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Syntheses, Crystal Structure, and Spectroscopic Properties of *Meso–Meso*-Linked Porphyrin–Corrole Hybrids

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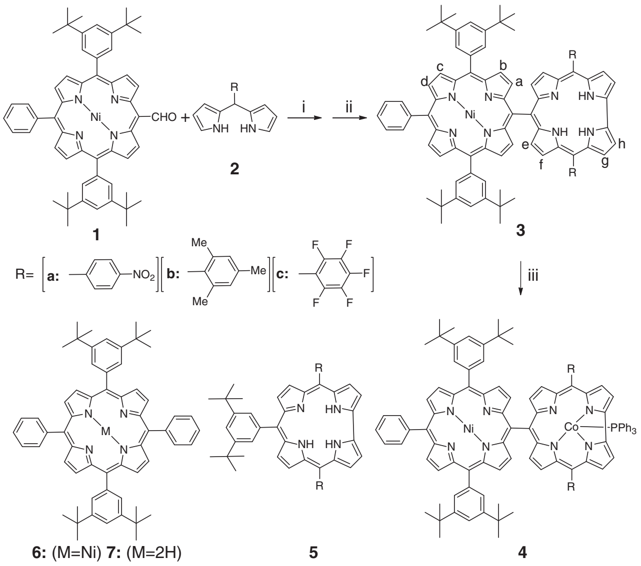
Meso–meso directly linked porphyrin (**Por**)–corrole (**Cor**) hybrids have been successfully achieved for the first time. The *meso–meso* linkage has been confirmed by X-ray diffraction analysis. The characteristic split Soret absorption band revealed the existence of strong exciton coupling between porphyrin and corrole subunits. Time-resolved and steady-state fluorescence has also been investigated.

In the past two decades, covalently linked multiporphyrin arrays have attracted considerable interest for their great potential applications, such as artificial photosynthetic systems, molecular wires, sensors, and nonlinear optical devices.[1] Among the reported structures, *meso–meso* directly linked porphyrin (**Por**) arrays possess an important position because they are favorable for achieving rapid energy- and electron-transfer owing to the direct linking and a short center-to-center distance between **Por** subunits.[2] The strong exciton interaction between two adjacent **Por** rings imparts predominant spectroscopic and photovoltaic properties to the molecules.[3]

Corroles (**Cors**), one carbon short analogs of porphyrins bearing a direct pyrrole–pyrrole linkage, have recently emerged as an independent research area.[4] In comparison with porphyrins, corroles exhibit some interesting properties, including trianionic character, smaller cavity, lower oxidation potential, higher fluorescence quantum yield, larger Stokes shift, and relatively more intense absorption of red light.[5] Many efforts have been devoted to the syntheses of directly linked corrole dyads.[6] With the aim of realizing the combination of specific properties of **Por** and **Cor**, several **Por**–**Cor** conjugates have also been studied.[7] To the best of our knowledge, the fascinating *meso–meso*-linked porphyrin–corrole hybrids have not been reported so far. As a continuous focus on the *meso–meso*-linked porphyrinoids,[8] we present herein the systematic investigation of synthesis, structure, and photophysical properties of *meso–meso* directly linked **Por**–**Cor** dyads.

An acid-catalyzed **2** + **1** condensation method with relatively accessible dipyrromethane and *meso*-formylporphyrin was adopted to avoid the difficulty in derivatization of corroles.[9] After screening the reaction conditions, $BF_3 \cdot Et_2O$/EtOH was found to be the most efficient catalyst, and the general procedure was carried out in CH_2Cl_2 at 0 °C with a subsequent oxidation by DDQ (Scheme 1). Compounds **3** have been obtained with a moderate yield of 8% for **3a**, 17% for **3b**, and 20% for **3c**, respectively. HR-MALDI-TOF mass spectra of all three target molecules showed obvious $[M + H]^+$ peaks. The ^1H NMR spectrum of **3a** displays broad signals, which is consistent with reported free-base corroles possessing unhindered substituents.[10] The spectra of **3b** and **3c** show much clearer splitting due to the steric effect of introducing 2,6-substituents. That will facilitate the assignment of proton signals and the determination of the mutual ring current effect of the adjacent **Por** and **Cor** chromophores.



Scheme 1. Synthesis procedures of **Por**–**Cor** dyads and structures of reference compounds studied herein. Reagents and conditions: (i) CH_2Cl_2, $BF_3 \cdot Et_2O$, EtOH, 0 °C; (ii) CH_2Cl_2, THF, DDQ; (iii) CH_2Cl_2, CH_3OH, $Co(OAc)_2 \cdot 4H_2O$, PPh_3.

The selected low-field chemical shift data of **3b**, Ni^{II}**Por 6**, and free-base **Cor 5b** are shown in Figure S10.[11] By carefully analyzing the ^1H–^1H COSY spectrum (Figure S9)[11] and the previously reported data of corroles and *meso–meso*-linked porphyrinoid arrays,[2,10] the β-H of **3b** has been assigned and labeled by lower-case letter a–f in Scheme 1. Comparing to the references **6** and **5b**, both the inner β-protons of porphyrin (H_a and H_b) and corrole (H_e and H_f) in **3b** show significant upfield shift due to the large shielding effect of macrocycles.

More intuitive evidence for the formation of *meso–meso* linkage was provided by crystallographic analysis of **4a**, a cobalt coordinated complex of **3a** (Figure 1). X-ray quality crystals of **4a** were obtained by slow diffusion of CH_3OH to a CH_2Cl_2 solution of **4a**.[12] Porphyrin and corrole subunits in the dyad **4a** are attached to each other at the *meso* position through a 1.50 Å C–C bond, and the dihedral angle between the two planes is 86°. Meanwhile, the nickel(II)–porphyrin moiety of **4a** displays slight distortion, while the plane of corrole moiety retains planar conformation with a 2.21 Å P–Co bond.

The absorption spectra of **3c**, the reference monomer **5c** and **6** are shown in Figure 2. Compound **3c** displays an obvious split Soret band. The high-energy Soret band of **3c** occurs at the same wavelength with respect to that of monomer **Cor 5c** and **Por 6** (414 nm), while a new low-energy Soret band appears at 445 nm.

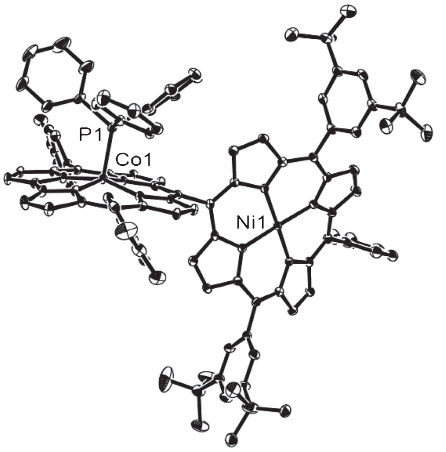


Figure 1. X-ray crystal structure of **4a**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability.

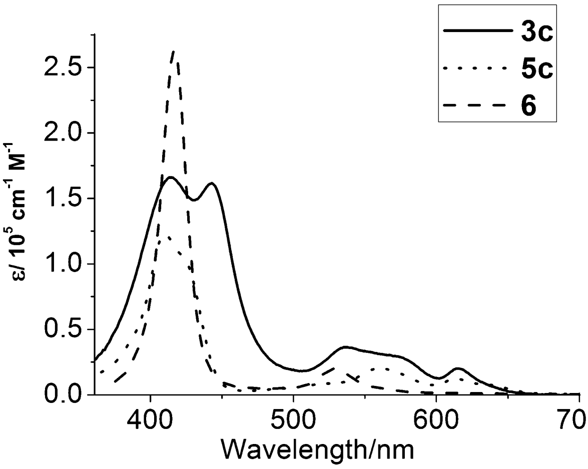
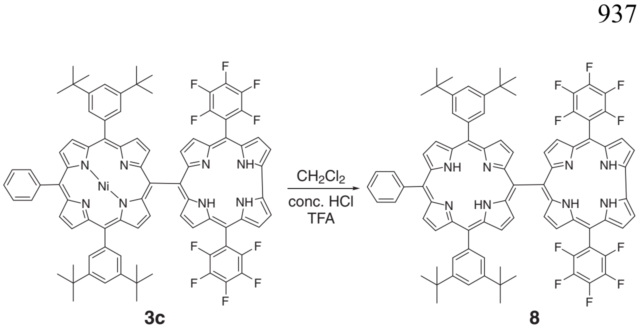


Figure 2. Electronic absorption spectra of dyad **3c**, reference compound **5c** and **6** in $CHCl_3$.

Such results reflect a strong exciton coupling between the neighboring porphyrin and corrole.[2] The Q-bands of **3c** represent the sum of Q-band of **5c** and **6** with a slight bathochromic-shift. This should be attributed to the weak electronic coupling between the directly linked chromophores with a nearly orthogonal conformation supported by the DFT calculations (Figure S43).[2e,11]

Since the fluorescent emission of porphyrin was seriously quenched by the introducing of Ni atom, a demetalization process is needed before exploring the luminescence properties of *meso–meso* directly linked **Por–Cor** hybrid. We initially treated **3c** with the mixture of trifluoroacetic acid (TFA) and concentrated H_2SO_4, a commonly used method, but severe decomposition was observed. In view of the lability of corroles toward oxidant, we modified the reaction by using concd HCl instead of concd H_2SO_4 and free-base **8** was obtained in 50% yield (Scheme 2).[13] A typical signal of inner 2H of porphyrin appeared at −2.18 ppm (Figure S36).[11]



Scheme 2. Synthesis procedure of free-base **Por–Cor** dyad.

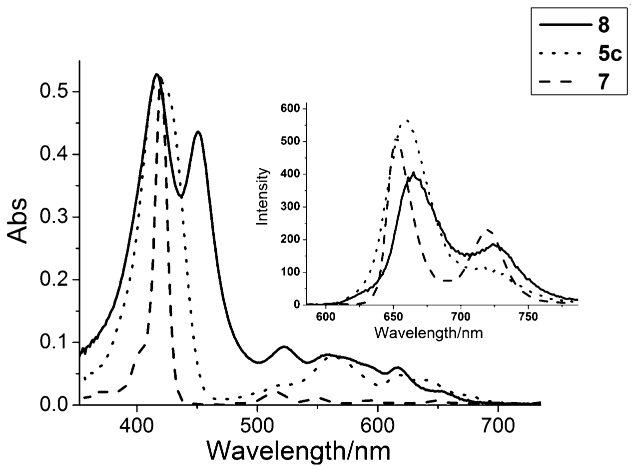


Figure 3. Absorption and emission spectra ($\lambda_{ex} = 420$ nm) of dyad **8**, reference compound **5c** and **7** in toluene.

Table 1. Fluorescence quantum yield and fluorescence lifetime of compound **5c**, **7**, and **8** in toluene

Compound	$\Phi_F{}^a$	τ/ns[a]
5c	0.16	3.9
7	0.11	9.6
8	0.14	6.7

[a]Measured at 298 K.

Figure 3 showed absorption and emission spectra of free-base **8**, **Cor 5c**, and **Por 7**. Similar to compound **3c**, the dyad **8** also exhibits obvious split Soret bands in toluene because of the same reason mentioned above. As shown in the inset of Figure 3, there is a large overlap between the emission of corrole **5c** and porphyrin **7**. The emission of corrole **5c** onsets at higher energy with respect to porphyrin **7** (600 nm compared to 625 nm), but its maximum emission (659 nm) is slightly longer than 652 nm for **7**. Comparing to the second distinct band at 720 nm of **7**, **5c** only shows a shoulder in the same region.[7b] The fluorescence quantum yield Φ_F and lifetime τ has further been determined (Table 1 and Figure S42[11]), $\Phi_F = 0.11$ with $\tau = 9.6$ ns for **7** and $\Phi_F = 0.16$ with $\tau = 3.9$ ns for **5c** are in agreement with the literature data.[5,7b] A sum of the emission features of **5c** and **7** have been observed for dyad **8**, and Φ_F and τ have been evaluated to be 0.14 and 6.7 ns, respectively. The values locate between those of **5c** and **7**. This phenomenon could be rationalized by the existence of reversible energy transfer tendency between porphyrin and corrole subunit in dyad **8** because of their nearly iso-energetic singlet excited states (both extending up at 770 nm). That has been found and demonstrated by Gryko in amide-linked porphyrin–corrole dyads.[7b]

In summary, *meso–meso* directly linked porphyrin–corrole hybrids have been successfully prepared and fully characterized by NMR, HR-MS, and X-ray diffraction analysis. Crystal structure and calculation results show that **Por** and **Cor** moiety in the dyads adopt orthogonal conformations, which results in minimizing the conjugate of neighboring chromophores. Obvious split Soret bands observed in absorption spectra reflect the existence of strong exciton coupling between the adjacent porphyrin and corrole. Luminescence properties of the free-base dyad indicate that reversible energy transfer should exist in the dyads.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

12 Crystal data for **4a**: CCDC No. 928176, triclinic, space group $P\bar{1}$, $a = 16.509(3)$ Å, $b = 16.672(2)$ Å, $c = 21.029(3)$ Å, $\alpha = 67.256(10)°$, $\beta = 76.733(12)°$, $\gamma = 68.391(9)°$, $V = 4937.1(12)$ Å^3, $Z = 2$, $\mu = 0.455\,\mathrm{mm}^{-1}$, $R = 0.0770$, $wR = 0.1854$.

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