 57 mg of corrole **Cu-90** (96%). R$_f$ (DCM/acetone, 95:5) = 0.63; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.67 (s, 3H, OCH_3), 6.85 (br s, 3H, quin.), 7.14 (br s, 2H, quin.), 7.42 (br s, 4H, β-H), 8.02 (br s, 4H, β-H); HRMS (TOF MS FD): [M$^+$]: 847.0458 $C_{41}H_{16}N_5OF_{10}Cu$ requires: 847.0491.

10-(8-Methoxyquinolin-4-yl)-5,15-bis(pentafluorophenyl)corrole (96).

Aldehyde **95** (160 mg, 0.85 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 530 mg, 1.7 mmol) were dissolved in DCM (55 mL). To the resulting mixture TFA (200 μL) was added and the reaction mixture was stirred for 30 min. Subsequently NEt_3 (400 μL)was added and, after diluting with DCM to 300 mL, solution of DDQ (550 mg, 2.38 mmol) in toluene (10 mL) was added, and the reaction was stirred at room temperature for a further 0.5 h. The reaction mixture was passed through a silica pad (silica, DCM/acetone, 95:5). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/acetone, 95:5) afforded title compound as a dark solid. The resulting solid was precipitated from hot DCM by adding hexanes. Crystals were filtered off and dried in vacuum to give 121 mg of corrole **96** (18%). R_f (DCM/MeOH 99:1) = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ (-3) – (-1) (br s, 3H, NH), 3.00 (s, 3H, OCH_3), 6.52 (d, 1H, J = 2.8 Hz, quin.), 7.42 (dd, 1H, J_1 = 2.8, J_2 = 9.4 Hz, quin.), 8.04 (d, 1H, J = 4.2 Hz, quin.), 8.24 (d, 1H, J = 9.4 Hz, quin.), 8.41 (d, 2H, J = 4.8 Hz, β-H), 8.59 (d, 2H, J = 4.1 Hz, β-H), 8.65 (d, 2H, J = 4.6 Hz, β-H), 9.07 (d, 1H, J = 4.2 Hz, quin.), 9.14 (d, 2H, J = 4.3 Hz, β-H); HRMS (TOF MS FD): [M^+]: 787.1457 $C_{41}H_{19}N_5OF_{10}$ requires: 787.1430. UV-vis (THF) λ 328, 412, 566, 609 nm.

[10-(8-Methoxyquinolin-4-yl)-5,10-bis(pentafluorophenyl)corrolato]copper (Cu-96).

Corrole **96** (55 mg, 70 μmol) was dissolved in 12 mL of $CHCl_3$/MeOH = 1:1 mixture and $Cu(OAc)_2$ (240 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature overnight. The crude product was passed through a short silica gel column with dichloromethane as eluent. The resulting solution was rotary evaporated to dryness and the resulting solid was crystallized from hot DCM by adding hexanes affording 20 mg of corrole **Cu-96** (34%). R_f (DCM/MeOH, 99:1) = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.60 (s, 3H, OCH_3), 6.55 (d, 1H, J = 2.4 Hz, quin.), 7.40 (dd, 1H, J_1 = 2.4, J_2 = 9.2 Hz, quin.), 8.04 (d, 1H, J = 4.0 Hz, quin.), 8.26 (d, 1H, J = 9.2 Hz, quin.), 7.56 (br s, 4H, β-H), 8.15 (br s, 4H, β-H), 8.27 (d, 1H, J = 4.0 Hz, quin.); HRMS (TOF MS FD): [M^+]: 847.0459 $C_{41}H_{16}N_5OF_{10}Cu$ requires: 847.0491.

[10-(2,7-Dimethoxynaphthalen-1-yl)-5,10-bis(pentafluorophenyl)corrolato]silver (Ag-77).

Corrole **77** (81.6 mg, 0.1 mmol) was dissolved in 10 mL of pyridine and AgOAc (55 mg, 0.33 mol) was added. The reaction mixture was stirred at 100 °C overnight. The crude product was passed through Celite. Flash column chromatography

(DCM/hexanes, 1:1) afforded title compound as red solid, which was then crystallized from hot DCM by adding hexanes affording 71 mg of corrole **Ag-77** (77%). R*f* (DCM/hexanes, 1:1) = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.85 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 6.10 (d, 1H, *J* = 2.5 Hz, naphth.), 7.04 (dd, 1H, J_1 = 2.5, J_2 = 9 Hz, naphth.), 7.57 (d, 1H, *J* = 9.1 Hz, naphth.), 7.98 (d, 1H, *J* = 9 Hz, naphth.), 8.24 (d, 1H, *J* = 9.1 Hz, naphth.), 8.59 (d, 2H, *J* = 4.8 Hz, *β*-H), 8.74 (d, 2H, *J* = 4.35 Hz, *β*-H), 8.77 (d, 2H, *J* = 4.6 Hz, *β*-H), 9.32 (d, 2H, *J* = 4.5 Hz, *β*-H); HRMS (ESI): [MH^+] 920.042 $C_{43}H_{19}N_4O_2F_{10}Ag$ requires: 920.039.

[10-(4,7-Dimethoxynaphthalen-1-yl)-5,10-bis(pentafluorophenyl)corrolato]silver (Ag-78).

Corrole **78** (81.6 mg, 0.1 μmol) was dissolved in 10 mL of pyridine and AgOAc (55 mg, 0.33 mmol) was added. The reaction mixture was stirred at 100 °C overnight. The crude product passed through Celite. Flash column chromatography (DCM/hexanes, 1:1) afforded title compound as red solid, which was then crystallized from hot DCM by adding hexanes affording 75 mg of corrole **Ag-78** (81%). R*f* (DCM/hexanes, 1:1) = 0.68; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.94 (s, 3H, OCH_3), 4.28 (s, 3H, OCH_3), 6.44 (d, 1H, *J* = 2.5 Hz, naphth.), 7.10 (d, 1H, *J* = 7.9 Hz, naphth.), 7.16 (dd, 1H, J_1 = 2.5, J_2 = 9.5 Hz, naphth.), 8.06 (d, 1H, *J* = 7.8 Hz, naphth.), 8.48 (d, 1H, *J* = 9.3 Hz, naphth.), 8.68 (d, 2H, *J* = 4.8 Hz, *β*-H), 8.76 (d, 2H, *J* = 4.4 Hz, *β*-H), 8.79 (d, 2H, *J* = 4.6 Hz, *β*-H), 9.34 (d, 2H, *J* = 4.5 Hz, *β*-H); HRMS (ESI): [M^+] 920.044 $C_{43}H_{19}N_4O_2F_{10}Ag$ requires: 920.039.

5-(4,7-Dimethoxynaphthalen-1-yl)-10,15-bis(pentafluorophenyl)corrole (98).

Method A.

Tripyrromethane **97** (224 mg, 0.40 mmol), aldehyde **73** (86 mg, 0.40 mmol) and pyrrole (**75**, 28 μL, 0.4 mmol) were dissolved in a pre-prepared solution (7.5 mL) of TFA (10 μL, 0.13 mmol) in DCM (10 mL). After 1.5 h at room temperature, the reaction mixture was dissolved in DCM (300 mL) and a solution of DDQ (236 mg, 1.04 mmol) in toluene (4 mL) was added, and the reaction mixture was stirred for a further 5 min. Subsequently, the reaction mixture was passed through a silica column (silica, DCM/hexanes, 4:1). All fractions containing corrole were combined and evaporated to the dryness. Flash column chromatography (silica, DCM/hexanes, 1:3 → 1:1) afforded contaminated title compound. Second chromatography (silica, DCM/hexanes, 1:1) afforded almost pure required corrole as a dark solid, which was subsequently purified using SEC (THF). Fraction containing fluorescent compound was collected and evaporated. The resulting solid was precipitated from hot DCM by adding cyclohexane. Crystals were filtered off and dried in vacuum to give 8 mg of corrole **98** (2.5%).

Method B.

Aldehyde **74** (411 mg, 2.25 mmol), 5-(pentafluorophenyl)dipyrrane (**76**, 2.11 g, 6.76 mmol) and dipyrrane **99** (747 mg, 2.25 mmol) were dissolved in MeOH (600 mL). Subsequently, a solution of HClaq (36%, 22.5 mL) in H_2O (225 mL) was added, and the reaction was stirred at room temperature for 2 h. The mixture was extracted with $CHCl_3$ (4x100mL), and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 2 L with $CHCl_3$. DDQ (2.1 g, 9.1 mmol) was added, and the mixture was stirred for 1h at room temperature. The reaction mixture was concentrated to half the volume and passed through a silica column (silica, DCM/hexanes, 4:1). All fractions containing corroles were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes, 1:1) afforded title compound as a dark solid. The resulting solid was precipitated from hot DCM by adding cyclohexane. Crystals were filtered off and dried in vacuum to give 523 mg of corrole **98** (16%).

R_f (DCM/hexanes, 1:1) = 0.50; ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si, ppm) δ (-2.5) – (-1) (br s, 3H, NH), 2.99 (s, 3H, OCH_3), 4.24 (s, 3H, OCH_3), 6.73 (d, 1H, J = 1.9 Hz, naphth.), 7.12 (d, 1H, J = 7.9 Hz, naphth.), 7.17 (dd, 1H, J_1 = 2.3 Hz, J_2 = 9.3 Hz, naphth.), 8.12 (d, 1H, J = 7.7 Hz, naphth.), 8.35 (d, 1H, J = 4.2 Hz, β-H), 8.41 (d, 1H, J = 4.4 Hz, β-H), 8.45 (d, 1H, J = 9.3 Hz, naphth.), 8.52 (d, 1H, J = 4.8 Hz, β-H), 8.55 (d, 1H, J = 3.3 Hz, β-H), 8.69 (d, 1H, J = 3.1 Hz, β-H), 8.71 (d, 1H, J = 4.4 Hz, β-H), 8.89 (d, 1H, J = 4.2 Hz, β-H), 9.07 (d, 1H, J = 4.2 Hz, β-H); HRMS (TOF MS FD): [M^+] 816.1583 $C_{43}H_{22}N_4O_2F_{10}$ requires: 816.1562. Anal. Calcd. for $C_{43}H_{22}F_{10}N_4O_2$: C, 63.24; H, 2.72; F, 23.26; N, 6.86. Found: C, 63.17; H, 2.95; F, 23.12; N, 6.76;

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15-bis(pentafluorophenyl)corrolato] copper (Cu-98).

Corrole **98** (50 mg, 61 μmol) was dissolved in 10 mL of DCM/MeOH = 1:1 mixture and $Cu(OAc)_2$ (250 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature overnight. The crude product was passed through a short silica gel column with dichloromethane as eluent. The resulting solution was rotary evaporated to dryness and the resulting solid was crystallized from hot DCM by adding hexanes affording 45 mg of corrole **Cu-98** (84%). R_f (DCM/hexanes, 1:1) = 0.55; ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.05 (s, 3H, OCH_3), 4.12 (s, 3H, OCH_3), 6.45 (d, 1H, J = 2.4 Hz, naphth.), 7.08 (d, 1H, J = 8.0 Hz, naphth.), 7.17 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz, naphth.), 8.12 (d, 1H, J = 8.0 Hz, naphth.), 8.40 (d, 1H, J = 4.4 Hz, β-H), 8.42 (d, 1H, J = 4.2 Hz, β-H), 8.44 (d, 1H, J = 9.2 Hz, naphth.), 8.50 (d, 1H, J = 4.6 Hz, β-H), 8.55 (d, 1H, J = 4.0 Hz, β-H), 8.69 (d, 1H, J = 4.0 Hz, β-H), 8.72 (d, 1H, J = 4.4 Hz, β-H), 8.80 (d, 1H, J = 4.0 Hz, β-H), 8.98 (d, 1H, J = 4.0 Hz, β-H); HRMS (TOF MS FD): [M^+] 876.0644 $C_{43}H_{19}CuF_{10}N_4O_2$ requires: 876.0673.

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15-bis(pentafluorophenyl)corrolato] silver (Ag-98).

Corrole **98** (81.6 mg, 0.1 μmol) was dissolved in pyridine (10 mL) and AgOAc (55 mg, 0.33 mmol) was added. The reaction mixture was stirred at 100 °C overnight. The crude product was passed through Celite. Flash column chromatography (DCM/hexanes, 1:1) followed by evaporation of the fraction containing complex afforded title compound as red solid, which was then crystallized from hot DCM by adding hexanes affording 88 mg of corrole **Ag-98** (95%). R_f (DCM/hexanes, 1:1) = 0.65; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.15 (s, 3H, OCH_3), 4.15 (s, 3H, OCH_3), 6.48 (d, 1H, J = 2.3 Hz, naphth.), 7.10 (d, 1H, J = 8.1 Hz, naphth.), 7.20 (dd, 1H, J_1 = 2.3 Hz, J_2 = 9.2 Hz, naphth.), 8.14 (d, 1H, J = 8.1 Hz, naphth.), 8.45 (d, 1H, J = 4.2 Hz, β-H), 8.47 (d, 1H, J = 4.2 Hz, β-H), 8.50 (d, 1H, J = 9.2 Hz, naphth.), 8.50 (d, 1H, J = 4.6 Hz, β-H), 8.56 (d, 1H, J = 4.0 Hz, β-H), 8.70 (d, 1H, J = 4.1 Hz, β-H), 8.72 (d, 1H, J = 4.2 Hz, β-H), 8.74 (d, 1H, J = 4.0 Hz, β-H), 9.02 (d, 1H, J = 4.1 Hz, β-H); HRMS (TOF MS FD) [M^+] 920.040 $C_{43}H_{19}N_4O_2F_{10}Ag$ requires: 920.036.

5-(4,7-Dimethoxynaphthalen-1-yl)dipyrrane (99).

The solution of aldehyde **73** (1.3 g, 6.0 mmol) in pyrrole (**75**, 42 mL, 0.6 mol) was degassed with a stream of argon for 10 min. $MgBr_2$ (1.104 g, 6.00 mmol, anhydrous) was added, and the mixture was stirred under argon at room temperature for 1.5 h. The mixture turned yellow during the course of the reaction. NaOH (4.0 g, 0.1 mol, powdered) was added to quench the reaction. After 1h the mixture was filtered through Celite. The contents of the flask and the filtered material were washed with a small amount of pyrrole. The filtrate was concentrated using a rotary evaporator; the collected pyrrole was set aside. The crude viscous residue was chromatographed (DCM/hexanes, 1:1 → 3:1). Suspending of resulted solid in cyclohexane gave 1.8 g of **99** as white crystals (90%). R_f (DCM/hexanes, 4:1) = 0.40; ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.74 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 5.98 - 6.03 (m, 2H, pyrr.), 6.04 (s, 1H, CH), 6.17 (q, 2H, J = 2.8 Hz, pyrr.), 6.60 (d, 1H, J = 8.0 Hz, naphth.), 6.64 – 6.67 (m, 2H, pyrr.), 7.04 (d, 1H, *J* = 8 Hz, naphth.), 7.10 (dd, 1H, J_1 = 4.4 Hz, J_2 = 9.2 Hz, naphth.), 7.23 (d, 1H, 2.4 Hz, naphth.), 7.89 (br s, 2H, NH), 8.21 (d, 1H, *J* = 9.2 Hz, naphth.); ^{13}C NMR (50 MHz, $CDCl_3$, Me_4Si, ppm) 36.1, 50.7, 51.0, 96.9, 98.5, 102.7, 104.1, 112.4, 116.6, 119.8, 122.6 (2), 124.2, 128.0, 129.4, 150.7, 153.8. HRMS (EI): [$M^{\cdot+}$] 332.1535 $C_{21}H_{20}N_2O_2$ requires: 332.1525. Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43. Found: C, 75.61; H, 6.34; N, 8.43.

10-(4,7-Dimethoxynaphthalen-1-yl)-5,15-bis(4-nitrophenyl)corrole (104).

Aldehyde **73** (298 mg, 1.38 mmol) and 5-(4-nitrophenyl)dipyrrane (**103**, 735 mg, 2.76 mmol) were dissolved in DCM (140 mL). To the resulting mixture TFA (30 μL) was added and the reaction mixture was stirred for 30 min. After dilution to 300 mL with $CHCl_3$, DDQ (940 mg, 4.14 mmol) was added, and the mixture was stirred for 1h at room temperature. The reaction mixture was concentrated to half the volume and passed over a silica pad (DCM/hexanes, 1:1). All fractions containing corrole were combined and evaporated to the dryness. Flash column chromatography (silica, DCM/hexanes, 1:1 → 2:1) afforded title compound as a brown solid. The resulting solid was crystallized from hot DCM by adding hexanes affording 100 mg of corrole **104** (10%). R_f (DCM/hexanes, 1:1) = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) signals are broadened and of low intensity, hence impossible to assign; HRMS (ESI): [M^+] 726.2320 $C_{43}H_{30}N_6O_6$ requires: 726.2301; Anal. Calcd. for $C_{43}H_{30}N_6O_6$: C, 71.07; H, 4.16; N, 11.56. Found: C, 71.08; H, 4.15; N, 11.27.

[10-(4,7-Dimethoxynaphthalen-1-yl)-5,15-bis(4-nitrophenyl)corrolato]copper (Cu-104).

Corrole **104** (73 mg, 0.1 mmol) was dissolved in 10 mL of DCM/MeOH = 1:1 mixture and $Cu(OAc)_2$ (250 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature overnight. The crude product was passed through a short silica gel column with dichloromethane as eluent. The solution was rotary evaporated to dryness and the resulting solid was crystallized from hot DCM by adding hexanes affording 74 mg of corrole **Cu-104** (95%). R$_f$ (DCM/hexanes, 1:1) = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.93 (s, 3H, OCH_3), 4.27 (s, 3H, OCH_3), 6.40 (d, 1H, J = 2.5 Hz, naphth.), 7.11 (d, 1H, J = 7.7 Hz, naphth.), 7.16 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.3 Hz, naphth.), 8.03 (d, 1H, J = 9.3 Hz, naphth.), 8.05 (d, 1H, J = 7.7 Hz, naphth.), 8.35 – 8.95 (m, 16H, Ar, β-H); HRMS (ESI): [M$^+$] 786.1421 $C_{43}H_{30}N_6O_6$ requires: 786.1432.

10-(4-Bromoindol-3-yl)-5,15-bis(pentafluorophenyl)corrole (106).

Aldehyde **105** (100 mg, 0.45 mmol) and 5-(pentafluorophenyl)dipyrrane (**76**, 280 mg, 0.9 mmol) were dissolved in DCM (30 mL). To the resulting mixture TFA (95 μL) was added and the reaction mixture was stirred for 1 h. Subsequently NEt_3 (210 μL) was added and, after diluting with DCM to 250 mL of volume, solution of DDQ (280 mg, 1.23 mmol) in toluene (5 mL) was added, and the reaction was stirred at room temperature for a further 0.5 h. The reaction mixture was passed through a silica pad (silica, DCM/hexanes, 3:1). All fractions containing corrole were combined and evaporated to dryness. Flash column chromatography (silica, DCM/hexanes, 1:3) afforded contaminated title compound. SEC (THF) afforded pure compound, which was then precipitated from hot DCM by adding hexanes. Crystals were filtered off and dried in vacuum to give 53 mg of corrole **106** (15%). R$_f$ (DCM/hexanes, 3:1) = 0.70; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ (-3) – (-1) (br s, 3H, NH), 7.16 (s, 1H, ind.), 7.58 (dd, 1H, J_1 = 8.4, J_2 = 7.0 Hz, ind.) 7.78 (d, 1H, J = 7.0 Hz, ind.), 7.88 (d, 1H, J = 8.4 Hz, ind.), 8.41 (br s, 1H, ind. NH), 8.56 (s, 2H, β-H), 8.63 (s, 4H, β-H), 9.1 (s, 2H, β-H); HRMS (ESI): [MH$^+$] 824.0511 $C_{39}H_{17}BrF_{10}N_5$ requires: 824.0502; UV-vis (THF) λ (ε) 281, 412, 509, 550, 581, 636 nm.

5,15-Bis(pentafluorophenyl)-10-(phenylethynyl)corrole (110).

HRMS (TOF MS FD): [M$^+$] 730.1209 $C_{39}H_{16}F_{10}N_4$ requires: 730.1215;

10-(4-Cyanophenylethynyl)-5,15-bis(pentafluorophenyl)corrole (117).

LRMS (ESI): [MH^+] 756.2 $C_{40}H_{15}F_{10}N_5$ requires: 756.12

Octaphyrin 122.

Acetal **121** (170 mg, 0.691 mmol), dipyrrane **76** (431 mg, 1.38 mmol) were dissolved in dichloromethane (25 mL). Argon was bubbled through the mixture. Subsequently, the TFA (35 μL) was added to the reaction and the mixture was stirred at room temperature for 1 h. Then the mixture was added dropwise to the suspension of DDQ (635 mg, 2.8 mmol) in DCM (200 mL). After 10 min the reaction mixture was filtered through silica pad affording a fraction containing non-polar products. Evaporation gave crude solid, which was dissolved in DCM/hexanes 1:3 mixture and purified using flash DCVC (silica, DCM/hexanes, 1:4 to 1:1). Suspension in small amount of cyclohexane afforded greenish-black solid **122** (15 mg, 4%). R_f (DCM/hexanes, 1:2) = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.89 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.27 (d, 1H, J = 4.2 Hz, β-H), 6.42 (d, 1H, J = 4.8 Hz, β-H), 6.70 (s, 1H, Ar.), 6.75 (d, 1H, J = 4.2 Hz, β-H), 6.78 (s, 1H, Ar), 6.85 (d, 1H, J = 4.2 Hz, β-H), 6.95 (d, 1H, J = 4.8 Hz, β-H), 6.96 (d, 1H, J = 4.2 Hz, β-H), 7.07 (d, 1H, J = 4.2 Hz, β-H), 7.11 (d, 1H, J = 4.2 Hz, β-H), 12.49 (s, 1H, NH), 12.55 (s, 1H, NH). ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si, ppm) 20.7, 21.0, 21.1, 111.5, 111.6, 111.8, 111.9, 117.0, 117.3, 118.6, 119.1, 119.2, 122.2, 123.1, 125.9, 126.1, 126.2, 128.0, 128.9, 129.3, 130.0, 135.0, 136.2, 136.7, 138.3, 139.6, 139.9, 140.7, 141.5, 142.4, 142.9, 143.9, 144.2, 144.3, 144.6, 145.6, 145.8, 147.2, 160.6, 169.0. LRMS (FD): [M^+] 1544.3 $C_{84}H_{44}F_{20}N_8$ requires: 1544.4. UV-vis (DCM) λ (ε) 277 (12600), 357 (26900), 458 (35300), 663 (14800) nm.

7,8-Dihydroxy-4-methylcoumarin (129).[140]

Sulphamic acid (2.43 g, 25 mmol) was added to the mixture of pyrogallol (**128**, 6.3 g, 50 mmol) and ethyl acetoacetate (**126**, 6.4 mL, 50 mmol). The reaction was heated at 130 °C for 0.5 h. Subsequently, water was added through the condenser while hot.

After cooling, the product was filtered and extensively washed with H_2O. White crystals of **129** were obtained in 46% yield, (4.44g).

4-Formyl-7,8-dimethoxycoumarin (130).

To a solution of 7,8-dimethoxy-4-methylcoumarin[140] (**127**, 1.8 g, 8.14 mmol) in chlorobenzene (100 mL), selenium dioxide (1.3 g, 11.72 mmol) was added and the mixture was stirred at 133 °C. After 20 h, hot reaction mixture was filtered through Celite, and chromatographed (silica, DCM/acetone, 99:1), to give aldehyde **130** (1.62 g, 92%): R_f (DCM/acetone, 95:5) = 0.55; mp = 177 – 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.99 (br s, 6H), 6.73 (s, 1H), 6.35 (d, 1H, J = 9.2 Hz), 8.31 (d, 1H, J = 9.2 Hz), 10.08 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si, ppm) 56.4, 61.5, 109.1, 120.2, 121.7, 122.3, 136.3, 143.8, 148.7, 156.3, 160.1, 191.7; HRMS m/z (ESI) 234.0502 $C_{12}H_{10}O_5$ requires 234.0528; Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30; Found: C, 61.42; H, 4.32.

5-(7,8-Dimethoxycoumarin-4-yl)-10,15,20-trimesitylporphyrin (133).

Aldehyde (**130**, 234 mg, 1 mmol), mesitaldehyde (**131**, 440 μL, 3 mmol) and pyrrole (**75**, 275 μL, 4 mmol) were dissolved in chloroform (400 mL), followed by adding the catalytic amount of boron trifluoride diethyl etherate (155 μL, 1.25 mmol). Subsequently, the reaction mixture was stirred at room temperature for 1.5 h and DDQ (908 mg, 4 mmol) was added and reaction mixture was stirred for an additional 15 min. After this time, the mixture was run through a pad of silica. DCVC (silica, DCM/acetone, 9:1) gave fraction containing only desired product. Crystallization from DCM/hexanes afforded A_3B-porphyrin as purple crystals in 10% yield: R_f (DCM/MeOH, 98:2) = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.54 (br s, 2H, NH), 1.83 (s, 6H, CH_3), 1.85 (s, 12H, CH_3), 2.62 (s, 9H, CH_3), 3.83 (s, 3H, OCH_3), 4.23 (s, 3H, OCH_3), 6.44-6.49 (m, 2H, coum.), 7.11 (s, 1H, coum), 7.27 – 7.28 (m, 6H, Ar), 8.65 (br s, 4H, β-H); 8.69 (d, 2H, J = 4.4 Hz, β-H), 8.56 (d, 2H, J = 4.4 Hz, β-H); HRMS (FD): 868.3943 $C_{58}H_{52}N_4O_4$ requires 868.3989; Anal. Calcd.

for $C_{58}H_{52}N_4O_4$: C, 80.16; H, 6.03; N, 6.45; Found: C, 80.01; H, 6.24; N, 6.16; UV-vis (THF) λ 418(424700), 513(20540), 589(6270) nm.

5-(7,8-Dimethoxycoumarin-4-yl)-10,15,20-tris(3,5-difluorophenyl)porphyrin (134).

Aldehyde **130** (234 mg, 1 mmol), 3,5-difluorobenzaldehyde (**132**, 335 μL, 3 mmol) and pyrrole (**75,** 275μL, 4 mmol) were dissolved in chloroform (400 mL), followed by adding the catalytic amount of TFA (500μL) and boron trifluoride diethyl etherate (9 μL). Subsequently, the reaction mixture was stirred at room temperature for 1.5 h and DDQ (908 mg, 4 mmol) was added and reaction mixture was stirred for an additional 15 min. Subsequently, the mixture was run through a pad of silica. Subsequent DCVC (DCM/acetone, 98:2) affording pure porphyrin fraction. Crystallization gave crystals in 12% of yield: R_f (DCM/MeOH, 98:2) = 0.50; ^1H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.88 (s, 2H, NH), 3.83 (s, 3H, OCH_3), 4.24 (s, 3H, OCH_3), 6.32 (d, 1H, *J* = 9.1 Hz, coum.), 6.47 (d, 1H, *J* = 9.1 Hz, coum.), 7.14 (s, 1H, coum.), 7.26 – 7.35 (m, 3H, Ar), 7.73 – 7.76 (m, 6H, Ar), 8.88 – 8.89 (m, 6H, β-H), 9.01 (d, 2H, *J* = 4.5 Hz, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 56.3, 61.8, 103.8, 104.0, 104.2, 108.5, 111.6, 117.8, 117.9, 117.9, 118.2, 118.8, 119.4, 119.7, 124.7, 131.6, 136.4, 144.4, 144.5, 144.5, 144.6, 144.7, 147.3, 155.6, 155.6, 159.9, 160.3, 160.4, 162.3, 162.4; HRMS (ESI): [MH^+] 851.2108 $C_{49}H_{28}F_6N_4O_4$ requires 851.2088; Anal. Calcd. for $C_{49}H_{28}F_6N_4O_4$: C, 69.18; H, 3.32; N, 6.59; Found: C, 69.30; H, 3.44; N, 6.58. UV-vis (DCM) λ (ε) 417 (344000), 512 (18000), 545 (3700), 586 (5500), 644 (1500) nm.

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[5-(7,8-Dimethoxycoumarin-4-yl)-10,15,20-trimesitylporphyrinato)]zinc (Zn-133).

To a solution of porphyrin **133** (432 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75mL) $Zn(OAc)_2 \cdot 2H_2O$ (19.0 g, 87 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried over $MgSO_4$ and evaporated.

Crystallization from $CHCl_3$/cyclohexane afforded pure product as purple crystals (455 mg, 99%): R_f (DCM/MeOH, 98:2) = 0.55; ^1H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.80 (s, 6H, CH_3), 1.83 (s, 3H, CH_3), 1.87 (s, 9H, CH_3), 2.62 (s, 9H, CH_3), 3.81 (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 6.40 (d, 1H, J = 4.3 Hz, coum.), 6.45 (d, 1H, J = 4.3 Hz, coum.) 7.02 (s, 1H, coum.), 7.26 (br s, 6H, Ar), 8.71 (d, 2H, J = 4.5 Hz, β-H), 8.73 (d, 2H, J = 4.4 Hz, β-H), 8.76 (d, 2H, J = 4.7 Hz, β-H), 8.92 (d, 2H, J = 4.7 Hz, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.5(2), 21.70(4), 56.2, 61.7, 108.3, 110.4, 118.7, 119.5, 119.9, 120.1, 124.9, 127.7 (2), 127.8, 129.9, 130.5, 131.3, 131.6, 131.7, 136.2, 137.6, 137.6, 138.6, 138.7, 138.9, 139.1, 139.2, 139.4, 147.1, 148.1, 149.8, 149.9, 150.4, 155.2, 157.2, 160.2; HRMS (FD): m/z (FD): [M^+] 930.3129 $C_{58}H_{50}N_4O_4Zn$ requires 930.3124; UV-vis (DCM) λ (ε) 401 (47000), 421 (559000), 549 (23400) nm.

[5-(7,8-Dimethoxycoumarin-4-yl)-10,15,20-tris(mesityl)porphyrinato)]copper (II) (Cu-133).

To a solution of porphyrin **133** (60 mg, 0.069 mmol) in the mixture of $CHCl_3$ (30 mL) and MeOH (15 mL), $Cu(OAc)_2$ (300 mg, 0.3 mmol) was added and the reaction was stirred for 1 h. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried over $MgSO_4$ and evaporated. Crystallization from DCM/hexanes afforded pure carmine crystals (58 mg, 91%): R_f (DCM/MeOH, 98:2) = 0.58; HRMS (FD):): [M^+] m/z 929.310 $C_{58}H_{50}CuN_4O_4$ requires 929.310; Anal. Calcd. for $C_{58}H_{50}CuN_4O_4$: C, 74.86; H, 5.42; N, 6.02; Found: C, 74.71; H, 5.49; N, 5,81; UV-vis (DCM) λ (ε) 308 (26800), 417 (458000), 540 (20500). HPLC confirmed the purity of complex **Cu–133** R_t = 5.46 min.

[5-(7,8-Dimethoxycoumarin-4-yl)-10,15,20-tris(3,5-difluorophenyl) porphyrinato] zinc(II) (Zn-134).

To a solution of porphyrin **134** (432 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75 mL) $Zn(OAc)_2{\cdot}2H_2O$ (19.0 g, 87 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried and evaporated. Crystallization from $CHCl_3$/cyclohexane afforded complex **Zn-134** as purple crystals (445 mg, 98%): R_f (DCM/MeOH, 98:2) = 0.70; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 3.75 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 6.09-6.16 (m, 2H, coum.), 6.35 – 6,38 (m, 1H, coum.), 7.30 (br s, 6H, Ar), 7.74 – 7.82 (m, 5H, 2 β-H, 3 Ar), 8.84 – 9.00 (m, 6H, β-H); HRMS (FD): [M^+] m/z 912.1112 $C_{49}H_{26}F_6N_4O_4Zn$ requires 912.1150; Anal. Calcd. for $C_{49}H_{26}F_6N_4O_4Zn$: C, 64.38; H, 2.87; N, 6.13; Found: C, 64.33; H, 3.03; N, 5.89; UV-vis (THF) λ (ε) 314 (25500), 398 (44000), 418 (512000), 546 (21700) nm.

7,8-Dihydroxy-[3-α-methylacetyl ester]-4-methylcoumarin (136).

Pyrogallol (**128**, 1.36 g, 10 mmol) was added to 2-acetyl-succinic acid dimethyl ester (**135**, 1.78 mL, 12 mmol) and $ZnCl_2$ (1.0 g) was added. The reaction was heated at 140 °C for 5 h. Subsequently, MeOH (50 mL) was added through the condenser while hot. The mixture was poured on water, extensively extracted with DCM and dried over $MgSO_4$. Evaporation gave 1.4g of white crystals of **136** (53%). R_f (DCM/MeOH, 9:1) = 0.50; ^{1}H NMR (600 MHz, DMSO-d_6, Me_4Si, ppm) δ 2.33 (s, 3H, Me), 3.20 – 3.45 (br s, 2H, OH), 3.61 (s, 3H, OCH_3), 3.66 (s, 2H, CH_2), 6.83 (d, 1H, J = 8.8 Hz, coum.), 7.16 (d, 1H, J = 8.7 Hz, coum.), ^{13}C NMR (150 MHz, DMSO-d_6, Me_4Si, ppm) 36.1, 50.7, 51.0, 96.9, 98.4, 102.7, 104.1 (2), 112.4, 116.4, 119.8, 122.6, 128.0, 129.0; LRMS m/z (EI): [$M^{\cdot+}$] 264.00 $C_{13}H_{12}O_6$ requires 264.06; Anal. Calcd. for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58; Found: C, 58.67; H, 4.46.

7,8-Dimethoxy-[3-α-methylacetyl ester]-4-methylcoumarin (137).

To a solution of K_2CO_3 (3 g, 21.5 mmol) in DMF (15 ml) 7,8-dihydroxy-[3-α-methylacetyl ester]-4-methylcoumarin (**136,** 1.4 g, 5.3 mmol), was added. The mixture was cooled to 10 °C and $(CH_3)_2SO_4$ (1.82 mL, 21.5 mmol) was added dropwise while stirring. The reaction was heated at 110 °C overnight. After cooling, water (50 mL) was added and the product was extracted with EtOAc (3x50 mL). The organic layer was washed subsequently with water and saturated aqueous NaCl, dried over Na_2SO_4, filtered through a pad of silica to eliminate colored impurities, and evaporated to dryness. The residue was dried in vacuum to give 1.43 g **137** (91%). R$_f$ (DCM/acetone, 95:5) = 0.75; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si, ppm) δ 2.35 (s, 3H, Me), 3.61 (s, 3H, OCH_3), 3.74 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 6.90 (d, 1H, *J* = 8.9 Hz, coum.), 7.14 (d, 1H, *J* = 8.9 Hz, coum.), HRMS m/z (EI): [$M^{\cdot+}$] 292.0912 $C_{15}H_{16}O_6$ requires 292.0921.

2-Oxo-2H-benzo[*h*]chromen-4-yl)-10,15,20-tris(mesityl)porphyrin (142).

Aldehyde (**141**, 224 mg, 1 mmol), mesitaldehyde (**131**, 440 μL, 3 mmol) and pyrrole (**75**, 275 μL, 4 mmol) were dissolved in chloroform (400 mL), followed by adding the catalytic amount of boron trifluoride diethyl etherate (155 μL, 1.25 mmol). Subsequently, the reaction mixture was stirred at room temperature for 1.5 h and DDQ (908 mg, 4 mmol) was added and reaction mixture was stirred for an additional 15 min. After this time, the mixture was run through a pad of silica. DCVC (silica, DCM/hexanes, 3:2) afforded pure porphyrin fraction. Crystallization gave porphyrin **142** as purple crystals in 16% of yield: R$_f$ (DCM/hexanes, 3:1) = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.48(br s, 2H, NH), 1.83 (s, 3H, CH_3), 1.85 (s, 6H, CH_3), 1.86 (s, 6H, CH_3), 1.87 (s, 3H, CH_3), 2.61 (s, 6H, CH_3), 2.63 (s, 3H, CH_3), 6.77 (d, 1H, *J* = 8.9 Hz, coum.), 7.26 – 7.27 (m, 7H, 1 coum. 6 Ar), 7.28 (s, 1H, coum.), 7.68 – 7.69 (m, 1H, coum.), 7.76 – 7.78 (m, 2H, coum.), 8.65 – 8.66 (m, 4H, *β*-H), 8.69 (d, 2H, *J* = 4.6 Hz, *β*-H), 8.85 (d, 2H, *J* = 4.6 Hz, *β*-H), 8.90 (d, 1H, *J* = 8.9 Hz, coum.); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.7(2), 21.9, 22.0(2), 27.2, 109.9, 119.1, 119.7, 119.8, 121.1, 123.4, 123.4, 124.5, 124.8, 127.8, 128.1(2), 128.2, 129.4, 130.5 (6), 135.1, 138.1 (2), 138.2 (2), 139.5, 139.6, 139.6, 139.7, 150.2, 157.4, 160.7; HRMS m/z (ESI) 859.4041 [MH^+] $C_{60}H_{51}N_4O_2$ requires 859.4007; UV-vis (DCM) λ (ε) 419 (372000), 514 (19400), 547 (5300), 589 (6000), 645 (2500) nm.

[2-Oxo-2H-benzo[*h*]chromen-4-yl)-10,15,20-tris(mesityl)porphyrinato]nickel (II) (Ni-142).

To a solution of porphyrin **142** (429 mg, 0.5 mmol) in toluene (120 mL), $Ni(acac)_2$ (1.3g, 5 mmol) was added and the reaction was refluxed for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:4). Crystallization from DCM/hexanes afforded pure deep orange crystals (448 mg, 98%): R$_f$ (DCM/hexanes, 3:2) = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.75 (s, 6H, CH_3), 1.80 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.89 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 2.57 (s, 3H, CH_3), 6.69 (d, 1H, *J* = 8.4 Hz, coum.), 7.19 – 7.23 (m, 7H, 1 coum. 6 Ar), 7.29 (d, 1H, *J* = 5.4 Hz, coum.), 7.66 – 7.68 (m, 1H, coum.), 7.74 – 7.77 (m, 2H, coum.), 8.56 (d, 2H, *J* = 4.8 Hz, *β*-H), 8.58 (d, 2H, *J* = 4.8 Hz, *β*-H), 8.60 (d, 2H, *J* = 5.4 Hz, *β*-H), 8.75 (d, 2H, *J* = 4.8 Hz, *β*-H), 8.85 (d, 1H, *J* = 8.4 Hz, coum.); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.6 (2), 21.8, 22.0 (2), 27.2, 109.8, 118.2, 118.5, 119.1, 120.4, 123.3, 123.4, 124.4, 124.6, 127.7, 128.0, 128.1, 129.3, 130.9, 131.9, 132.2, 132.4, 135.1, 137.2, 137.3, 138.1, 139.1, 139.2, 139.2, 139.3, 141.1, 142.9, 143.1, 143.4, 150.2, 156.5, 160.7; HRMS (ESI): [MH$^+$] 915.3133 $C_{60}H_{48}N_4NiO_2$ requires 915.3125. UV-vis (DCM) λ (ε) 415 (203000), 528 (16800), 559 (4800) nm.

5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(mesityl)porphyrin (148).

Aldehyde **73** (216 mg, 1 mmol), mesitaldehyde (**131**, 440 μL, 3 mmol) and pyrrole (**75**, 275 μL, 4 mmol) were dissolved in chloroform (400 mL), followed by adding the catalytic amount of boron trifluoride diethyl etherate (155 μL, 1.25 mmol). Subsequently, the reaction mixture was stirred at room temperature for 1.5 h and DDQ (908 mg, 4 mmol) was added. The reaction mixture was filtered through silica pad affording a mixture of A_4- and A_3B-type porphyrins, which were then separated using DCVC (DCM/hexanes, 1:4 → 2:1). Crystallization from DCM/hexanes afforded purple-violet solid (170 mg, 20%): R$_f$ (DCM/hexanes, 3:2) = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.43 (s, 2H, NH), 1.82 (s, 3H, CH_3), 1.84 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 2.60 (s, 6H, CH_3), 2.62 (s, 3H, CH_3), 2.89 (s, 3H, OCH_3), 4.24 (s, 3H, OCH_3), 6.57 (d, 1H, *J* = 2.6 Hz, naphth.), 7.07 (d, 1H, *J* = 7.9 Hz, naphth.), 7.14 (dd, 1H, J_1 = 2.6 Hz, J_2 = 9.3 Hz, naphth.), 7.25 – 7.29 (m, 6H, Ar), 8.04 (d, 1H, *J* = 7.9 Hz, naphth.), 8.45 (d, 1H, *J* = 9.3 Hz, naphth.), 8.57 – 8.59 (m, 4H, *β*-H), 8.62 – 8.63 (m, 4H, *β*-H); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.5, 21.5, 21.7 (2), 21.8, 26.9, 54.7, 55.7, 100.9, 107.1, 117.1, 117.6, 117.8, 117.85, 120.1, 123.5, 127.74 (3), 130.00 (5), 130.50, 133.9, 137.7, 137.7, 138.2, 138.3, 138.9, 139.4(2), 139.44, 139.5, 156.0, 158.3; HRMS (ESI): [MH^+] 851.4284 $C_{59}H_{54}N_4O_2$ requires: 851.4278. Anal. Calcd. for $C_{59}H_{55}N_4O_2$: C, 83.26; H, 6.40; N, 6.58. Found: C, 83.38; H, 6.60; N, 6.28; UV-vis (THF) λ (ε) 303 (17900), 420 (330000), 515 (20800), 548 (6700), 592 (5500) nm.

5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(3,5-difluorophenyl)porphyrin (149).

Aldehyde **73** (216 mg, 1 mmol), aldehyde **132** (335 μL, 3 mmol) and pyrrole **(75)** (275 μL, 4 mmol) were dissolved in chloroform (400 mL), followed by adding the catalytic amount of boron trifluoride diethyl etherate (155 μL, 1.25 mmol). Then the reaction mixture was stirred at room temperature for 1.5 h and DDQ (908 mg, 4 mmol) was added. The reaction mixture was filtered through silica pad afforded mixture of A_4- and A_3B-type porphyrins, which were then purified on DCVC using (DCM/hexanes, 1:10 → 1:1). Crystallization from DCM/hexanes afforded porphyrin **149** as deep-violet solid (233 mg, 28%): R_f = (DCM/hexanes, 3:2) = 0.50; ^{1}H NMR (600 MHz; $CDCl_3$; Me_4Si) δ -2.77 (s, 2H, NH), 2.89 (s, 3H, OCH_3), 4.26 (s, 3H, OCH_3), 6.35 (d, 1H, J = 2.5 Hz, naphth.), 7.1 (d, 1H, J = 7.8 Hz, naphth.), 7.16 (dd, 1H, J_1 = 2.5 Hz, J_2 = 9.4 Hz, naphth.), 7.24 – 7.27 (m, 3H, Ar), 7.74 – 7.76 (m, 6H, Ar), 8.06 (d, 1H, J = 7.8 Hz, naphth.), 8.48 (d, 1H, J = 9.4 Hz, naphth.), 8.74 (m, 4H, β-H), 8.89 (s, 4H, β-H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si, ppm) 55.0, 56.0, 101.3, 103.8, 104.1, 104.3, 107.6, 117.6, 117.9, 118.1, 118.1, 118.3, 119.7, 120.4, 123.9, 130.1, 131.5 (4), 134.2, 139.3, 145.2, 145.3, 145.4, 156.6, 158.8, 160.3, 160.4, 162.8, 162.9; HRMS (FD): [M^+] m/z 832.2296 $C_{50}H_{30}F_6N_4O_2$ requires 832.2273; UV-vis (DCM) λ (ε) 418 (283000), 514 (21000), 549 (5400), 589 (6400), 644 (2000) nm.

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(mesityl)porphyrinato]zinc(II) (Zn-148).

To a solution of porphyrin **148** (425 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75 mL) $Zn(OAc)_2 \cdot 2H_2O$ (19.0 g, 87 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried and evaporated. Crystallization from $CHCl_3$/cyclohexane afforded complex **Zn-148** as purple crystals (455mg, 100%): R_f (DCM/hexanes, 3:2) = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.83 (s, 6H, CH_3), 1.84 (s, 6H, CH_3), 1.86 (s, 3H, CH_3), 1.88(s, 3H, CH_3), 2.61 (s, 6H, CH_3), 2.63 (s, 3H, CH_3), 2.84 (s, 3H, OCH_3), 4.25 (s, 3H, OCH_3), 6.41 (d, 1H, J = 3.0 Hz, naphth.), 7.07 – 7.13 (m, 2H, naphth.), 7.25 – 7.27 (m, 6H, Ar), 8.12 (d, 1H, J = 8.0 Hz, naphth.), 8.44 (d, 1H, J = 9.2 Hz, naphth.), 8.63 – 8.72 (m, 8H, β-H), HRMS (ESI): [MH$^+$] m/z 912.3376 $C_{59}H_{52}N_4O_2Zn$ requires 912.3356; UV-vis (THF) λ (ε) 313 (18400), 407 (43600), 427 (477000), 558 (18800), 596 (4200) nm.

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5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(3,5-difluorophenyl) porphyrinato]zinc (II) (Zn-149).

To a solution of porphyrin **149** (416 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75mL) $Zn(OAc)_2 \cdot 2H_2O$ (19.0 g, 87 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried and evaporated. Crystallization from $CHCl_3$/cyclohexane afforded complex **Zn-149** as red crystals (447 mg, 100%): R_f (DCM/hexanes, 3:2) = 0.55; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si) δ 2.70 (s, 3H, OCH_3), 4.23 (s, 3H, OCH_3), 6.19 (d, 1H, J = 2.0 Hz, naphth.), 6.91 (dd, 1H, J_1 = 2.0 Hz, J_2 = 9.6 Hz, naphth.), 7.07 (d, 1H, J = 7.6 Hz, naphth.), 7.25 – 7.30 (m, 3H, Ar), 7.72 – 7.80 (m, 6H, Ar), 8.05 (d, 1H, J = 8.0 Hz, naphth.), 8.37 (d, 1H, J = 9.2 Hz, naphth.), 8.79 (d, 2H, J = 4.8 Hz, β-H), 8.84 (d, 2H, J = 4.8 Hz, β-H), 8.98 (s, 4H, β-H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si, ppm) 54.5, 55.8, 101.0, 103.3, 103.5, 103.62, 107.7, 116.7, 117.7, 117.8, 118.5, 119.9, 120.0, 123.4, 130.5, 131.7, 131.8, 131.9, 132.9, 133.5, 138.8, 145.7, 145.7, 149.5, 149.5, 149.7, 151.8, 155.9, 157.9, 160.4, 162.0; HRMS (FD): [M$^+$] m/z 894.1382 $C_{50}H_{28}N_4O_2F_6Zn$ requires 894.1408; UV-vis (DCM) λ 312 (16170), 419 (251000), 547 (17800) nm.

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(mesityl)porphyrinato] copper(II) (Cu-148).

To a solution of porphyrin **148** (425 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75 mL), $Cu(OAc)_2$ (2.0 g, 10 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried and evaporated. Crystallization from DCM/hexanes afforded complex **Cu-148** as reddish crystals (450 mg, 98%): R_f (DCM/hexanes, 1:1) = 0.60; HRMS (FD): $[M^+]$ m/z 911.3357 $C_{59}H_{52}CuN_4O_2$ requires 911.3386, El. Anal. Calc. for $C_{59}H_{52}CuN_4O_2$: C, 77.65; H, 5.74; N, 6.14; Found C, 77.90; H, 5.62; N, 6.20; UV-vis (THF) λ (ε) 419 (380000), 542 (18000) nm. HPLC confirmed the purity of complex **Cu–148** (R_t = 5.12 min).

5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(3,5-difluorophenyl) porphyrinato]copper (II) (Cu-149).

To a solution of porphyrin **149** (416 mg, 0.5 mmol) in the mixture of $CHCl_3$ (150 mL) and MeOH (75 mL) $Cu(OAc)_2$ (2.0 g, 10 mmol) was added and the reaction was stirred overnight. Then water (30 mL) was added and the mixture was extracted with $CHCl_3$. Organic layer was dried over $MgSO_4$ and evaporated. Crystallization from DCM/hexanes afforded complex **Cu-149** reddish crystals (425 mg, 96%): R_f (DCM/hexanes, 2:1) = 0.76; HRMS (FD): $[M^+]$ 893.1373 $C_{50}H_{28}N_4O_2F_6Cu$ requires 893.1412 El. Anal. Calc. for $C_{50}H_{28}CuF_6N_4O_2$: C, 67.15; H, 3.16; N, 6.26 Found C, 66.95; H, 3.02; N, 6.20; UV-vis (THF) λ (ε) 309 (19700), 414 (337000), 539 (22700) nm. HPLC confirmed the purity of complex **Cu-149** (R_t = 4.85 min).

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(mesityl)porphyrinato]nickel (II) (Ni-148).

To a solution of porphyrin **148** (425 mg, 0.5 mmol) in the toluene (120 mL) $Ni(acac)_2$ (1.3 g, 5 mmol) was added and the reaction was refluxed for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:2). Crystallization from DCM/hexanes afforded complex **Ni-148** as deep orange crystals (422 mg, 93%): R*f* (DCM/hexanes, 3:2) = 0.63; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.78 (s, 6H, CH_3), 1.84 (s, 12H, CH_3), 2.56 (s, 6H, CH_3), 2.57 (s, 3H, CH_3), 3.03 (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 6.40 (d, 1H, *J* = 2.5 Hz, naphth.), 7.01 (d, 1H, *J* = 7.9 Hz, naphth.), 7.12 (dd, 1H, J_1 = 2.5 Hz, J_2 = 9.5 Hz, naphth.), 7.19 – 7.26 (m, 6H, Ar), 7.94 (d, 1H, *J* = 7.7 Hz, naphth.), 8.41 (d, 1H, *J* = 9.3 Hz, naphth.), 8.47 – 8.48 (m, 2H, *β*-H), 8.52 – 8.54 (m, 6H, *β*-H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si, ppm) 21.4, 21.4, 21.4 (2), 21.5, 26.9, 54.8, 55.7, 100.9, 107.3, 116.4, 117.0, 117.1 (2), 120.1, 123.5, 127.7 (3), 129.7, 130.8, 131.0, 131.2, 132.4, 133.1, 137.5, 137.6, 138.5, 138.9, 139.0, 139.1, 142.6, 142.7, 142.8, 144.1, 155.9, 158.2; HRMS (ESI) [M^+] 906.3449 $C_{59}H_{52}N_4O_2Ni$ requires 906.3438; UV-vis (DCM) λ (ε) 416 (199000), 528 (17000) nm.

[5-(4,7-Dimethoxynaphthalen-1-yl)-10,15,20-tris(3,5-difluorophenyl) porphyrinato]nickel (II) (Ni-149).

To a solution of porphyrin **149** (416 mg, 0.5 mmol) in the toluene (120 mL) $Ni(acac)_2$ (1.3 g, 5 mmol) was added and the reaction was refluxed for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:3). Crystallization from DCM/hexanes afforded complex **Ni-148** as deep orange crystals (440 mg, 99%): R*f* (DCM/hexanes, 3:2) = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 3.08 (s, 3H, OCH_3), 4.22 (s, 3H, OCH_3), 6.32 (d, 1H, *J* = 2.3 Hz, naphth.), 7.03 (d, 1H, *J* = 7.9 Hz, naphth.), 7.14 (dd, 1H, J_1 = 2.6 Hz, J_2 = 9.2 Hz, naphth.), 7.17 – 7.25 (m, 3H, Ar), 7.54 – 7.55 (m, 6H, Ar), 7.86 (d, 1H, *J* = 7.7 Hz, naphth.), 8.44 (d, 1H, *J* = 9.2 Hz, naphth.), 8.63 – 8.67 (m, 4H, *β*-H), 8.76 – 8.79 (m, 4H, *β*-H); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 55.2, 55.9, 101.2, 103.7, 103.9, 104.2, 107.5, 116.8, 117.2, 117.2, 117.4, 117.4, 118.4, 120.4, 123.9, 128.8, 132.2, 132.2, 132.3, 133.5, 133.7, 138.5, 142.3, 142.4, 142.5, 143.9, 144.1, 144.2, 144.7, 156.5, 158.7, 160.4, 160.5, 162.9, 163.0; HRMS (FD) [M^+] 888.1429 $C_{50}H_{28}N_4O_2F_6Ni$ requires 888.1470; UV-vis (DCM) λ (ε) 413(186400), 527(19440) nm.

Fused free-base porphyrin H_2-151.

To a solution of **Zn-149** (6.3 mg, 0.007 mmol) in DCM (4 mL), $FeCl_3$ (5.6 mg) in $MeNO_2$ (1ml) was added and the reaction was stirred for 30 min. Subsequent chromatography afforded pure fraction of **H_2-151**. Crystallization from DCM/hexanes gave crystals (2.8 mg, 47%): R_f (DCM/hexanes, 3:2) = 0.65; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ -1.46 (s, 2H, NH), 4.19 (s, 3H, OCH_3), 4.41 (s, 3H, OCH_3), 7.26 – 7.33 (m, 4H, 1 naphth. 3 Ar), 7.64 (d, 1H, J = 9.2 Hz, naphth.), 7.72 – 7.83 (m, 6H, Ar), 8.50 (d, 1H, J = 8 Hz, naphth.), 8.64 – 8.75 (m, 6H, β-H), 8.95 (br s, 1H, β-H), 9.55 (s, 1H, naphth.); HRMS m/z (ESI) 831.2170 [MH^+] $C_{50}H_{28}F_6N_4O_2$ requires 831.2189); UV-vis (DCM) λ (ε) 315 (28800), 362 (27800), 380 (28400), 479 (13100), 571 (11800), 617 (23600), 642 (25400), 701 (27000) nm.

General procedure for oxidation of porphyrin complexes:

Sample of porphyrin complex (0.01 mmol) was dissolved in dry DCM (4 mL) and $Fe(ClO_4)_3 \cdot 2H_2O$ (0.1 mmol) in $MeNO_2$ was added via syringe within 5 min. After 25 min. the reaction was filtered directly through a pad of silica. Additional DCVC (DCM/hexanes) gave pure product. Crystallization from DCM/hexanes afforded product as dark crystals. Purification details are described for each case as follows.

Fused complex Cu-150.

Chromatography (DCM/hexanes, 2:3). Yield = 83%. R_f (DCM/hexanes, 3:2) = 0.65; HRMS (FD): [M^+] m/z 909.3202 $C_{59}H_{50}CuN_4O_2$ requires 909.3230; UV-vis (THF) λ (ε) 312 (12900), 377 (10000), 485 (73800), 551 (3000), 609 (5200), 660 (18600) nm. HPLC confirmed the purity of complex **Cu-150** (R_t = 5.73 min).

Fused complex Cu-151.

Chromatography (DCM/hexanes, 1:1). Yield = 60%. R_f (DCM/hexanes, 2:1) = 0.78; HRMS m/z (FD) [M^+] 891.1281 $C_{50}H_{26}N_4O_2F_6Cu$ requires 891.1256; UV-vis (THF) *λ* (*ε*) 310 (29000), 379(23000), 460 (72500), 487 (183000), 553 (6500), 600 (12000), 658 (43000) nm. HPLC confirmed the purity of complex **Cu-151** (R_t = 5.97 min).

Fused complex Ni-150.

Chromatography (DCM/hexanes, 1:1). Yield = 60%. R_f (DCM/hexanes, 3:2) = 0.70; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.87 (s, 6H, CH_3), 1.92 (s, 12H, CH_3), 2.53 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 4.19 (s, 3H, OCH_3), 4.31 (s, 3H, OCH_3), 7.16 – 7.26 (m, 7H, 1 naphth. 6 Ar), 7.62 (d, 1H, *J* = 9.2 Hz, naphth.), 8.26 (d, 1H, *J* = 8.4 Hz, naphth.), 8.30 – 8.39 (m, 4H, *β*-H), 8.61 (d, 1H, *J* = 9.2 Hz, naphth.), 8.65 (d, 1H, *J* = 4.4 Hz, *β*-H), 9.05 (d, 1H, *J* = 4.4 Hz, *β*-H), 9.17 (br s, 1H, *β*-H); HRMS m/z (FD) [M^+] 904.3267 $C_{59}H_{50}N_4O_2Ni$ requires 904.3287; UV-vis (THF) *λ* (*ε*) 310 (22200), 379 (17700), 481 (106000), 585 (1100), 648 (35000) nm.

Fused complex Ni-151.

Chromatography (DCM/hexanes, 1:2). Yield = 40%. R_f (DCM/hexanes, 3:2) = 0.65; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si, ppm) δ 4.16 (s, 3H, OCH_3), 4.38 (s, 3H, OCH_3), 7.14 – 7.25 (m, 5H, 2 naphth. + 3 Ar), 7.51 – 7.62 (m, 6H, Ar), 8.18 (br s, 1H, naphth.), 8.53 – 8.61 (m, 5H, *β*-H), 8.79 (br s, 1H, naphth.), 8.99 (d, 1H, *J* = 4.8 Hz, *β*-H), 9.36 (br s, 1H, *β*-H); ^{13}C NMR (150 MHz, $CDCl_3$, Me_4Si, ppm) 55.9, 56.3, 103.2, 103.3, 103.5, 103.5, 103.6, 104.8, 111.9, 111.9, 114.4, 114.5, 116.0, 116.7, 116.8, 117.00, 119.8, 123.3, 124.4, 125.9, 126.2, 131.1, 131.6, 131.7, 132.2, 133.2, 136.5, 137.3, 138.1, 138.6, 140.6, 140.6, 141.6, 141.9, 142.1, 142.4, 143.7, 143.7, 143.9, 143.9, 157.2, 158.3, 160.5, 160.6, 160.7, 160.8, 162.5, 162.6, 162.7, 162.8; HRMS m/z (FD) [M^+] 886.1301 $C_{50}H_{26}N_4O_2F_6Ni$ requires 886.1313; UV-vis (DCM) *λ* (*ε*) 310 (26400), 378 (21500), 399 (18400), 484 (127000), 591 (13000), 648 (43000) nm.

5-(Indol-4-yl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (154).

Aldehyde **152** (181 mg, 1.25 mmol), aldehyde **153** (880 mg, 3.75 mmol) and pyrrole **(75)** (350 μL, 5 mmol) were dissolved in chloroform (500 mL), followed by adding the catalytic amount of boron trifluoride diethyl etherate (9 μL) and TFA (579 μl). Subsequently, the reaction mixture was stirred at room temperature for 1 h and DDQ (1.14 g, 5 mmol) was added. The reaction mixture was filtered through silica pad affording a mixture of A_4- and A_3B-type porphyrins, which were then separated using DCVC (DCM/hexanes, 1:3 → 1:1). Crystallization from DCM/MeOH afforded purple-violet solid (100 mg, 11%): R_f (DCM/hexanes, 1:1) = 0.45; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ -2.59 (s, 2H, NH), 1.50 (s, 18H, CCH_3), 1.51 (s, 18H, CCH_3), 1.52 (s, 9H, CCH_3), 1.53 (s, 9H, CCH_3), 5.90-5.92 (m, 1H, indole-pyrrole), 7.04-7.06 (m, 1H, indole-pyrrole), 7.54-7.57 (m, 1H, Ar, indole-benzene), 7.68 – 7.71 (m, 1H, indole-benzene), 7.76-7.80 (m, 3H, Ar), 7.90-7.92 (m, 1H, indole-benzene), 8.05-8.10 (m, 6H, Ar), 8.25 (s, 1H, indole-NH), 8.76 (d, 2H, J = 4.7 Hz, β-H), 8.80 (d, 2H, J = 4.7 Hz, β-H), 8.88 – 8.90 (m, 4H, β-H); HRMS (ESI): [MH^+] 990.6408 $C_{70}H_{80}N_5$ requires 990.6418; Anal. Calcd. for $C_{70}H_{80}N_5$: C, 84.89; H, 8.04; N, 7.07. Found: C, 84.94; H, 7.94; N, 7.04. UV-vis (DCM) λ (ε) 404 (134000), 513 (35800) nm.

[5-(Indol-4-yl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrinato] nickel (II) (Ni-154).

To a solution of porphyrin **154** (99 mg, 0.1 mmol) in the toluene (50 mL) $Ni(acac)_2$ (255 mg, 1 mmol) was added and the reaction was refluxed for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:4). Crystallization from DCM/MeOH afforded complex **Ni-154** as orange crystals (84 mg, 80%): R_f (DCM/hexanes, 1:1) = 0.40; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 1.38 (s, 36H), 1.39 (s, 18H), 5.78-5.80 (m, 1H, indole-pyrrole), 7.02-7.04 (m, 1H, indole-pyrrole), 7.42-7.44 (m, 1H, indole-benzene), 7.60 – 7.61 (m, 1H, indole-benzene), 7.62 – 7.63 (m, 3H, Ar), 7.69 (d, 1H, J = 7.05 Hz, indole-benzene), 7.8 (br s, 6H, Ar), 8.24 (s, 1H, indole-NH), 8.62 (d, 2H, J = 4.8 Hz, β-H), 8.64 (d, 2H, J = 4.8 Hz, β-H), 8.72 (d, 2H, J = 5 Hz, β-H), 8.73 (d, 2H, J = 5 Hz, β-H); HRMS (ESI):

[M$^+$] m/z 1045.5527 $C_{70}H_{77}N_5Ni$ requires 1045.5541. UV-vis (DCM) λ (ε) 415 (123300), 520 (33500) nm.

Fused porphyrin Ni-155.

Chromatography (DCM/hexanes, 1:1). Yield = 56%. R_f (DCM/hexanes, 2:1) = 0.45; ^{1}H NMR, LRMS (FD): m/z 1043.7 $C_{70}H_{75}N_5Ni$ requires 1043.5. UV-vis (DCM) λ (ε) 424 (19300), 462 (24800), 584 (2300), 644 (6600) nm.

5,15-Bis(fluoranthen-3-yl)-10,20-bis(mesityl)porphyrin (162).

Dipyrrane **158** (264 mg, 1 mmol) and fluoranthene-3-carbaldehyde **161** (230 mg, 1.0 mmol) were dissolved in DCM (100 mL), and then TFA (0.137 mL, 1.78 mmol) was added slowly over 30 s. The reaction was stirred at room temperature with the progress of the reaction monitored by TLC. After 1h, DDQ (554 mg, 2.0 mmol) was added, and the reaction mixture was stirred at room temperature for a further 1 h. The complete reaction mixture was poured onto a pad of alumina and eluted with DCM/Acetone (98:2). Note: addition of acetone is crucial because of porphyrin **162** poor solubility in DCM. The black residue was chromatographed (DCM/hexanes, 2:1). Crystallization from DCM/EtOH afforded porphyrin **162** as violet solid (162 mg, 34%): R_f (DCM/hexanes, 2:1) = 0.79; ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.38 (s, 2H, NH), 1.83 (s, 3H, CH_3), 1.86 (s, 6H, CH_3), 1.90 (s, 3H, CH_3), 2.58 (s, 6H, CH_3), 7.15 (s, 1H, Ar), 7.17 (s, 1H, Ar), 7.21-7.24 (m, 4H, 2 Ar, 2 fluoranth.), 7.34-7.40 (m, 2H, fluoranth.), 7.49 – 7.56 (m, 4H, fluoranth.), 7.99 (d, 2H, J = 3.4 Hz, fluoranth.), 8.06 (d, 2H, J = 3.8 Hz, fluoranth.), 8.16 (d, 2H, J = 3.4 Hz, fluoranth.), 8.29 – 8.32 (m, 2H, fluoranth.), 8.42 (d, 1H, J = 3.6Hz, fluoranth.), 8.46 (d, 1H, J = 3.4 Hz, fluoranth.), 8.63 (br s, 8H, β-H); HRMS (ESI): [MH$^+$] 947.4108 $C_{70}H_{51}N_4$ requires: 947.4068. UV-vis (DCM) λ (ε) 324 (22640), 365 (28150), 423 (187900), 515 (23650), 549 (16700), 588 (12000), 645 (5500) nm.

5,15-Bis(4,7-dimethoxynaphthalen-1-yl)-10,20-bis(mesityl)porphyrin (163 a/b).

Dipyrrane **158** (264 mg, 1.0 mmol) and aldehyde **73** (216 mg, 1.0 mmol) were dissolved in DCM (100 mL), then TFA (0.137 mL, 1.78 mmol) was added slowly within 30 s. The reaction was stirred at room temperature. After 30 min, DDQ (227 mg, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature for a further 1 h. The complete reaction mixture was poured onto a pad of alumina and eluted with DCM with a few drops of acetone. The solvent was removed under vacuum to give a black solid which was dissolved in toluene (100 mL) and heated under reflux for 2 hrs in the presence of DDQ (227 mg, 1.0 mmol) to oxidize any remaining chlorin. After cooling to room temperature, the entire reaction mixture was passed through a pad of alumina and eluted with DCM until the purple material had completely eluted. Only one unpolar spot was observed on TLC. Crystallization from DCM/EtOH afforded porphyrins **163 a/b** as violet solid (94 mg, 21%): R_f (DCM/hexanes, 3:1) = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$, Me_4Si, ppm) δ -2.37 (s, 2H, NH), 1.84 (s, 12H, CH_3), 2.59 (s, 6H, CH_3), 2.86 (s, 3H, OCH_3), 2.93 (s, 3H, OCH_3), 4.25 (s, 6H, OCH_3), 6.49 (d, 1H, J = 2.4 Hz, naphth.), 6.62 (d, 1H, J = 2.4 Hz, naphth.), 7.09 (dd, 2H, J_1 = 1.8 Hz, J_2 = 7.8 Hz, naphth.), 7.12-7.18 (m, 2H, naphth.), 7.24 (br s, 4H, Ar), 8.07-8.09 (m, 2H, naphth.), 8.45 – 8.48 (m, 2H, naphth.), 8.57 – 8.63 (m, 8H, β-H); HRMS (TOF MS FD): [M^+] 918.4115 $C_{62}H_{54}N_4O_4$ requires: 918.4145. UV-vis (DCM) λ (ε) 438 (143000), 505 (98800), 585 (13300), 640 (7000) nm.

5,15-Bis(4,7-dimethoxynaphthalen-1-yl)-10,20-bis(mesityl)porphyrinato]nickel (II) (Ni-163).

To a solution of porphyrins **163 a/b** (92 mg, 0.1 mmol) in toluene (50 mL), $Ni(acac)_2$ (255 mg, 1 mmol) was added and the reaction was refluxed for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:1). Crystallization from DCM/EtOH afforded complex **Ni-163** as deep-orange crystals (97 mg, 99%): R_f (DCM/hexanes, 3:1) = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.81 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 2.56 (s, 6H, CH_3), 3.04 (s, 6H, OCH_3), 4.10 (s, 6H, OCH_3), 6.38 (d, 2H, J = 1.5 Hz, naphth.), 7.00 (d, 2H, J = 8.0 Hz, naphth.), 7.11 (dd, 2H, J_1 = 1.5 Hz, J_2 = 8 Hz, naphth.), 7.20 (br s, 4H, Ar), 7.93 (d, 2H, J = 8 Hz, naphth.), 8.40 (d, 2H, J = 9 Hz, naphth.), 8.47 – 8.56 (m, 8H, β-H); ^{13}C NMR (125 MHz, $CDCl_3$, Me_4Si, ppm) 21.4 (4), 21.5 (2), 54.9 (2), 55.6 (2), 100.9, 107.3, 116.6, 116.8, 117.0, 117.3, 120.1, 123.5, 127.7, 129.6, 131.0, 131.2, 132.2, 132.4, 133.0, 137.4, 137.6, 138.5, 139.0, 142.5, 142.6, 144.1, 155.9, 158.2. UV-vis (DCM) λ (ε) 420 (145000), 504 (95600), 562 (13300), 624 (5600) nm.

Mono fused *trans*-A_2B_2-porphyrin Ni-164.

The mixture of porphyrin complexes **Ni-163 a/b** (9.8 mg, 0.01 mmol) was dissolved in dry DCM (4 mL) and $Fe(ClO_4)_3{\cdot}2H_2O$ (78 mg, 0.2 mmol) in $MeNO_2$ (1 mL) was added via syringe within 5 min. After 25 min the reaction was filtered through a pad of silica. Additional DCVC (DCM/hexanes, 1:1) gave pure **Ni-164**. Crystallization from DCM/MeOH afforded product as green crystals (4.9 mg, 50%). R_f (DCM/hexanes, 1:1) = 0.65; ^1H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.74 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.05 (s, 3H, OCH_3), 4.12 (s, 3H, OCH_3), 4.15 (s, 3H, OCH_3), 4.28 (s, 3H, OCH_3), 6.41 (s, 1H, naphth.), 7.02 (d, 1H, J = 7.8 Hz, naphth.), 7.08 (dd, 1H, J_1 = 1.4 Hz, J_2 = 9.2 Hz, naphth.), 7.14 (s, 1H, naphth.), 7.17 (s, 1H, naphth.), 7.21-7.26 (m, 4H, Ar), 7.59 (d, 1H, J = 9.2 Hz, naphth.), 8.00 (d, 1H, J = 7.6 Hz, naphth.), 8.27 (d, 1H, J = 8.2 Hz, naphth.), 8.23 – 8.30 (m, 5H, β-H), 8.57 (d, 1H, J = 8.9 Hz, naphth.), 8.66 (d, 1H, J = 4.3 Hz, β-H), 8.97 (d, 1H, J = 4.9 Hz, β-H), 9.06 (d, 1H, J = 4.7 Hz, β-H). HRMS (ESI): [M^+] 972.3194 $C_{62}H_{50}N_4O_4Ni$ requires: 972.3180. UV-vis (DCM) λ (ε) 312 (31300), 379 (21900), 484 (134000), 587 (13200), 650 (41000), 730 (2000) nm.

Bis-fused *trans*-A_2B_2-porphyrin Ni-165.

The mixture of porphyrin complexes **Ni-163 a/b** (19.6 mg, 0.02 mmol) was dissolved in dry DCM (6 mL) and $Fe(OTf)_3$ (100 mg, 0.2 mmol) in $MeNO_2$ (2 mL) was added via syringe within 5 min. Subsequently, catalytic amount of $BF_3{\cdot}Et_2O$ (20 μL) was added. After 1h at room temperature the reaction was filtered through a pad of silica. Additional DCVC (DCM/hexanes, 1:1) gave pure **Ni-165**. Crystallization from DCM/MeOH afforded product as green crystals (7 mg, 36%). R_f (DCM/hexanes, 1:1) = 0.55; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.99 (br s, CH_3), 2.57 (s, CH_3), 2.60 (s, CH_3), 2.63 (s, CH_3), 4.17 (s, OCH_3), 4.30 (s, OCH_3), 4.31 (s, OCH_3), 7.20-7.24 (m, Ar + naphth.), 7.58-7.61 (m, naphth.), 8.22 – 8.28 (m, *β*-H), 8.51-8.59 (m, naphth.), 8.90-8.96 (m, *β*-H), 9.02 (s, *β*-H), 9.04 (s, *β*-H). HRMS (ESI): [M^+] 970.3023 $C_{62}H_{48}N_4O_4Ni$ requires: 970.3026. UV-vis (DCM) λ (ε) 307 (32000), 389 (14800), 498 (142700), 622 (8400), 666 (21300), 733 (98000) nm.

5,15-Bis(4,7-dimethoxynaphthalen-1-yl)-10,20-bis[(triisopropylsilyl)ethynyl]porphyrin (167).

$BF_3{\cdot}Et_2O$ (84 μl, 0.64 mmol) was added to an oxygen-free solution of dipyrrane **99** (660 mg, 2.0 mmol) and 3-(triisopropylsilyl)propynal (**166**) (620 mg, 2 mmol) in DCM (140 ml). The mixture was stirred for 20 min, over which time it turned deep blue. DDQ (684 mg, 3 mmol) was then added and the mixture was stirred for additional 10 min. The resulting brown solution was filtered through silica gel with DCM as eluent, then the solution was evaporated with silica gel, loaded on the column and chromatographed on silica gel (DCM/hexanes 1:4 → 2:1). After solvent removal, **167** was recrystallized from DCM/hexanes to give 425 mg of title compound (43%). R_f (DCM/hexanes, 3:2) = 0.45; ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si, ppm) δ -1.90 (s, 2H, NH), 1.36-1.45 (m, 42H, TIPS), 2.91 (s, 3H, OCH_3), 2.94 (s, 3H, OCH_3), 4.27 (s, 6H, OCH_3), 6.40 (d, 1H, J = 1.2 Hz, naphth.), 6.47 (d, 1H, J = 1.4 Hz, naphth.), 7.09 (d, 2H, J = 4.0 Hz, naphth.), 7.12 (d, 2H, J = 4.6 Hz, naphth.), 8.01 (d, 2H, 4.0 Hz, naphth.), 8.47 (d, 2H, J = 4.6 Hz, naphth.), 8.66 (s, 4H, *β*-H), 9.54 (s, 4H, *β*-H); LRMS (TOF MS FD): [M^+] 1042.5 $C_{66}H_{74}N_4O_4Si_2$ requires: 1042.5. UV-vis (DCM) λ (ε) 337 (20000), 438 (150700), 537 (10800), 585 (13300), 670 (7000) nm.

10,20-Bis(triisopropylsilylethynyl)-5,15-bis(4,7-dimethoxynaphthalen-1-yl) porphyrinato] nickel (II) (Ni-167).

To a solution of porphyrin **167** (104 mg, 0.1 mmol) in toluene (50 mL), Ni(acac)$_2$ (255 mg, 1 mmol) was added and the reaction was heated to reflux for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:2). Crystallization from DCM/MeOH afforded complex **Ni-167** as deep-orange crystals (109 mg, 99%). R$_f$ (DCM/hexanes, 3:2) = 0.55; ^{1}H NMR (500 MHz, CDCl$_3$, Me$_4$Si, ppm) δ 1.31-1.40 (m, 42H, TIPS), 3.07 (s, 3H, OCH$_3$), 3.10 (s, 3H, OCH$_3$) , 4.21 (s, 6H, OCH$_3$), 6.36 (d, 1H, J = 2.5 Hz, naphth.), 6.40 (d, 1H, J = 3 Hz, naphth.), 7.02 (d, 2H, J = 7.5 Hz, naphth.), 7.15-7.17 (m, 2H, naphth.), 7.84 (d, 1H, J = 6 Hz, naphth.), 7.86 (d, 1H, J = 6 Hz, naphth.), 8.42 (d, 1H, J = 3.5 Hz, naphth.), 8.44 (d, 1H, J = 3.5 Hz, naphth.), 8.58 – 8.60 (m, 4H, β-H), 9.43-9.45 (s, 4H, β-H); ^{13}C NMR (125 MHz, CDCl$_3$, Me$_4$Si, ppm) 11.7 (6), 19.0 (12), 55.0 (2), 55.8 (2), 99.3, 99.4, 100.5, 100.6, 101.0, 106.8, 106.9, 107.0, 107.1, 117.2, 117.3, 118.6, 118.7, 120.1, 120.2, 123.6, 128.8, 128.9, 131.6, 131.7, 132.9, 133.0, 133.1, 138.2, 144.1, 144.2, 145.3, 145.3, 156.1, 158.4, 158.5. LRMS (TOF MS FD): [M$^+$] 1098.4 $C_{66}H_{72}N_4NiO_4Si_2$ requires: 1098.4. UV-vis (DCM) λ (ε) 439 (196800), 515 (4600), 555 (14500), 592 (19700) nm.

Mono-fused porphyrin Ni-168.

R$_f$ (DCM/hexanes, 3:2) = 0.53; LRMS (TOF MS FD): [M$^+$] 1096.4 $C_{66}H_{70}N_4NiO_4Si_2$ requires: 1096.4. UV-vis (DCM) λ (ε) 308 (20800), 333 (19600), 388 (18300), 509 (111800), 617 (13700), 666 (30600) nm.

Bis- fused porphyrin Ni-169.

Porphyrin complex **Ni-167** (10 mg, 9.1 μmol) was dissolved in dry DCM (3 mL) and Fe(OTf)$_3$ (46 mg, 91 μmol) in MeNO$_2$ (5 mL) was added via syringe within 5 min. Subsequently, catalytic amount of BF$_3$·Et$_2$O (10 μL) was added. After 1h of stirring at room temperature and additional 30 min. at 40 °C the reaction was filtered through a pad of silica. DCVC (silica, DCM/hexanes, 1:1) gave pure **Ni-169**. Crystallization from DCM/MeOH afforded product as green crystals (3.3 mg, 36%). R$_f$ (DCM/hexanes, 3:2) = 0.45; HRMS (TOF MS FD): [M$^+$] 1095.4205 $C_{66}H_{69}N_4NiO_4Si_2$ requires: 1095.4194. UV-vis (DCM) λ (ε) 320 (14100), 392 (7300), 435 (9000), 537 (66900), 673 (6800), 743 (28800) nm.

5-(4,7-Dimethoxynaphthalen-1-yl)-tris-10,15,20-(triisopropylsilylethynyl) porphyrin (170).

Porphyrin **170** was separated from a crude reaction mixture obtained after synthesis of porphyrin **167** by chromatography (silica, DCM/hexanes, 1:4) and crystallization from DCM/MeOH (44 mg, 4%). R$_f$ (DCM/hexanes, 1:2) = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ -1.75 (s, 2H), 1.41-1.54 (m, 63H, TIPS), 2.94 (s, 3H, OCH_3), 4.25 (s, 3H, OCH_3), 6.41 (d, 1H, *J* = 2.3 Hz, naphth.), 7.07 (d, 1H, *J* = 7.8 Hz, naphth.), 7.15 (dd, 1H, J_1 = 2.3 Hz, J_2 = 9.5 Hz, naphth.), 7.97 (d, 1H, *J* = 7.7 Hz, naphth.), 8.46 (d, 1H, *J* = 9.4 Hz, naphth.), 8.60 (d, 2H, *J* = 4 Hz, *β*-H), 9.47 (d, 2H, *J* = 4.6 Hz, *β*-H), 9.65 (s, 4H, *β*-H); LRMS (TOF MS FD): [M$^+$] 1036.8 $C_{65}H_{84}N_4O_2Si_3$ requires: 1036.6. UV-vis (DCM) λ (ε) 424 (16800), 462 (21500), 583 (2500), 644 (5700) nm.

[5-(4,7-Dimethoxynaphthalen-1-yl)-tris-10,15,20-(triisopropylsilylethynyl)porphyrinato] nickel (II) (Ni-170).

To a solution of porphyrin **170** (104 mg, 0.1 mmol) in toluene (50 mL) $Ni(acac)_2$ (255 mg, 1 mmol) was added and the reaction was heated to reflux for 5 h. The reaction mixture was evaporated to dryness and chromatographed (DCM/hexanes, 1:4). Crystallization from DCM/MeOH afforded complex **Ni-170** as orange crystals (109 mg, 99%). R$_f$ (DCM/hexanes, 1:2) = 0.65; ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si, ppm) δ 1.34 – 1.42 (m, 63H, TIPS), 3.04 (s, 3H, OCH_3), 4.21 (s, 3H, OCH_3), 6.30 (d, 1H, *J* = 2.4 Hz, naphth.), 7.00 (d, 1H, *J* = 7.8 Hz, naphth.), 7.13 (dd, 1H, J_1 = 2.7 Hz, J_2 = 9.4 Hz, naphth.), 7.81 (d, 1H, 7.8 Hz, naphth.), 8.41 (d, 1H, *J* = 9.2 Hz, naphth.), 8.52 (d, 2H, *J*= 4.8 Hz, *β*-H), 9.36 (d, 2H, *J* = 5.1 Hz, *β*-H), 9.53 (s, 4H, *β*-H); LRMS

(TOF MS FD): [M$^+$] 1092.5 $C_{65}H_{82}N_4NiO_2Si_3$ requires: 1092.5. UV-vis (DCM) λ (ε) 433 (13800), 482 (18500), 572 (2200), 645 (5600) nm.

Fused porphyrin Ni-171.

Porphyrin complex **Ni-170** (10.9 mg, 0.01 mmol) was dissolved in dry DCM (3 mL) and $Fe(OTf)_3$ (51 mg, 0.1 mmol) in $MeNO_2$ (5 mL) was added via syringe within 5 min. Subsequently, catalytic amount of $BF_3 \cdot Et_2O$ (10 μL) was added. After 1h at room temperature and additional 30 min. at 40 °C the reaction was filtered through a pad of silica. DCVC (silica, DCM/hexanes 1:2) gave pure **Ni-171**. Crystallization from DCM/MeOH afforded title compound as brownish crystals (3.9 mg, 36%). R_f (DCM/hexanes, 1:2) = 0.45; LRMS (TOF MS FD): [M$^+$] 1090.5 $C_{65}H_{80}N_4NiO_2Si_3$ requires: 1090.5. UV-vis (DCM) λ (ε) 368 (26400), 444 (13500), 583 (17200), 640 (32000), 725 (1500) nm.

List of abbreviations

Ac acetyl

Acac acetylacetonato

Aq aqueous

Ar aryl

***t*-Bu** *tert*-Butyl

°C temperature in degrees Centigrade

DCM dichloromethane

DCVC dry column vacuum chromatography

DDQ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

DMF *N,N*-dimethylformamide

DMSO dimethylsulfoxide

h hour(s)

HPLC high pressure liquid chromatography

Me methyl

Mes mesityl

MS mass spectrometry

NMR nuclear magnetic resonance

Ph phenyl

PIFA phenyliodine bis(trifluoroacetate)

R_f retention factor

SEC size exclusion chromatography

TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography

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Synteza *mezo*-podstawionych porfiryn i koroli o rozszerzonym chromoforze

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1. Wprowadzenie

Na przestrzeni ostatnich kilku lat wiele uwagi zostało poświęcone syntezie porfiryn o rozszerzonym chromoforze.[1] Analiza wieloletniej pracy chemików badających możliwości rozszerzenia układu sprzężonych wiązań wielokrotnych w porfirynach dowodzi, że wartość batochromowego przesunięcia absorpcji bardziej zależy od sposobu modyfikacji tego chromoforu niż od ilości dodanych wiązań wielokrotnych.[2] Spośród wielu możliwości otrzymania tego typu związków[3] na uwagę zasługuje wewnątrzcząsteczkowe oksydatywne sprzęgnięcie *mezo-mezo* połączonych porfiryn przeprowadzone przez Osukę i współpracowników.[4] Rezultatem badań było otrzymanie posiadającej dwa dodatkowe wiązania, zupełnie płaskiej diporfiryny wykazującej w konsekwencji właściwości wskazujące na całkowite zdelokalizowanie elektronów π, jak na przykład znacząco poszerzone i przesunięte batochromowo widmo absorpcji.[5] Analogiczne układy można potencjalnie otrzymać przez oksydatywne sprzęganie porfiryn zawierających inne bogate w elektrony jednostki (homo- i heteroaromatyczne) w pozycjach *mezo*.[6] Porównanie maksimów absorpcji różnych rozszerzonych porfiryn wykazuje, że dobudowanie jednostek aromatycznych w ten sposób jest metodą modyfikacji pierścienia porfiryny prowadzącą do wyjątkowo silnego przesunięcia batochromowego.

2. Cel i wyniki

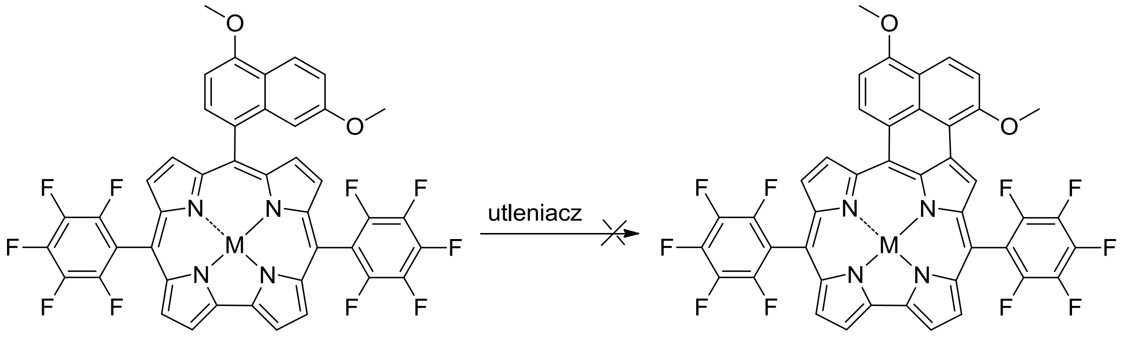
Cel mojej pracy można sprecyzować jako:

- Badanie szeregu ścieżek syntetycznych mających na celu rozszerzenie chromoforu korolu
- Badanie wewnątrzcząsteczkowej reakcji oksydatywnego sprzęgania dla *mezo*-podstawionych A_3B- i *trans*-A_2B_2-porfiryn

Po sprawdzeniu szeregu koncepcji dotyczących rozszerzenia chromoforu koroli, takich jak:

1 zmiana metalu w makrocyklu [Cu, Ag]
2 modulowanie struktury podstawnika w pozycji *mezo* (pochodne naftalenu, chinoliny)
3 zamiana pozycji podstawnika podlegającego potencjalnie reakcji sprzęgania [5 lub 10]
4 przebadanie szeregu utleniaczy

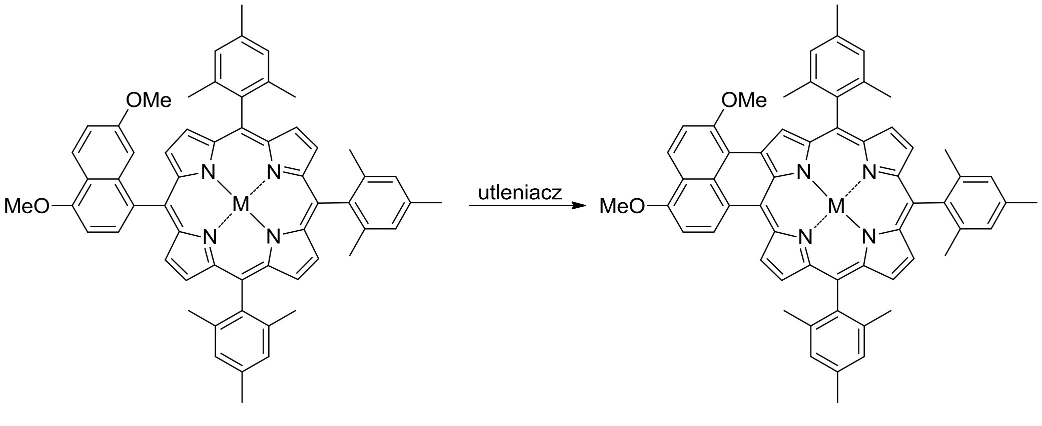
mogę stwierdzić, że jest to cel trudny do zrealizowania (Schemat 1). Spośród wszystkich prób tylko w jednej udało się uzyskać pożądany produkt, był on jednak wysoce niestabilny, przez co jego analiza była możliwa jedynie częściowo.



Schemat 1

Wobec braku możliwości otrzymania stabilnego sprzęgniętego korolu, zdecydowałem się na syntezę korolu zawierającego w pozycji *mezo*- ugrupowanie arylopropargilowe. Literatura nie odnotowuje dotychczas syntezy takiego korolu. Dowiodłem, że spodziewane *trans*-A_2B-korole powstają w reakcji z użyciem typowych dla syntezy koroli warunków, sa one jednak zbyt nietrwałe żeby można je było doczyścić. Podejście to, zastosowane dla reakcji acetalu dietylowego aldehydu mezytylopropargilowego z 5-(pentafluorofenylo)dipirometanem zaowocowało powstaniem produktu, będącego prawdopodobnie pochodną oktafiryny (1.1.1.0.1.1.1.0).

Następnie przedstawione zostały badania oksydatywnego sprzęgania porfiryn typu A_3B, posiadających bogaty w elektrony podstawnik naftalenowy (Schemat 2).

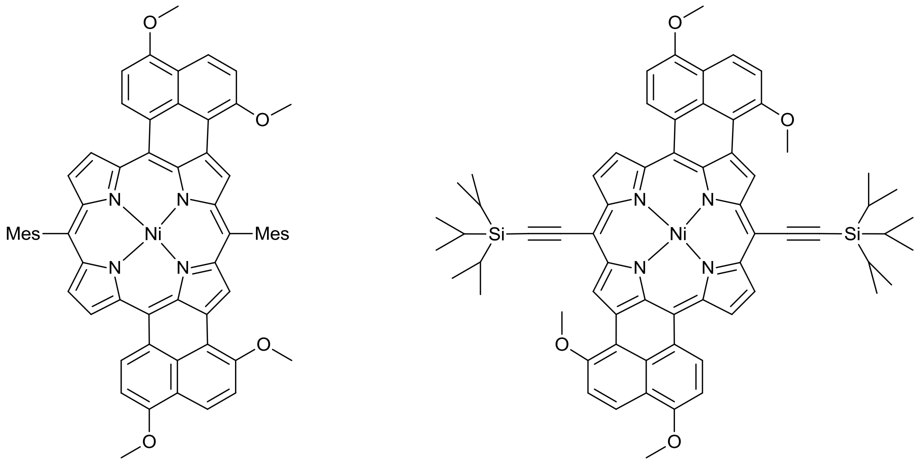


Schemat 2

Ta część pracy zaowocowała otrzymaniem pięciu *mezo-β*-sprzęgniętych kompleksów porfirynowych. Dodatkowo opracowałem metodę oksydatywnego sprzęgania za pomocą $Fe(ClO_4)_3$. Pozwala ona na uniknięcie ubocznego procesu chlorowania, oferując jednocześnie dobre wydajności.

Opracowałem również metodę syntezy *mezo-β*-sprzęgniętej indolo-porfiryny.
Kolejną częścią rozprawy były badania oksydatywnego sprzęgania *trans*-A_2B_2-porfiryn zawierających dwa podstawniki naftalenowe. Zastosowanie analogicznej procedury jak dla porfiryn A_3B doprowadziło do utworzenia mono-sprzęgniętych porfiryn. Próby przeprowadzenia drugiego oksydatywnego sprzęgnięcia doprowadziły do odkrycia tryflanu żelaza (III) jako bardzo dobrego utleniacza dla tego typu reakcji. Porfiryny bis-sprzęgnięte otrzymałem jako mieszaninę regioizomerów (Rys. 1).

Ostatnia część pracy poświęcona jest badaniom sprzęgania *trans*-A_2B_2-porfiryn posiadających zarówno jednostki naftalenowe jak i podstawniki zawierające wiązanie potrójne w pozycji *mezo*. Również w tym przypadku otrzymałem bis-sprzęgnięte porfiryny (Rys. 3).



Rysunek 1

3. Wnioski

Zaprojektowałem i otrzymalem substraty niezbędne do przebadaniareakcji oksydatywnego sprzęgania koroli. Pomimo wielu podejść i różnych koncepcji nie udało się otrzymać stabilnego sprzęgniętego korolu.
W reakcji mającej w założeniu prowadzić do otrzymania korolu zawierającego potrójne wiązanie otrzymałem produkt zawierający prawdopodobnie szkielet oktafiryny (1.1.1.0.1.1.1.0).
Z dobrymi wydajnościami otrzymałem sprzęgnięte porfiryny typu A_3B, A_2B_2 oraz A_2B_2 zawierające wiązania potrójne w pozycji *mezo*.

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