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Fused Corrole Dimers Interconvert between Nonaromatic and Aromatic States through Two-Electron Redox Reactions**

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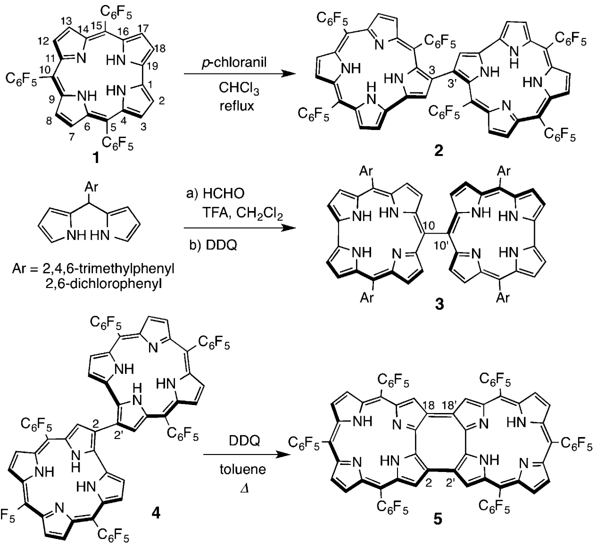
Abstract: *A singly linked corrole dimer was synthesized by condensation of a dipyrromethane-1-carbinol with 1,1,2,2-tetrapyrroethane. Oxidation of the dimer gave doubly linked corrole dimers* ***9*** *and* ***10*** *as the first examples of fused corrole dimers involving a meso–meso linkage. Dimers* ***9*** *and* ***10*** *exhibit characteristic* ^1H *NMR spectra, absorption spectra, excited-state dynamics, and two-photon absorption (TPA) values, which indicate the nonaromatic nature of* ***9*** *and the aromatic nature of* ***10****. Interestingly,* ***9*** *is fairly stable despite its unusual 2H-corrole structure, which has been ascribed to the presence of two direct connections between the individual corrole units.*

Conjugated porphyrin arrays have been extensively studied for the last two decades in light of their attractive electronic, optical, and electrochemical properties.[1] Various porphyrinoids have been employed in numerous studies to demonstrate their potential.[1,2] Corrole is a ring-contracted porphyrin bearing a direct pyrrole–pyrrole linkage. In most cases, corroles bear three pyrrolic protons (3*H*-corroles) and those bearing two pyrrolic protons (2*H*-corroles) are electronically frustrated and very rare.[3] After the initial reports by the groups of Gross, Gryko, and Paolesse describing reliable synthetic protocols, corroles have been widely used as chromophores, sensors, and catalysts.[4,5] Despite these studies, only a limited number of directly linked corrole dimers have been reported so far. Oxidation of 5,10,15-tris(pentafluorophenyl)corrole (**1**) with *p*-chloranil afforded the 3,3′-linked dimer **2** (Scheme 1).[6] Corrole dimers with the same connection were also produced upon metalation of **1** with either Cu^{III} or Co^{III} ions.[7] As an interesting example, Gryko et al. have synthesized the 10,10′-linked corrole dimers **3** by acid-catalyzed condensation reactions of 5-aryldipyrromethanes with formaldehyde, but attempts to obtain fused dimers from **3** were unsuccessful.[8] We synthesized the 2,2′-linked corrole dimer **4** by oxidative homocoupling of a 2-borylated corrole,[9a] and **4** was further oxidized to the doubly linked 2*H*-corrole dimer **5** which exists as a stable singlet biradicaloid.[3c,9b] The scarcity of directly linked corrole dimers may be ascribed to the intrinsically high reactivity of corroles as well as limited synthetic transformations applicable to corroles.



Scheme 1. Syntheses of corrole dimers.

Recently we reported a facile synthesis of corroles by condensation of 5-aryldipyrromethane and dipyrromethane-1-carbinol **6** (for structure see Scheme 2).[10] This success led us to envision that the 5,5′-linked corrole dimer **8** may be accessed by condensation of **6** with the 1,1,2,2-tetrapyrroethane **7**.[11,12] Herein we report the synthesis of **8** and its oxidative transformation into the doubly linked corrole dimers **9** and **10** as the first example of fused corrole dimers involving a meso–meso direct linkage. Importantly, **9** is fairly stable in spite of its 2*H*-corrole structure.

The corrole dimer **8** was synthesized by a 2:1 condensation of **6** and **7** with the assistance of $BF_3{\cdot}OEt_2$ (Scheme 2). After stirring for 5 minutes, a bilane intermediate was separated though a short pad of silica gel and was immediately oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Repeated separation through silica gel columns gave **8** in 3.4% yield as the only isolable product. High-resolution atmospheric-pressure chemical-ionization time-of-flight mass

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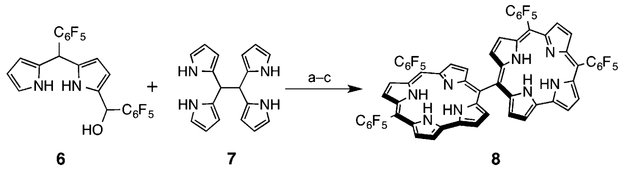


Scheme 2. Synthesis of **8**. Reaction conditions: a) $BF_3{\cdot}OEt_2$ (0.33 mol%), CH_2Cl_2, room temperature, 5 min. b) purification by silica-gel column chromatography. c) DDQ (2.8 equiv), CH_2Cl_2, room temperature, 1 h.

spectroscopy (APCI-TOF-MS) revealed its parent ion peak at *m/z* 1258.1610 (calcd for $C_{62}H_{22}N_8F_{20}$, *m/z* 1258.1643). The ^{1}H NMR spectrum of **8** exhibited eight doublet peaks resulting from the pyrrolic β-protons in the range of $\delta =$ 8.1–9.2 ppm, thus indicating a diamagnetic ring current of the constitutional corroles. The structure of **8** was revealed by X-ray diffraction analysis (Figure 1).[13] The central C5–C5′ bond length is 1.480(5) Å, which is similar to the lengths previously reported for meso–meso linked diporphyrins, while the dihedral angle between the mean planes of the corroles is only 50.0°, which is considerably smaller than those of meso–meso linked diporphyrins (75–88°).[11,14]

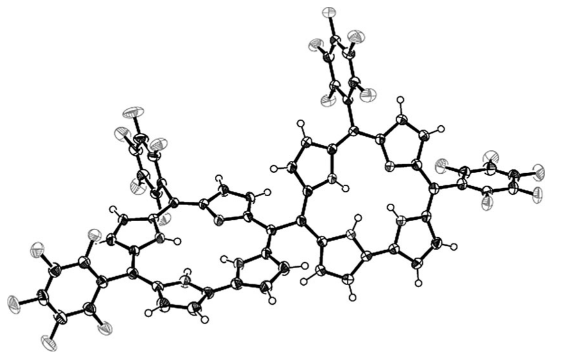


Figure 1. X-Ray crystal structure of **8**. Thermal ellipsoids were scaled to 50% probability level. Solvent molecules were omitted for clarity.

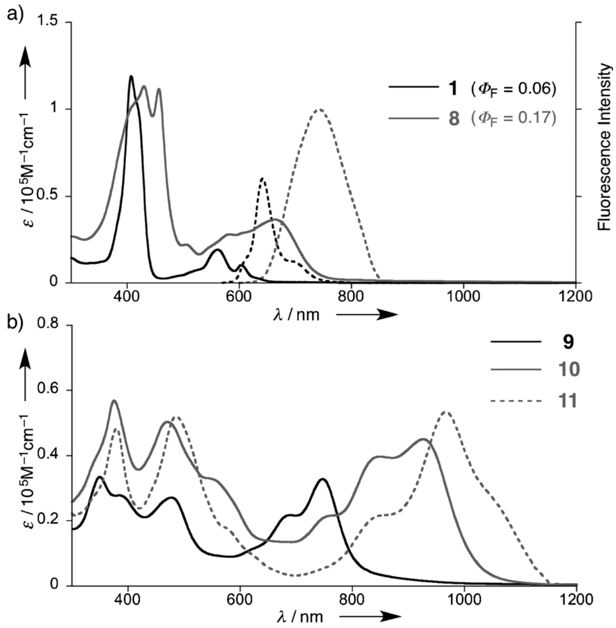
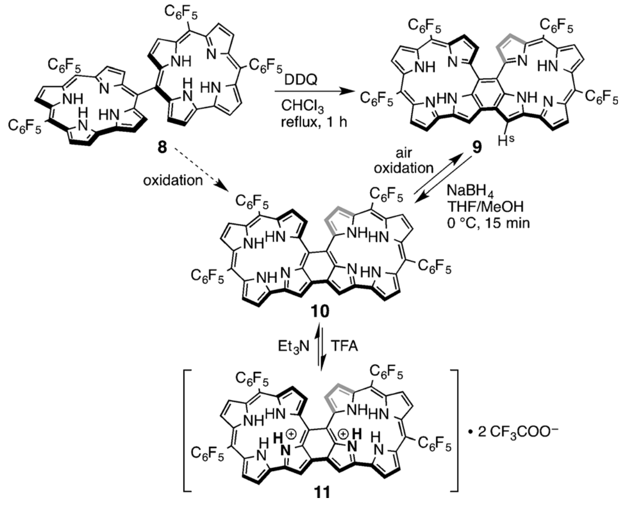


Figure 2. a) UV/Vis absorption (solid lines) and fluorescence spectra (dashed lines) of **1** (black) and **8** (gray). b) UV/Vis/NIR absorption spectra of **9** (solid black), **10** (solid gray), and **11** (dashed gray) in CH_2Cl_2.

The UV/Vis absorption spectra of **1** and **8** in CH_2Cl_2 are shown in Figure 2a. The dimer **8** exhibits a split Soret band at $\lambda = 430$ and 457 nm and red-shifted Q bands in the range of $\lambda = 500$–800 nm. The observed split Soret band arises from exciton coupling of the two corroles, while the red-shifted absorption bands indicate considerable conjugative communication between the two corroles, and it is notably larger than those in meso–meso linked diporphyrins.[11,14] The fluorescence of **8** is red-shifted with respect to the monomer, whilst the quantum yield ($\Phi_F = 0.17$) is enhanced. Cyclic voltammetry of **8** in benzonitrile revealed that the first and second oxidation take place at 0.13 and 0.33 V, respectively, whilst two reduction potentials can be observed at −1.51 and −1.71 V versus the ferrocene/ferrocenium ion couple. The two oxidation waves have been assigned as split first oxidation waves (one electron per corrole), as judged from the results of meso–meso linked diporphyrins.[15] The potential difference (splitting energy) between the first and second oxidation waves ($\Delta E_{ox} = E_{ox2} - E_{ox1}$) of **8** is 0.20 V, which is larger than that of meso–meso linked Zn^{II} diporphyrin ($\Delta E_{ox} =$ 0.11 V).[15]

In the next step, the intramolecular oxidative fusion reaction of **8** was performed under high dilution conditions (ca. 0.1 mM) with DDQ (3 equiv) in refluxing $CHCl_3$ for 30 minute to avoid undesirable intermolecular coupling (Scheme 3). To our delight, **9** was obtained in 63% yield as a black solid.[16] HR-APCI-TOF-MS analysis revealed its parent ion peak at *m/z* 1254.1319 (calcd for $C_{62}H_{18}N_8F_{20}$, *m/z* 1254.1330), thus indicating a loss of four hydrogen atoms from **8**. The ^{1}H NMR spectrum of **9** displayed six doublets at $\delta =$ 6.43, 6.38, 6.30, 5.92, 5.61, and 5.52 ppm resulting from the



Scheme 3. Oxidative fusion reaction of **8** and interconversions among **9**, **10**, and **11**.

pyrrolic β-protons, one doublet at $\delta = 5.88$ ppm (H^{s} in Scheme 3) coupled with the pyrrolic NH ($J = 2.3$ Hz), and two broader peaks at $\delta = 19.28$ and 18.70 ppm resulting from the pyrrolic NH protons. Assignment of the latter two signals has been confirmed by deuterium exchange experiments. Therefore, this product has been assigned as a doubly linked 2*H*-corrole dimer **9** bearing only two pyrrolic NH protons. Interestingly, **9** is chemically fairly stable in spite of its 2*H*-corrole constitution.[17] The observed ^{1}H NMR chemical shifts of **9** indicate its non-aromatic character, which is consistent with its structural features, which one cannot depict as either an 18π aromatic circuit of corrole or an overall conjugated circuit. Here it is interesting to compare doubly linked 2*H*-corrole dimers **5** and **9**, in that the connecting location dictates the electronic state of the dimers, that is, singlet biradicaloid and nonaromatic, respectively.

Then, **9** was reduced with $NaBH_4$ to give the 3*H*-corrole dimer **10** in 83 % yield, which was isolated in pure form but steadily reverted to **9** under aerobic conditions. The oxidation of **10** to **9** proceeded gradually in open air and immediately upon treatment with DDQ. The ^{1}H NMR spectrum of **10** exhibits seven signals which result from the β-protons in the range of $\delta = 8.7$–7.9 ppm, thus indicating the full recovery of aromaticity. Despite numerous attempts under various conditions, we could not obtain single crystals of eitehr **9** or **10** because of the poor solubility of **9** and readily oxidizable nature of **10**. In the meantime, single crystals of doubly protonated **10**, namely **11**, were obtained from slow vapor diffusion of pentane to a 1,2-dichlorobenzene solution of **10** containing a trace amount of trifluoroacetic acid (TFA). The structure of **11** is depicted in Figure 3,[18] in which the two corroles are doubly connected at the 3,3′- and 5,5′-positions with C−C bond lengths of 1.433(6) and 1.442(5) Å, respectively. The corrole planes are severely distorted to avoid steric interaction between the two protons at the 7- and 7′-positions. The mean-plane deviation values are calculated to be 0.258 and 0.285 Å, which are clearly larger than those in **8** (0.118 and 0.146 Å).[19]

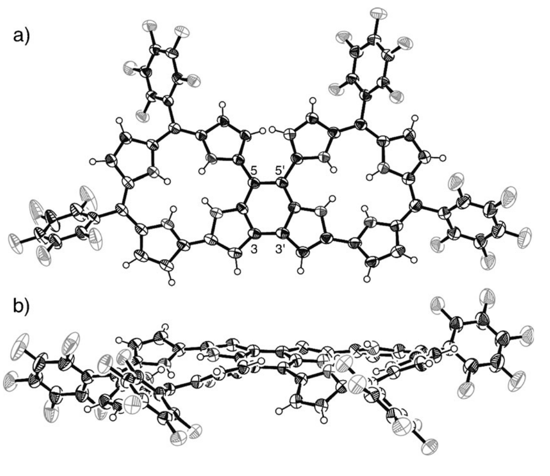


Figure 3. X-Ray crystal structure of **11**: a) Top view and b) side view. Thermal ellipsoids were scaled to 50% probability level. Solvent molecules and counter anions were omitted for clarity.

The absorption spectrum of **9** exhibits high-energy bands at $\lambda = 349$, 382, and 478 nm, low-energy bands at $\lambda = 690$ and 748 nm, and a very weak absorption tail reaching out to around $\lambda = 1100$ nm (Figure 2b). The weak absorption tail is characteristic of antiaromatic porphyrinoids,[20] which suggests that **9** possesses some degree of antiaromatic character. In comparison, **10** displays a more perturbed absorption spectrum without a weak tail, whilst the absorption bands of **11** are further red-shifted. Cyclic voltammetry revealed two oxidation potentials at 0.56 and 0.73 V and four reversible reduction potentials at −0.48, −0.65, −1.75, and −1.99 V for **9**, and the first oxidation and reduction potentials at −0.13 and −0.98 V, respectively, for **10**.[21] The observed low oxidation potential of **10** is consistent with its facile oxidation under ambient conditions. The electrochemical HOMO–LUMO gaps (ΔE) are thus calculated to be 1.04 eV for **9** and 0.85 eV for **10**, which match roughly with the respective optical band gaps ($\Delta E_o = 1.12$ eV for **9** and $\Delta E_o = 1.07$ eV for **10**).

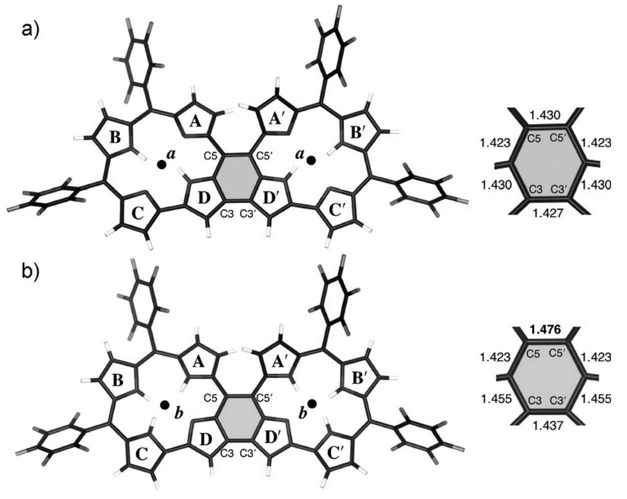


Figure 4. The lowest energy forms of **9** and **10** obtained by DFT calculation. The bond lengths of internal six-membered rings (in Å) are shown on the right.

DFT calculations have been performed at the B3LYP/6-31G* level of theory to optimize the structures of **9** and **10**. The lowest energy tautomer of **9** is shown in Figure 4a, in which the pyrroles A and C are imine-type and the pyrroles B and D are amino-type, and is in line with the ^{1}H NMR data. In contrast, the most stable tautomer of **10** possesses an imine-type pyrrole at the pyrrole D (Figure 4b). The nucleus-independent chemical shift (NICS) values at the gravity centers of corrole rings (position *a* in **9** and position *b* in **10**) are calculated to be 8.07 and −9.37 ppm, respectively.[22] In **9**, the central benzene ring has been calculated to be an almost hexagonal shape, thus suggesting the importance of the local benzene aromaticity at the expense of macrocyclic conjugation. In contrast, the C5−C5′ bond length in **10** has been calculated to be distinctly longer than the other sides of the central benzene ring, thus implying less contribution of the local benzene aromaticity.

Excited-state dynamics of **8**, **9**, and **10** were studied using femtosecond transient absorption (TA) spectroscopy. In the case of **8**, characteristic TA spectral shape changes were observed in NIR absorption bands. These changes are a signature of excited-state conformational relaxation along the inter-ring torsional coordinate as seen in various meso–meso linked diporphyrins.[23] The excited-state lifetime is 0.78 ns, which is significantly shorter than that of a corrole monomer (4.87 ns).[9b] The shorter S_1 lifetime seems to originate from electronic perturbation arising from the direct linkage. In contrast, such TA spectral changes were not observed for **9**. The decay dynamics probed at ground-state bleaching ($\lambda = 680$ nm) was analyzed with biexponential decay. The fast component, 0.4 ps, corresponds to internal conversion from the optically allowed state, which appears at around $\lambda = 740$ nm, to the optically forbidden state located in the NIR region. Because of a significantly reduced energy gap, the excited-state lifetime of **9** is reduced to 11 ps. The dimer **10** displays a longer excited-state lifetime of 140 ps, thus reflecting its recovered aromaticity. A fast decay with a time constant of 15 ps is presumably attributed to a vibrational cooling process, as in the case of fused diporphyrins.[23] To investigate nonlinear optical properties, two-photon absorption (TPA) cross-section values were measured using an open-aperture Z-scan method. The TPA cross-section values for **9** and **10** were 410 GM at 1500 nm and 1300 GM at 1800 nm, respectively. A large difference in the TPA cross-section values of **9** and **10** indicates that **10** possesses a more effective aromatic conjugation pathway,[25] which is also supported by the excited-state lifetimes and NICS values.

In summary, the 3,3′- and 5,5′-doubly linked corrole dimers **9** and **10** were synthesized as the first examples of fused corrole dimers from the oxidation of 5,5′-singly linked corrole dimer **8**. The dimers **9** and **10** have been assigned as nonaromatic and aromatic, respectively, on the basis of their ^{1}H NMR spectra, DFT calculation, excited-state dynamics, and TPA values. Curiously, **9** is fairly stable despite its 2*H*-corrole structure. These unusual properties of the fused corrole dimers may be ascribed to the direct double linkage between the corroles. Explorations of aromatic-fused corroles and oligomeric fused corrole systems are ongoing in our laboratory.

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