

Lipophilic Corrole–Porphyrin–Corrole Linear Triad

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Herein, a novel lipophilic corrole-porphyrin-corrole triad has been synthesized and characterized. The electronic structure study was carried out by the spectroscopic investigations and electrochemical characterizations to provide better understanding of the electronic structure of this novel macrocyclic linear triad. In addition, the triad exhibits a highly efficient energy transfer process from the excited porphyrin part to the corrole core units.

Keywords: Porphyrin, corrole, electronic structure, spectroscopy, electrochemistry, tautomerism.

Липофильная линейная триада коррол–порфирин–коррол

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#Авторы внесли равный вклад

Получена и охарактеризована новая липофильная триада коррол-порфирин-коррол. С целью более глубокого понимания электронной структуры этой новой макроциклической линейной триады были изучены ее спектральные свойства и получены электрохимические характеристики. Показано, что триада демонстрирует высокоэффективный процесс передачи энергии от возбужденной порфириновой части к корролу.

Ключевые слова: Порфирин, коррол, электронная структура, спектроскопия, электрохимия, таутомерия.

Introduction

Porphyrins having extended π -electronic networks have received considerable attentions to create a wide range of functional materials, such as high performance organic conducting soft matters, near-infrared dyes, and non-linear optical materials.^[1] As the representative of such

molecules, various molecules including *meso-meso*, β - β , *meso*- β , and even highly conjugated porphyrin dimer, trimer and oligomers have been successfully isolated and characterized.^[2] In addition, these highly conjugated porphyrin derivatives mainly provided red-shifted absorp-

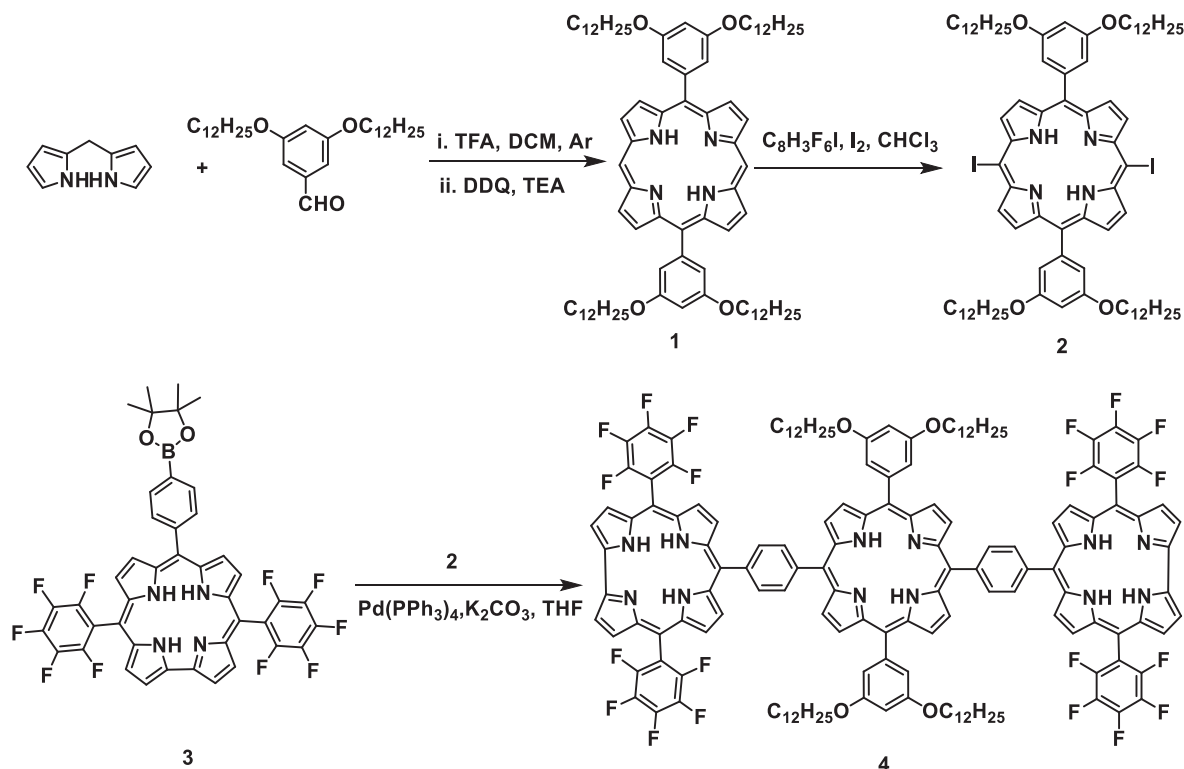
tion bands, narrow HOMO–LUMO gaps, multi-charge storage capabilities, high single-molecule conductance.^[3] Unfortunately, the main disadvantages of porphyrin in this regard is that their lowest energy π – π^* band (usually referred to as the Q band) tends to be relatively weak with molar extinction coefficients of $\epsilon > 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, and the poor solubility of these porphyrin oligomers limit the progress of this field.^[4] Compared with porphyrin, corrole with a direct linked “C–C” bond that resulting the ring-contracted molecular structure and novel optical and electrochemical properties have received the considerable attention in recent years.^[5] Also, the three inner N–H protons can support corrole stabilizing metallic and/or non-metallic ions at the higher oxidation states.^[6] Thus, the novel covalently linked corrole oligomers have displayed extremely attractive properties compared with that of porphyrin oligomers. Besides, various corroles have also been explored as catalysts, pigments for artificial photosynthesis, solar cells, sensors, and so on.^[7] For example, the face-to-face porphyrin-corrole hybrids as well as corrole dimers act as promising models of catalyst for the four-electron reduction of oxygen to water.^[8] On the other hand, molecular tautomerism is also one of the most attractive research areas in the past years, and the tautomerism of free base H_3 -corrole derivatives have been well demonstrated by Ziegler and us to understand the effect of the solvent polarity on the inner N–H isomerism of corrole core.^[9] Herein, we will synthesize and characterize a lipophilic corrole-porphyrin-corrole linear triad by introducing several highly soluble $-\text{OC}_{12}\text{H}_{25}$ units, and the satisfied molecular solubility is truly helpful for us to understand the molecular structure, electronic structure of this highly conjugated porphyrinic chromophore, and its tautomerism will also be illustrated.

Experimental

General. ^1H NMR spectra were recorded on a Bruker AVANCE 600 spectrometer (operating at 600.13 MHz), and ^{13}C NMR spectra was recorded on a Bruker AVANCE 600 spectrometer (operating at 150.00 MHz). All reagents and solvents used were of reagent grade and were used as received unless noted otherwise. Cyclic voltammetry was carried out on a Chi-730D electrochemistry station with a three-electrode cell. A glassy carbon disk, a platinum wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. An inert nitrogen atmosphere was introduced during all electrochemical measurements, which were carried out at room temperature. The UV and visible regions of the electronic absorption spectra were recorded with an HP 8453A diode array spectrophotometer.

Synthesis of 5,15-H-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin (1). A solution of 3,5-di(dodecyloxy)benzaldehyde (1.43 g, 3 mmol) and dipyrromethane (440 mg, 3 mmol) in CH_2Cl_2 (500 mL) was purged with nitrogen for 20 min, and then trifluoroacetic acid (TFA) (0.15 mL) was added. The mixture was stirred for 3 h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.01 g) was added. After the mixture was stirred at room temperature for an additional 2 h, the reaction was quenched by adding triethylamine (2 mL). The solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane/petroleum ether as the eluent. Recrystallization from CH_2Cl_2 /methanol gave a purple solid in 60 % yield (1.08 g). ^1H NMR (600 MHz, chloroform- d) δ_{H} ppm: 10.29 (s, 2H), 9.38–9.37 (d, $J = 4.8 \text{ Hz}$, 4H), 9.19–9.18 (d, $J = 4.8 \text{ Hz}$, 4H), 7.42 (d, $J = 1.8 \text{ Hz}$, 4H), 6.92–6.91 (t, $J = 1.8 \text{ Hz}$, 2H), 4.16–4.14 (t, $J = 6.6 \text{ Hz}$, 8H), 1.91–1.86 (m, 8H), 1.39–1.33 (m, 8H), 1.31–1.23 (m, 72H), 0.86–0.83 (m, 12H), –3.15 (s, 2H).

Synthesis of 5,15-diiodo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin (2). 5,15-Bis(3,5-di(dodecyloxy)phenyl)porphyrin (100 mg, 0.083 mmol) was dissolved in 80 mL of dry chloroform



Scheme 1. Synthesis of corrole-porphyrin-corrole triad **4**.

under argon. Iodine (109 mg, 0.39 mmol) and 20 drops of pyridine were added, followed by [bis(trifluoroacetoxy)iodo]benzene (66 mg, 0.2 mmol). The reaction flask was then shielded from ambient light and the reaction mixture was stirred for 48 h at room temperature. The reaction mixture was washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$, dried over Na_2SO_4 , and evaporated to dryness. The residue was purified by flash column chromatography on silica gel using dichloromethane/petroleum ether as the eluent. Recrystallization from CH_2Cl_2 /methanol gave a purple solid in 79 % yield (95 mg). ^1H NMR (600 MHz, chloroform-*d*) δ_{H} ppm: 9.57–9.56 (d, $J = 4.8$ Hz, 4H), 8.90–8.89 (d, $J = 4.2$ Hz, 4H), 7.29–7.28 (d, $J = 2.4$ Hz, 4H), 6.88 (t, $J = 2.4$ Hz, 2H), 4.11–4.09 (t, $J = 6.6$ Hz, 8H), 1.49–1.47 (m, 8H), 1.36–1.34 (m, 8H), 1.29–1.22 (m, 72H), 0.84–0.82 (m, 12H), –2.66 (s, 2H).

Synthesis of corrole-porphyrin-corrole triad (3). 5,15-Diiodo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin **2** (63 mg, 0.043 mmol), H_3 -5,15-pentafluorophenyl-10-benzopinacolborate-corrole **3** (100 mg, 0.12 mmol),^[11] K_2CO_3 (17 mg, 0.12 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (5 mg, 0.004 mmol) were placed in a Schlenk tube and dissolved in water/methanol/THF (2 mL/2 mL/8 mL) under Ar. The resulting solution was deoxygenated through three freeze-pump-thaw cycles, and then the reaction mixture was heated under reflux and stirred for 12 h under argon. After completion of the reaction, the organic phase was diluted with CH_2Cl_2 , washed with saturated NH_4Cl solution, and dried by anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was purified via column chromatography on silica gel with CH_2Cl_2 -petroleum ether to afford the deep-purple solid state compound in a 34% yield (38 mg). MALDI-TOF: $m/z = 2609.829$ (Calcd. for $\text{C}_{154}\text{H}_{146}\text{F}_{20}\text{N}_{12}\text{O}_4$ $[\text{M}+\text{H}]^+ = 2609.910$). ^1H NMR (600 MHz, chloroform-*d*) δ_{H} ppm: 9.34–9.33 (d, $J = 6.6$ Hz, 4H), 9.26–9.25 (d, $J = 7.2$ Hz, 4H), 9.21–9.18 (m, 8H), 8.95–8.94 (d, $J = 6.6$ Hz, 4H), 8.68–8.66 (d, $J = 12$ Hz, 4H), 8.65–8.62 (m, 8H), 7.58–7.57 (d, $J = 2.4$ Hz, 4H), 7.01–7.00 (d, $J = 3.0$ Hz, 2H), 4.24–4.21 (t, $J = 9.6$ Hz, 8H), 1.96–1.92 (m, 8H), 1.35–1.24 (m, 72H), 0.84–0.81 (t, $J = 9.6$ Hz, 12H), –2.46 (s, 2H).

Results and Discussion

Synthesis and Characterization

Firstly, 5,15-bis(3,5-di(dodecyloxy)phenyl)porphyrin **1** was synthesized from^[10] *meso*-H-dipyrrromethane 3,5-di(dodecyloxy)benzaldehyde through [2+2] type cyclization reaction catalyzed by TFA in the dry CH_2Cl_2 , and the crude mixture was directly oxidized with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to provide the target compound 5,15-H-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin **1** in a moderate yield of 60 %. In the next step, the iodination of **1** using an excess amount of iodine and [bis(trifluoroacetoxy)iodo]benzene gave 5,15-diiodo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin **2** as the sole compound in a 79 % yield. On the other hand, H_3 -5,15-pentafluorophenyl-10-benzopinacolborate-corrole **3** was prepared from H_3 -5,15-pentafluorophenyl-10-(*p*-bromophenyl)corrole according to the literature reported procedure.^[11] When iodinated porphyrin **2** and excess amount of **3** were placed to Schlenk tube and dissolved in water/methanol/THF (2 mL/2 mL/8 mL) under argon atmosphere, the whole mixture was heated under reflux and stirred for 12 h under argon catalyzed by $\text{Pd}(\text{PPh}_3)_4$. The resulting solution was deoxygenated through three freeze-pump-thaw cycles, and then the reaction mixture was heated under reflux and stirred for 12 h under argon.

Finally, the target compound corrole-porphyrin-corrole triad **4** was isolated as a deep-purple solid in 34% yield. Additionally, the structural characterization of these synthesized compounds were investigated by mass and NMR spectra. Firstly, MALDI-TOF mass spectra of **4** (Figure S1, see ESI) revealed the parent ion peaks at $m/z = 2609.829$ (Calcd. for $\text{C}_{154}\text{H}_{146}\text{F}_{20}\text{N}_{12}\text{O}_4$ $[\text{M}+\text{H}]^+ = 2609.910$) provided the direct evidences that corrole-porphyrin-corrole triad **4** was clearly observed. Due to introduction of lipophilic $-\text{OC}_{12}\text{H}_{25}$ units, the clear ^1H NMR was facially obtained. The ^1H NMR and ^{13}C NMR spectra of **4** (Figure S4, see ESI) showed clearly proton signals ascribed to the aromatic protons in the range 7.52–9.13 ppm. The protons from long alkyl chain $-\text{OC}_{12}\text{H}_{25}$ could be assigned from 0.77–2.14 ppm. ^{13}C NMR spectra of **4** were also measured to confirm the target lipophilic corrole-porphyrin-corrole linear triad **4** (Figure S5, see ESI). Similarly, porphyrins **1** and **2** (Figures S1–S2, see ESI) showed reasonable proton signals ascribed to the aromatic protons and *meso*-substitutions.

Optical Spectroscopy

Electronic absorption spectroscopy is one of the most useful methods for characterization of porphyrin, corrole and their analogues due to the presence of intense π - π^* bands in the visible region, but porphyrin and corrole have their own characteristic peaks independently. The optical spectroscopy of corrole and their analogues can be understood based on a consideration of perturbations to an $M_L = 0$, ± 1 , ± 2 , ± 3 , ± 4 , ± 5 , ± 6 and ± 7 sequence in ascending energy terms for the orbital angular momentum quantum number for the MOs of a D_{15h} symmetry parent hydrocarbon perimeter. The HOMO and LUMO have $M_L = \pm 4$ and ± 5 , respectively, and are linked by forbidden and allowed $\Delta M_L = \pm 9$ and ± 1 transitions, which are associated with the Q and B bands of Gouterman's four-orbital model,^[12] respectively, that are observed in the 500–600 and 400–450 nm regions of UV-Vis spectra. The absorption spectrum of **4** in low-polar CH_2Cl_2 contains a splitted intense B band at $\lambda = 422$ and 433 nm with an unclear shoulder band at slightly longer wavelength region, while five relatively intense bands are observed in the Q band region at 516, 556, 570, 612 and 645 nm. Interestingly, we can clearly identify the split of the Q band arising from both porphyrin and corrole absorptions. Thus, the spectroscopic investigations of synthetic precursors **1**, **2** and **3** should be carried out to understand the assignments of these complicated absorption bands (Figure 1, Table 1). We should point out that the changes on all peak values could be illustrated as the energy transfer between porphyrin and corrole core. Interestingly, when these compounds were measured in various high and/or low polar organic solvents, it is noteworthy that marked changes are only observed in the absorption spectra of corrole **3** and corrole-porphyrin-corrole triad **4** due to the tautomerism of inner N-H bond of corrole core (Figure 1 and Table 1). In the case of corrole monomer **3**, when the solvent polarity is increased by using DMF, PhCN and DMSO, three Q-band absorptions were gradually increased from shorter to longer wavelength (originally decreased), and the clear red-shift of the Soret-band absorptions were also observed. Similar spectral changes of Q-band absorptions of corrole-

porphyrin-corrole triad **4** were also observed when higher polar solvents were tested, and the larger split of the Soret band absorptions could also be assigned as the changes from *meso*-linked corrole units. It has been reported previously by Ziegler and us that a significant splitting is observed in the B band region in polar solvents, such as DMF, that is not observed in a low-polar solvent, such as CH_2Cl_2 , THF. The observed solvent-dependent spectroscopic changes of corrole **3** and corrole-porphyrin-corrole triad **4** could be explained as two possible reasons: the self-tautomerism of inner protons of corrole rings, as well as N-basicity and thermodynamic stability of two tautomers. In addition, the fluorescence spectra of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** were also measured in CH_2Cl_2 . As it is shown in Figure 2, the porphyrins **1** and **2** have similar emission spectra at around 630 and 690 nm, and corrole **3** has red-shifted emission bands at 650 and 710 nm. Interestingly, corrole-porphyrin-corrole triad **4** performs fluorescent properties mainly from corrole core (at 651 and 711 nm) which is possibly ascribed to the photoinduced energy transfer process from the excited porphyrin part to the corrole unit.

Electrochemistry

In order to better understand the electronic structure of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4**, their electrochemistry was also investigated, and $E_{1/2}$ values are derived from both CV and DPV characterizations (Figure 3, Table 2). It has been clearly shown that porphyrin **1** has two ring-reductions at $E_{1/2} = -0.86$ (quasi-reversible) and -1.63 V (reversible) and one reversible ring-oxidation at $E_{1/2} = 1.11$ V, respectively. Upon

introducing two iodine atoms at *meso*-positions, the redox potentials of porphyrin **2** has been slightly changed. In the case of corrole **3**, two reversible ring-reductions at $E_{1/2} = -1.14$ and -1.57 V and two reversible ring-oxidation were observed at $E_{1/2} = 1.23, 1.56$ V, respectively. Based on these assignments, all redox curves of corrole-porphyrin-corrole triad **4** could be correctly assigned. Compound **4** has three reversible reductions, the 1st reduction at $E_{1/2} = -0.98$ V was assigned as the 1st reduction from porphyrin ring, and the negative shift of the redox potential could be attributed to the introduction of corrole units as the electron-donating substituents at *meso*-positions. similarly, the 2nd reduction at $E_{1/2} = -1.29$ V was assigned as the 1st reduction from corrole ring, and the 3rd reduction at $E_{1/2} = -0.98$ V could be assigned as the 2nd reductions from both porphyrin and corrole rings. On the other hand, the 1st and 2nd oxidation of **4** could be assigned as the oxidation from both porphyrin and corrole rings ($E_{1/2} = 1.54$ V). Thus, we should point out that the changes on all redox potentials could be illustrated as the energy transfer between porphyrin and corrole core. The CV measurements were additionally tested at various scan speed from $50 \text{ mV}\cdot\text{s}^{-1}$ to $500 \text{ mV}\cdot\text{s}^{-1}$ (Figure 4), what provided an insight into the reversibility of the system on an experimental time-scale. The good linear correlations were observed, that confirms that all of the oxidation and reduction processes are diffusion controlled.

Conclusions

In summary, the novel lipophilic corrole-porphyrin-corrole triad were successfully synthesized, isolated

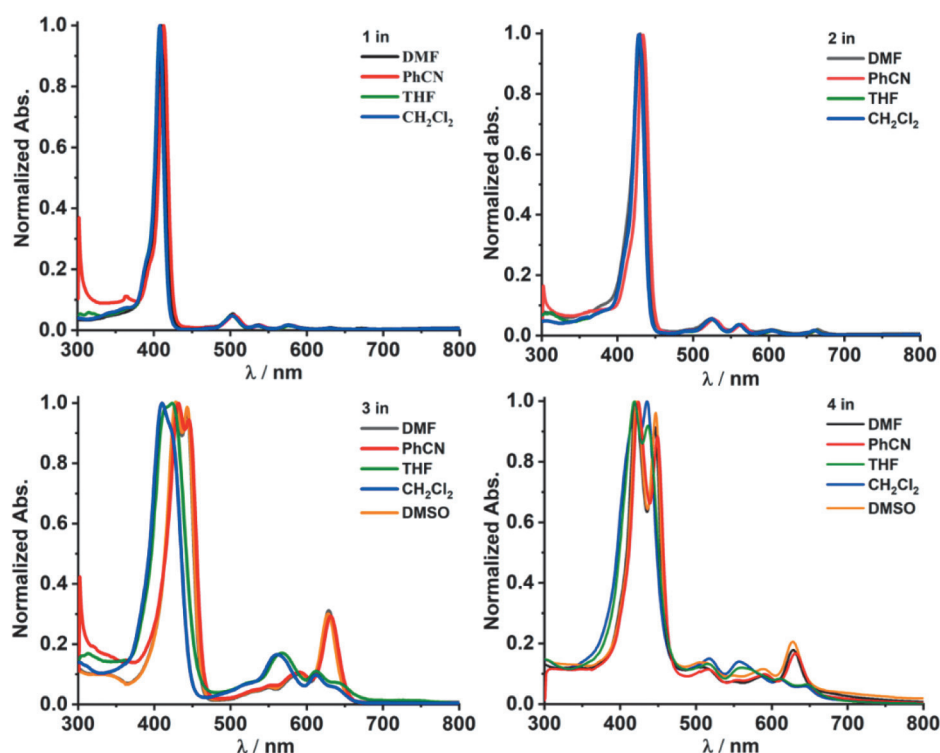


Figure 1. UV-vis absorption spectra of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in various solvents.

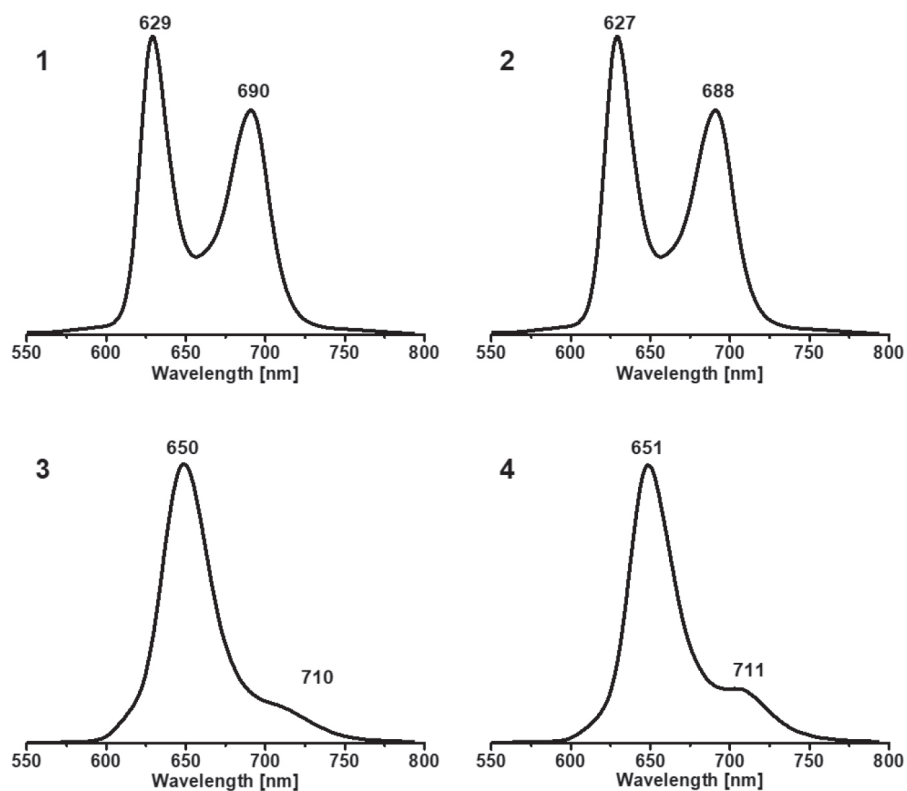


Figure 2. Fluorescence spectra of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in CH_2Cl_2 .

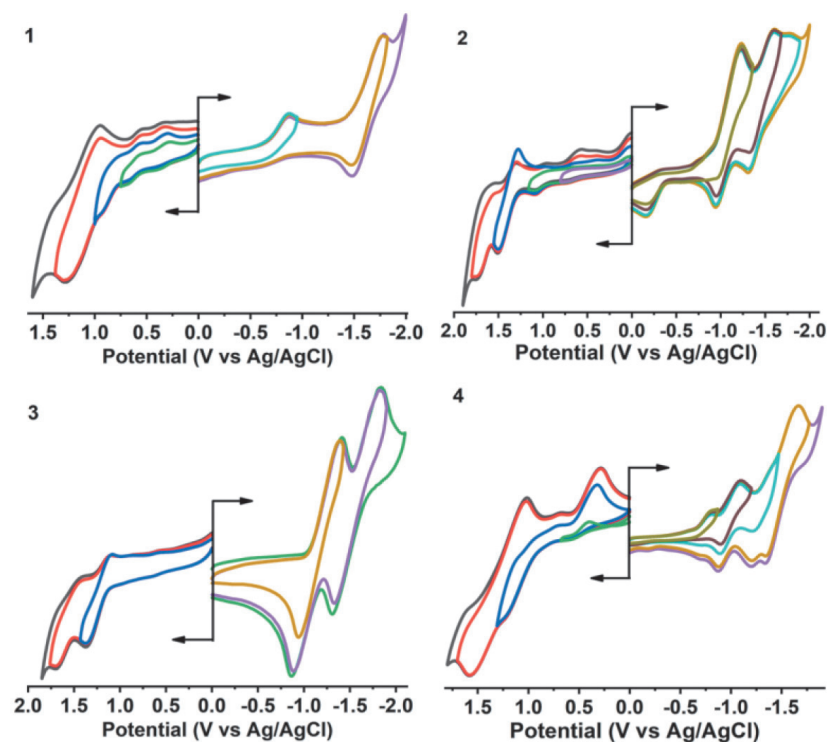


Figure 3. Cyclic voltammetry diagram of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in *o*-dichlorobenzene (*o*-DCB) containing 0.1 M TBAP, scan speed: $0.1 \text{ V} \cdot \text{s}^{-1}$.

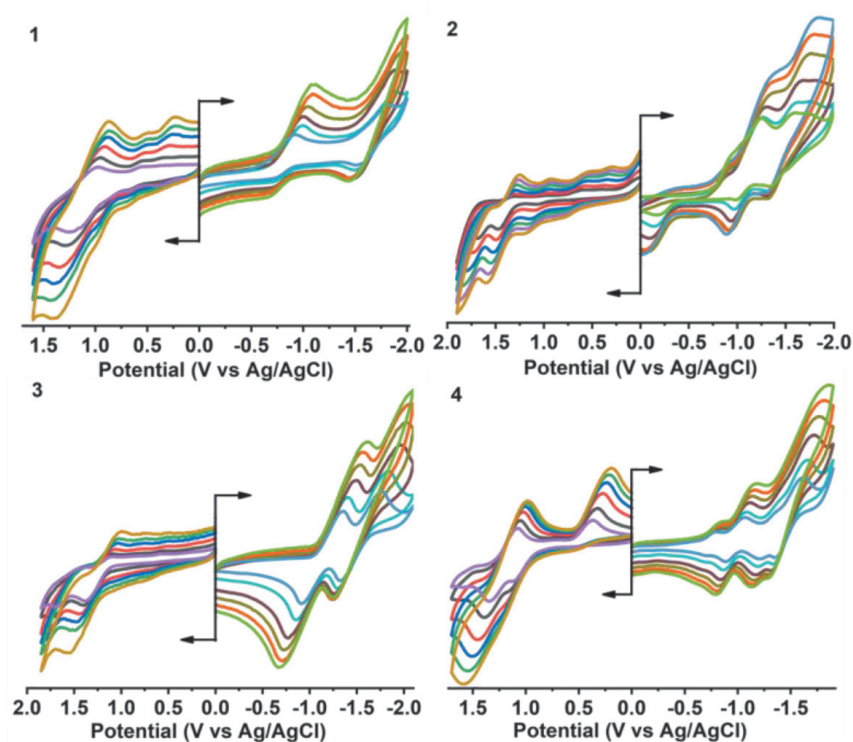


Figure 4. Cyclic voltammetry diagram of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in *o*-dichlorobenzene (*o*-DCB) containing 0.1M TBAP at scan speed from 50 to 500 mV·s⁻¹.

Table 1. UV-Vis absorption data of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in various solvents.

	1		2		3		4	
	Soret-band	Q-band	Soret-band	Q-band	Soret-band	Q-band	Soret-band	Q-band
DMF	410	503, 536, 578, 631	430	526, 565, 603, 666	428, 443	530, 551, 590, 629	422, 433	516, 556, 612, 645
PhCN	413	505, 539, 578, 632	433	527, 565, 604, 664	432, 445	531, 552, 589, 632	424, 449	516, 552, 591, 631
THF	408	501, 536, 577, 631	428	524, 566, 605, 663	415, 423	552, 567, 613, 643	419, 437	518, 560 610, 647
CH ₂ Cl ₂	407	502, 535, 577, 629	428	524, 561, 602, 660	410, 422	518, 563, 612, 638	422, 433	516, 556, 612, 645
DMSO	—	—	—	—	428, 443	527, 548, 590, 628	422, 449	510, 549, 590, 628

Table 2. Redox potentials of porphyrins **1** and **2**, corrole **3** and corrole-porphyrin-corrole triad **4** in *o*-dichlorobenzene containing 0.1 M TBAP.

No./Potential ($E_{1/2}/V$)	Ox II	Ox I	Red I	Red II	Red III
1	—	+1.11	−0.86	−1.63	—
2	+1.51	+1.38	−1.09	−1.45	—
3	+1.56	+1.23	−1.14	−1.57	—
4	+1.54	+1.17	−0.98	−1.29	−1.51

and fully characterized and the electronic structure was investigated by comparing with their synthetic precursors based on the spectroscopy including UV-Vis and fluorescence, along with electrochemistry. We can confirm that the energy transfer was observed from corrole-por-

phyrin-corrole triad between porphyrin and corrole core. Considering porphyrin/corrole derivatives have various advantages in high-tech field, the results may provide useful information for future investigation of porphyrin/corrole chemistry.

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