Meso–meso linked corroles†

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The cascade reaction of sterically hindered dipyrromethanes and formaldehyde furnished *meso*(10)–*meso*(10′) linked corroles—a new type of porphyrinoid—compounds with interesting photophysical properties.

In a search towards new chromophores with interesting properties, the existing ones are often combined in different fashions.[1] One of the striking examples of such an approach was recently demonstrated by Osuka *et al.* Porphyrins bearing *meso* position(s) free were first oxidized to form a *meso–meso* link[2] and then treated with DDQ/Sc(OTf)$_3$ to form two additional bridges between the β positions. This structural change caused an extension of the conjugated π-system with concurrent strong bathochromic absorption and emission shift.[3] An elegant example of such a multiplied effect is shown in so-called 'porphyrin tapes' (10 nm molecular size), which display absorption at 3500 cm^{-1}.[4] In principle, such an approach towards new interesting NIR-absorbing chromophores can be utilized for other compounds from the porphyrinoid family. A natural barrier though is often lack of suitably developed methodology for the synthesis of required building blocks. Among others, corroles[5]—one-carbon short analogs of porphyrins—fill this precondition, since they have become easily available after recent developments.[6,7] The methodology for the synthesis of *meso*-substituted corroles is in a mature state and allows for the introduction of various groups at the periphery of the macrocycle.[8]

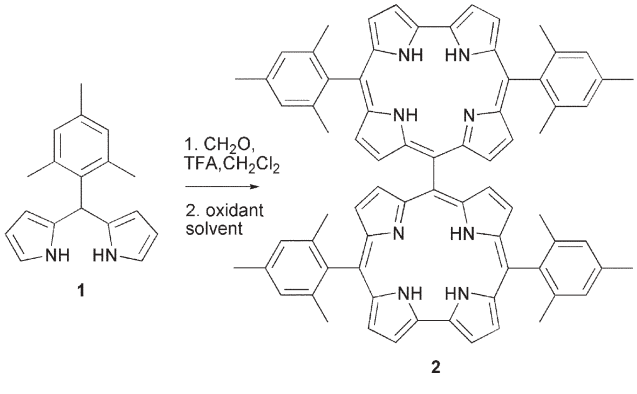
In fact, Gross and co-workers have already demonstrated that some complexes of tris(pentafluorophenyl)corrole (Cu, Co) undergo spontaneous dimerization to give β–β dimers.[9] Very recently, two methods for the preparation of 2,2′,18′,18′-linked corrole dimers were published independently by Osuka and co-workers[10] and Cavaleiro and co-workers.[11] Herein we describe our approach towards the synthesis of *meso–meso* linked corrole dimers and their basic photophysical properties.[12]

Lower symmetry of corroles in respect to porphyrins inevitably leads to a higher number of possible *meso–meso* linked corrole dimers (5–5′, 5–10′, 10–10′) as possible synthetic targets. However, since our additional aim was also to explore the possibility of triple linked dimer formation, only the 10–10′ dimer was a prospective goal. Further oxidation of 5–5′ and 5–10′ dimers would inevitably lead to a complex mixture of two regioisomers.

Following Osuka's work we designed an approach based on a substrate that would incorporate appropriate functional handles to allow the eventual installation of *meso–meso* link. We thus set as a target 5,15-diarylcorroles bearing *meso*(10)-position free, which might undergo oxidative dimerization upon the exposure to AgPF$_6$[2] to provide *meso–meso* dimers. Corroles with this pattern of substituents are unknown but one can assume that they can be synthesized from the corresponding bilanes. Since the reaction of unhindered dipyrromethanes with aldehydes in the HCl–H$_2$O–MeOH system[7] affords the highest yields of corroles reported up to date, we decided to investigate the reaction of 4-cyanophenyldipyrromethane with formaldehyde under such conditions. In the event, although we were pleased to find that the respective bilene was formed (identified based on MS), the subsequent oxidative macrocyclization reaction (in the presence of DDQ) could not be achieved. We therefore turned our attention to the reaction of sterically hindered mesityldipyrromethane (**1**) with formaldehyde. Quenching of this reaction mixture with DDQ delivered a red-fluorescent compound which was separated and identified as the *meso–meso* linked dimer **2** (Scheme 1).

The direct formation of dimer **2** can be rationalized as a DDQ mediated coupling[13] between two molecules of initially formed 5,15-dimesitylcorrole. Since the oxidation potential of corroles[14] is significantly lower than that of porphyrins such reaction should be in principle easier to perform. Low yield (0.5%) and tedious separation forced us to optimize this reaction (ESI,† Table S1).

Changing factors, such as: the solvent in the first step, concentration of an acid, time of the first step, type of oxidant as well as the dilution of the reaction mixture did not improve the yield of corrole **2**. Finally the combined effect of changing the ratio of mesityldipyrromethane (**1**) to formaldehyde and of THF addition as a co-solvent‡ to the reaction mixture before the second step afforded the product in 3.3% yield. The same reaction performed in the HCl–H$_2$O–MeOH system[7] did not lead to the formation of corrole **2**. All attempts to further improve the yield by performing the reaction with other forms of formaldehyde failed.



Scheme 1

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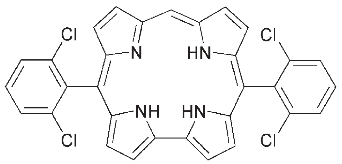
† Electronic supplementary information (ESI) available: Full experimental procedures for the synthesis of compounds **2–4**, their ^{1}H NMR spectra as well as detailed optimization of the synthesis of corrole **2**, comparison of absorption of **3** and **4**. See DOI: 10.1039/b703279j

Unsatisfactory yield of *meso–meso* dimer **2** inclined us to apply the optimized reaction conditions to the analogous sterically hindered 5-(2,6-dichlorophenyl)dipyrromethane.[15] In this case we obtained the expected *meso–meso* linked dimer **4** in overall 5% yield (Fig. 1). It is worth to mention that the respective 5,15-bis(2,6-dichlorophenyl)corrole (**3**) can be obtained in 2.4% yield when CH_2Cl_2 is used as a solvent for the oxidation step (Fig. 1). Additional refining of the reaction conditions by adding hydrazine hydrate[7] allowed to increase the yield of dimer **4** to 6.1%. Sterically unhindered dipyrromethanes (bearing such substituents such as: 4-cyanophenyl, 4-methylphenyl, 4-trifluoromethylphenyl and 3,5-bis(trifluoromethyl)phenyl) submitted to optimized reaction conditions gave neither *meso–meso* linked dimer nor corresponding monomeric corrole, based on ESI-MS.

Absorption and emission spectra of corrole **4** are presented on Fig. 2. The absorption spectrum of the *meso–meso* dimer displays differences in regard to the parent corrole **3** (see ESI†). The Soret band is split (42 nm difference), which indicates that the electronic structure has been significantly altered. One should note that moderate splitting of the Soret band (~15–20 nm) is an intrinsic property of corroles bearing sterically hindered substituents.[14,16,17] A large splitting of the Soret bands observed for corrole **4** is due to the strong exciton coupling, as was observed by Osuka and co-workers,[2] but not by Chandrashekar, for 5,5′-linked oxacorrole dimers.[12] The low-energy Soret band is shifted to longer wavelength while the high energy Soret band remains at nearly the same wavelength as for monomer (403 and 408 nm, see ESI†). On the contrary, the Q-bands of the directly linked corrole are much less perturbed as evidenced by a smaller bathochromic shift (12–15 nm) presumably due to the much weaker oscillator strength of Q transition. The emission properties of the corrole dimer were probed in view of its different electronic structure. The emission maximum for **4** was observed at 658 nm upon excitation at 413 nm. We also measured the fluorescence quantum yield in various solvents. In all solvents studied (CH_2Cl_2, toluene, THF), $\Phi = 0.04$, which is considerably lower than for corrole **3** (Φ = 0.14) and slightly lower than for 5,15-bis(2,6-dichlorophenyl)-10-(4-methylphenyl)corrole (Φ = 0.06).[18] This is in striking contrast to the *meso–meso* linked porphyrin where the fluorescence quantum yield slightly increases *vs.* that of the monomer.[19] The Stokes shift (1035 cm^{-1}) is higher than for typical *meso*-substituted corroles.[17] Unperturbed Soret transition at 403–408 nm suggests the perpendicular conformation of the corrole subunits in the dimer, which tends to minimize electronic interaction.



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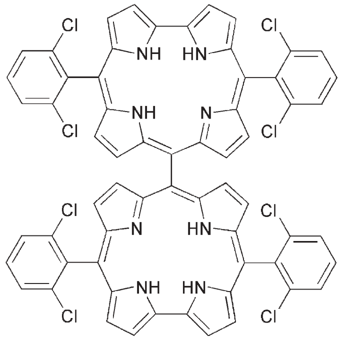

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Fig. 1

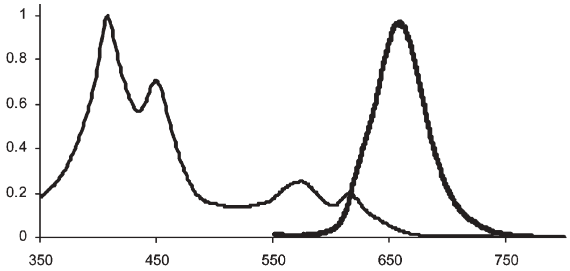

Fig. 2 Normalized absorption (thin line) and emission (thick line) spectra of corrole **4** (THF).

Standard ^1H NMR spectrum of *meso–meso* dimer **4** showed significant line broadening regardless the solvent used (see ESI†). Especially signals derived from β-pyrrole protons and NH protons were broadened. One has to note that there is no such effect for *meso–meso* dimer **3**. These intriguing results, which indicated some complex dynamic processes taking place prompted us to study the variable-temperature ^1H NMR spectra for corrole **4** in DMSO-d_6. The most interesting regions are shown on Fig. 3. The spectrum recorded at 303 K displayed sharper signals than in previously studied solvents ($CDCl_3$, CD_2Cl_2, THF-d_8). On the other hand, the spectrum recorded at 363 K shows significantly broadened aromatic signals in comparison to spectrum recorded at 303 K. For NH, the spectrum at lower temperature has two distinct

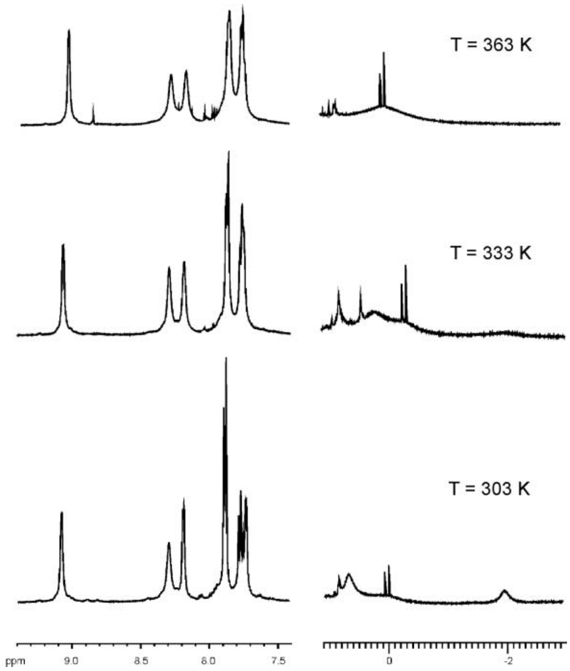

Fig. 3 Variable-temperature ^1H NMR spectra of **4** (DMSO-d_6, aromatic and NH regions).

signals (at −1.95 and 0.6 ppm) which coalesce at 363 K to give a very broad signal (0.0 ppm) (Fig. 3). The striking difference in the ^{1}H NMR spectra of dimers **3** and **4** is puzzling. In general, the type of spectra of corrole **4** suggested the presence of hindered rotation and/or NH tautomeric equilibrium of two conformers with slow exchange relative to the NMR time scale at 303 K. However, we may assume that for dimers **3** and **4** the free rotation of both corrole moieties is restricted to a similar extent. This complex picture could be clarified to a certain extent by X-ray crystallographic analysis. However, so far it has not been possible to obtain crystals of any *meso–meso* corrole dimers suitable for an X-ray crystal structure analysis.

At this point in our studies we decided to investigate if *meso-meso* corrole dimers can be converted into *meso–meso*, *β–β*, *β–β* triply linked corrole dimers. Owing to the higher yield and stability we focused on compound **4** as a substrate in these studies.

We explored the reactivity of the free base **4** as well as its *in situ* formed gallium complex under Osuka's conditions (DDQ/$Sc(OTf)_3$),[4] and in the presence of PIFA[20] or PIFA/TMSBr,[21] but this led to recovery of starting material in all cases. One of the promising approaches was the reaction with copper acetate, which can act as both a complexing and an oxidating agent. In the event, standard methods to synthesize copper complexes, however, led to mixtures in which the expected complex of triple linked corrole could not be detected using MS.

In conclusion, our studies have clearly documented the ability of a [2 + 1] strategy to assemble previously unknown *meso*(10)–*meso*(10′) linked corrole dimers. The target compounds were obtained in a one-pot synthesis from sterically hindered dipyrromethanes and formaldehyde. Sterically unhindered dipyrromethanes failed to give *meso–meso* linked corrole dimers under the same conditions. Overall yields from pyrrole are comparable to those calculated for *meso–meso* linked porphyrin dimers. The whole cascade process consists of acid-catalyzed bilane formation, its oxidation to corrole and subsequent DDQ-mediated oxidative dimerization. The latter step is so preferred that obtaining corroles unsubstituted in position 10 is very difficult. Spectroscopic properties suggest that the components are weakly electronically linked. Fluorescence data demonstrate that linking two corrole units in *meso*(10) positions induce a different response than in the case of *meso–meso* linked porphyrins. Attempts leading to oxidation of *meso–meso* linked corrole dimers to *meso–meso*, *β–β*, *β–β*-linked dimer failed, probably due to limited stability and/or preferable formation of bonds in positions 2 and 18 rather than 9 and 11.

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Notes and references

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