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Synthesis and Biradicaloid Character of Doubly Linked Corrole Dimers

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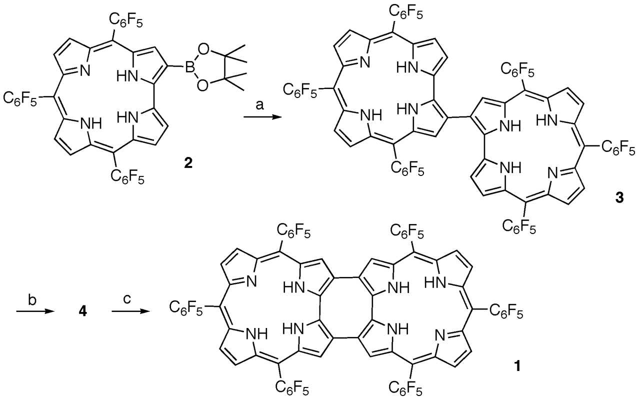
Cyclic π-conjugated systems have attracted considerable interest in terms of their applications as molecular materials having conductive or nonlinear optical properties, as building blocks for supramolecular structures, and for complexation with metals or ions. Our group has developed *meso*−*meso*, β−β, β−β, triply linked porphyrin oligomers, which exhibit extremely low-energy electronic absorption bands that reach into the infrared region because of the extensive full π-conjugation.[1] Recently, this strategy has been extended to a two-dimensional porphyrin sheet that bears a planar cyclooctatetraene (COT) core, which exhibits paratropic magnetic effects.[2] This direct fusion strategy has been now applied to corrole, a porphyrin-like 18-π aromatic macrocycle except for one direct pyrrole−pyrrole linkage, which displays a unique ability to stabilize unusually high valence state transition metals.[3,4] Some nickel(II) and copper(II) corroles have been reported to show radical character.[5] We report the synthesis and anomalous properties of the doubly linked corrole dimer **1** and its metal complexes that hold a formal COT moiety in the center of the molecule. Notably, oxidized counterparts of **1** and its zinc(II) complex exhibit biradicaloid character.

The synthesis of doubly linked corrole dimer **1** began with 2-borylcorrole **2** (Scheme 1).[6] Palladium-catalyzed oxidative coupling of **2** using chloroacetone as an oxidant afforded the 2,2′-linked corrole dimer **3** in excellent yield.[7] Further oxidation of **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene provided one product, **4**, as an air- and moisture-stable solid in moderate yield. The electronic absorption spectrum of **4** showed a broad spectrum reaching the near-infrared region. Reduction of **4** with $NaBH_4$ resulted in a solution color change from brown to green and gave **1** quantatively. Its parent mass ion peak was observed at $m/z = 1587.1096$ (calcd for $(C_{74}H_{17}N_8F_{30})^- = 1587.1103$ [(M − H)$^-$]) in its high-resolution electrospray ionization time-of-flight (HR ESI-TOF) mass spectrum. The ^1H NMR spectrum of **1** elucidated its symmetrical structure, exhibiting one singlet peak (8.91 ppm) and two doublet peaks (8.66 and 8.48 ppm) in the deshielded region. The electronic absorption spectrum of **1** exhibits three main bands at 396, 472, and 721 nm, which are characteristic of corroles but slightly red-shifted compared to those of monomers (Figure 1).

DDQ oxidation of **1** yielded **4** quantitatively, indicating that **4** is an oxidized form of **1** (Scheme 2). To gain knowledge about these compounds, we performed the metalation of **1** and **4**. When **1** was subjected to the conditions for cobalt metalation of corrole monomers, the bis-cobalt(III) complex **5** was obtained in good yield. On the other hand, **4** was zincated with $Zn(OAc)_2/2H_2O$ in refluxing $CHCl_3$ to afford the bis-zinc complex **6** as a stable brown solid. Since corroles usually serve as ligands for trivalent metals, it is quite rare that a corrole can accommodate divalent metal ions such as the zinc ion.[8] These complexes showed electronic absorption spectra similar to those of the corresponding free bases **1** and **4**, respectively, indicating preservation of their electronic and geometric structures upon metalation. Complex **6** showed its parent mass ion peak at $m/z = 1714.5249$ (calcd for $(C_{74}H_{12}F_{30}N_8Zn_2)^- = 1714.5272$ ([M]$^-$)) and exhibited very broad (virtually no signal) ^1H NMR spectra in CD_2Cl_2 and THF-d_8, even at −90 °C. The structures of the two complexes were finally confirmed by X-ray single-crystal analysis. Curiously, both complexes exhibited quite planar structures, including the COT cores (Figure 2). These

Scheme 1[a]



[a] Reaction conditions: (a) $PdCl_2$(dppb), chloroacetone, THF, H_2O at 70 °C, 6 h, 82%; (b) DDQ, toluene, at 50 °C, 1.5 h; (c) $NaBH_4$, THF, MeOH, room temperature, 30 min, 67% from **3**.

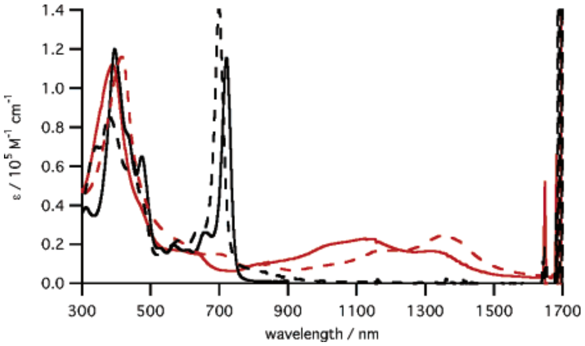
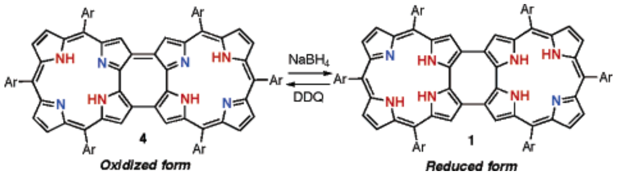


Figure 1. Electronic absorption spectra of **1** (black solid line), **4** (red solid line), **5** (black dashed line), and **6** (red dashed line). All spectra were recorded in CH_2Cl_2 solution.

Scheme 2



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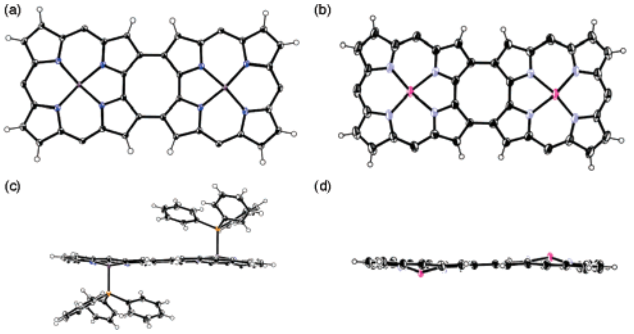

Figure 2. X-ray crystal structures of **5**·$(PPh_3)_2$ and **6**·(dioxane)$_2$. Top views of **5**·$(PPh_3)_2$ (a) and **6**·(dioxane)$_2$ (b), and side views of **5**·$(PPh_3)_2$ (c) and **6**·(dioxane)$_2$ (d). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Substituents are omitted for clarity.

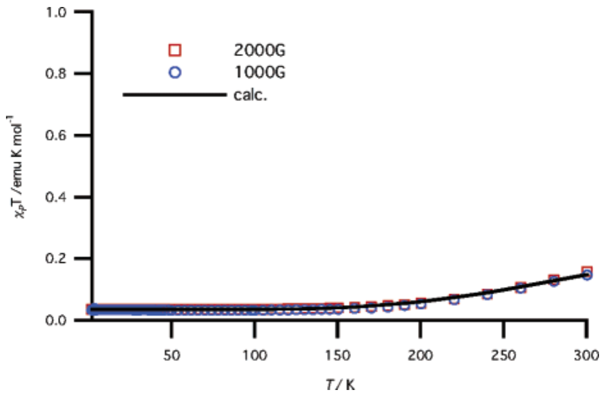

Figure 3. Temperature-dependent SQUID magnetic susceptibility of **6**.

structures suggest that the ligand of **6**, free base **4**, has two NH protons in each of the corrole cores. This suggestion is also supported by the observation of its parent mass ion peak at $m/z = 1586.1007$ for **4** (calcd for $(C_{74}H_{17}F_{30}N_8)^- = 1586.1024$ ($[M]^-$)).

The ESR spectrum of **6** was measured at room temperature, and a single peak was observed at $g = 2.0053$, indicating the existence of an unpaired electron. Furthermore, the temperature-dependent magnetic susceptibility of **6** was measured for the powder sample (Figure 3), which revealed that the χ_pT value was temperature independent, ~0.0 emu K mol^{-1}, below 150 K, and gradually increased above 150 K. These results indicated that **6** has a biradical character, with the singlet ground state[9] having a coupling value $J_{S-T} = -330$ cm^{-1}, as calculated from the Bleaney−Bowers equation.[10] The result is well consistent with ESR measurement of **6** (Supporting Information). Cyclic voltammetry of **6** also supported its biradical structure, exhibiting two reversible oxidation potentials at 0.20 and 0.38 V (vs ferrocene/ferrocenium couple (Fc/Fc^+)) and two reversible and one irreversible reduction potentials at −0.19, −0.34, and −1.9 V, respectively. The gap between the first oxidation and reduction potentials ($\Delta E = E^1_{Ox} - E^1_{Red}$) was only 0.40 V, suggesting nonbonding character of the frontier orbital of **6**.[9a]

The observed biradical character was supported by theoretical calculations at the BLYP/631TZVP level.[11] Symmetry-breaking of the UDFT solution lowered the energy 5.1 kJ/mol from the nonradical state. In addition, the UDFT calculations confirmed that the $S = 0$ state lies below the $S = 1$ state, and the J_{S-T} value was calculated to be −178 cm^{-1}. Calculation at the CASSCF(2,2)/631TZVP//UBLYP/631TZVP level gave an admixture of 43.5% of the doubly excited configuration $^1\Phi_{H,H\rightarrow L,L}$ into the singlet ground state. From this result, the singlet biradical character of **6** is estimated to be approximately 87%.

In summary, we have synthesized and characterized doubly linked corrole dimers. The oxidized corrole dimer **6** shows unusual biradical character, which has been indicated by UV−vis absorption spectra, ^{1}H NMR spectra, magnetic measurements, and DFT calculations. X-ray analysis of **6** has revealed a planar COT core. Although several stable singlet biradicals have been reported, this is the first report of biradicaloids based on porphyrinoids, to the best of our knowledge. The high stability of **6** in the air at ambient temperature is notable, and its application in molecular devices and material science is of worthy of further investigation.

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Supporting Information Available: General procedures, spectral data for compounds, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) 631TZVP denotes a basis set consisting of TZVP for Zn and 6-31G(d) for the rest.

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