PCCP

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/pccp

Journal Name

ARTICLE

An ionic charge-transfer dyad prepared cost-effectively from tetrathiafulvalene carboxylate anion and TMPyP cation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Li-Jun Xue,[a] Peng Huo,[a] Yan-Hong Li,[a] Jin-Le Hou,[a] Qin-Yu Zhu*[a] and Jie Dai*[a]

Great progresses have been made in combining a TTF moiety with a porphyrin unit by covalent bonds, but only a few examples were reported in which the TTF and porphyrin assembled by noncovalent interactions. In contrast to the energy- and time-consuming synthetic procedures for the covalent system, assembly of non covalent ionic system would be a cost-effective way to construct donor–acceptor ensembles. Herein a new type of ionic TTF-porphyrin dyad is obtained. A methylated tetra(4-pyridyl) porphyrin (5,10,15,20-tetrakis-(*N*-methyl-4-pyridyl)-porphyrin, TMPyP) is selected as the cation, and TTF-bicarboxylate (L^1) or TTF–tetracarboxylate (L^2) is used as the anion. Crystal structures of two TTF-TMPyP ionic D-A compounds {TMPyP-(HL^1)$_4$}·$3H_2O$ (**1**) and {TMPyP-(H_2L^2)$_2$}·$5H_2O$ (**2**) were characterized by single-crystal X-ray diffraction. The strong ionic interaction enhances the charge-transfer between the regular mixed-stacking donors and acceptors, which are investigated comprehensively by spectral, electrochemical and theoretical studies. The variation in properties between L^1 and L^2 is of great advantage in understanding the influence factors for charge-transfer. The charge-transfer property can be modulated by not only the nature of the donor or acceptor, but also the cation-anion ratio in the salt, which shows great flexibility of D-A ionic dyad in design and preparation of new charge-transfer systems.

Introduction

The global urgent need for clean energy sources has resulted in extensive research to develop systems capable of converting light energy into chemical energy. In this vein, electron donor–acceptor (D–A) compounds involving porphyrin are of great significance due to their applications in artificial light-harvesting antenna,[1] photonic wires,[2] photo reaction centers,[3] and photovoltaic cells.[4] In most cases, porphyrins and metalloporphyrin complexes usually act as electron donors in D–A ensembles.[5] Such properties can be tuned as electron acceptors by introducing strongly electron-withdrawing substituents,[6] high-valent metal ions,[7] and protons[8] to the macrocycles. On the other hand, tetrathiafulvalene (TTF) and its derivatives (TTFs) are well-known systems for their two-step reversible redox processes upon chemical or electrochemical oxidation.[9] TTFs as electron donors paired with suitable acceptors have been well exploited in controlled self-assembled nanostructures,[10] environmentally responsive devices,[11] nonlinear optical arrays,[12] as well as light harvesting complexes.[13] Considerable efforts have been devoted recently to incorporating TTF moieties onto the cores of porphyrins or metalloporphyrins, because they contain both redox active sites and a chromophoric unit, and also both electron donor and acceptor.[14] It is expected that such multicomponent molecules can act as effective chemical sensors and organoelectronic materials.

The direct combination of TTF and porphyrin moieties in one molecule had been unsuccessful until 2001 most likely due to the lack of an effective synthetic route. The first fully conjugated TTF-porphyrins was obtained[14a] using the appropriate pyrrolo-TTF unit. However, the multistep synthetic procedures are energy- and time-consuming and the yields are very low even for the symmetrical derivatives. The use of noncovalent binding such as metal–ligand coordination, electrostatic interaction, hydrogen bonds and rotaxane host-guest interaction would provide a simpler but more cost-effective way to construct electron donor–acceptor ensembles.[15] Developing a simple TTF-porphyrin supramolecular system could represent an important step forward in this research field. However, to the best of our knowledge, only a few examples including TTF and porphyrin assembled by the noncovalent interaction were reported. A protonated dodecaphenylporphyrin acts as a host and neutral TTF acts as a guest forming a supramolecular D-A compound in a 1:1 fashion based on intermolecular π-π interactions.[8d] The other examples are using metal–ligand coordination to get D-A dyads or triads .[16]

In contrast to the neutral TTF-porphyrin supramolecular systems,[8d] we report herein a new type of TTF-porphyrin cation-anion ionic supramolecular dyad. A methylated tetra(4-pyridyl)

---

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China.*
E-mail: zhuqinyu@suda.edu.cn; daijie@suda.edu.cn .

Electronic Supplementary Information (ESI) available: Crystallographic data CCDC 1426992-1426993 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data and structural refinement parameters, the energy of the frontier orbitals and the energy gaps of 2, frontier molecular orbitals, UV-vis, CV, fluorescence spectra. See DOI: 10.1039/x0xx00000x porphyrin [5,10,15,20-tetrakis-(*N*-methyl-4-pyridyl)-porphyrin, TMPyP] is selected as the cation, and TTF-bicarboxylate (L^1) or TTF–tetracarboxylate (L^2) is used as the anion (Chart 1). With these charge enhanced TTF donor and porphyrin acceptor, two TTF-TMPyP ionic D-A compounds {TMPyP-$(HL^1)_4$}·$3H_2O$ (**1**) and {TMPyP-$(H_2L^2)_2$}·$5H_2O$ (**2**) are easily obtained and their crystal structures were characterized by single-crystal X-ray diffraction. The regular D-A mixed-stacking structures of these two compounds are different from the host-guest structures mentioned above for the neutral TTF-porphyrin compounds. The strong ionic interaction enhances the charge-transfer between the anions and cations, which are investigated comprehensively by spectral, electrochemical and theoretical studies. The variation in properties between L^1 and L^2 is of great advantage in understanding the influence factors for the charge-transfer system. Not only the nature of the donor or acceptor, but also the cation-anion ratio in the salt are important for the charge-transfer process.

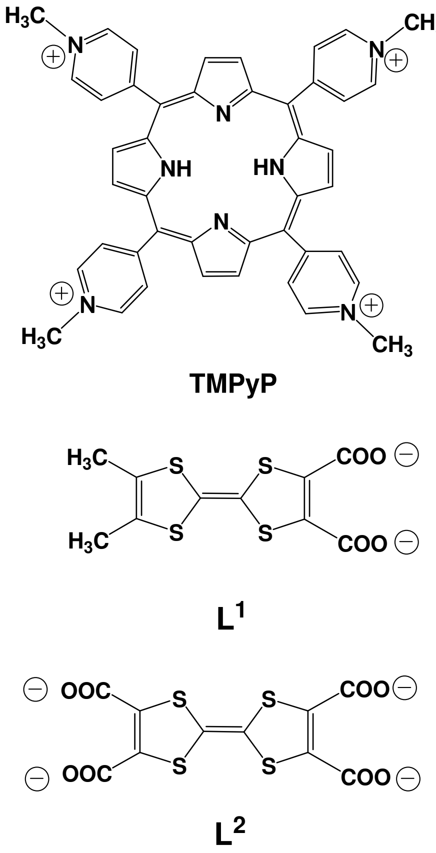


Chart 1 Structures of TMPyP (Top), TTF–bicarboxylate L^1 (middle), and TTF–tetracarboxylate L^2 (Bottom).

Experimental Section

General remarks Starting material $TMPyP(PF_6)_4$ was prepared according to the literature method.[17] TTF–bicarboxylate L^1, 2,3-bis(carboxyl)-6,7-bimethylthio-tetrathiafulvalene sodium salt, Na_2L^1, was prepared according to the literature methods.[18] Tetrathiafulvalene–tetracarboxylate sodium salt (Na_4L^2) was prepared using the method reported previously.[19] All other analytically pure reagents were purchased commercially and used without further purification. The IR spectra were recorded using KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C, H, and N were performed using an VARIDEL III elemental analyzer. Solid-state room-temperature optical diffuse reflectance spectra of the microcrystal samples were obtained with a Shimadzu UV-3150 spectrometer. ESR spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in X band at 110 K. The fluorescence was recorded on an HITACHI F2500 fluorescent photometer. ^1H NMR spectra were measured in *d*6-DMSO using tetramethylsilane, $Si(CH_3)_4$, as an internal standard on UNITYNOVA-400 spectrophotometer.

Synthesis

{TMPyP-$(HL^1)_4$}·$3H_2O$ (1) A solution of Na_2L^1 (8.6 mg, 0.02mmol) in methanol (2 mL) was mixed with a solution of $TMPyP(PF_6)_4$ (6.3mg, 0.005 mmol) in methanol (2 mL). The mixed solution was stirred for 0.5h at room temperature and filtered into a glass tube. Black rectangular crystals of **1** were obtained in 2 days from the filtrate by controlled evaporation of the solvent, washed with ethanol, dried in vacuum and used for all measurements (2.3 mg, yield 20.3 %). Anal. Calcd for $C_{84}H_{72}N_8O_{19}S_{24}$ (MW: 2267.07): C, 44.50; H, 3.20; N, 4.94. Found: C, 44.32; H, 3.09; N, 5.04. IR data (cm^{-1}): 2971(w), 2915(w), 1637(s), 1597(s), 1561(w), 1524(w), 1507(w), 1456(w), 1422(w), 1401(w), 1342(s), 1184(w), 1159(m), 1082(m), 1050(m), 974(m), 884(m), 859(m), 799(m), 774(m).

{TMPyP-$(H_2L^2)_2$}·$5H_2O$ (2) An aqueous solution (2 mL) of Na_4L^2 (4.7 mg, 0.01 mmol) was placed into the underlayer of a glass tube. A solution of $TMPyP(PF_6)_4$ (6.3mg, 0.005 mmol) in methanol (2 mL) was put into the superstratum dropwise carefully. The dark-purple block single crystals of **2** were obtained in 5 days by slow diffusion at room temperature, washed with ethanol, dried in vacuum and used for all measurements (1.8 mg, yield 23.7 %). Anal. Calcd for $C_{64}H_{52}N_8O_{21}S_8$ (MW: 1525.61): C, 50.38; H, 3.44; N, 7.34. Found: C, 50.13; H, 3.25; N, 7.06. IR data (cm^{-1}): 2974(w), 2923(w), 1640(s), 1573(s), 1510(w), 1459(w), 1403(m), 1385(w), 1345(s), 1279(w), 1181(w), 1162(m), 1074(b), 1000(w), 968(w), 859(m), 793(m).

X-ray Crystallographic Study The measurement was carried out on a Rigaku Mercury CCD diffractometer at low temperature with graphite–monochromated Mo Kα (λ = 0.71073 Å) radiation. X-ray crystallographic data for all compounds were collected and processed using CrystalClear (Rigaku).[20] The structure was solved by direct methods using SHELXS-97 for **1**[21] and SHELXS-2014 for **2**, and the refinement against all reflections of the compound was performed using SHELXL-97 for **1**[22] and SHELXL-2014 for **2**. All of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added theoretically, except that the H atoms of O–H of **2** were located from the Fourier map. Relevant crystal data, collection parameters, and refinement results can be found in Table S1 (ESI).

Electrode Preparation and Photocurrent Measurement The photoelectrodes of the compounds were prepared by powder coating method. As a typical procedure, the crystals (0.003 mmol) were ground and pressed uniformly on the cleaned ITO glass (100 Ω/□). A 150 W high-pressure xenon lamp, located 20 cm away from the surface of the ITO electrode, was employed as a full-wavelength light source. The photocurrent experiments were performed on a CHI650E electrochemistry workstation in a three-electrode system, with the sample coated ITO glass as the working electrode mounted on the window with an area of 0.385 cm2 (Φ = 0.7 cm), a Pt plate as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte solution was a 0.1 mol·L-1 sodium sulfate aqueous solution. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light.

Theoretical Calculations Density functional theory (DFT) calculation was carried out using Gaussian09 program package.[23] All calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee–Yang–Parr correlation functional (B3LYP) employing the 6-311G** basis set for all atoms.[24]

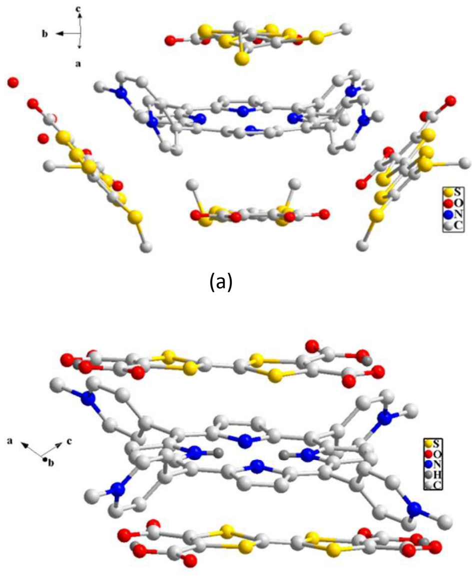
Results and Discussion

Design and synthesis

As a good series among porphyrin derivatives, tetra(4-pyridyl) porphyrin (PyP) has been attracted much attention to create coordination assemblies with novel structures and intriguing properties.[25] Geremia group utilized methylated PyP (TMPyP) to self-assemble host-guest supramolecular complexes with calixarene tweezers.[26] However, the study on TMPyP as an electron acceptor in electron donor–acceptor systems remains underexplored. The TMPyP is a porphyrin based positively charged tetravalent cation and, therefore, can act as a strong electron acceptor in D-A ensembles. The selection of TMPyP in this work rather than a metalated or protonated porphyrin as an electron acceptor originates also from its highly charged structure and, consequently, can improve the physical properties of the TTF-porphyrin compounds. Likewise, in comparison with neutral TTF, the negatively charged TTF-carboxylates can act as strong electron donors and match well with the positive charged TMPyP cation acceptor. The ionic TTF-porphyrin ensembles **1** and **2** were obtained in a simple manner by controlled evaporation of the mixed methanol solutions or two layers diffusion methods at room temperature. Compared with the preparation of covalently linked TTF–porphyrin compounds, it is an energy- and time-economic procedure.

Cation-anion coupled structures

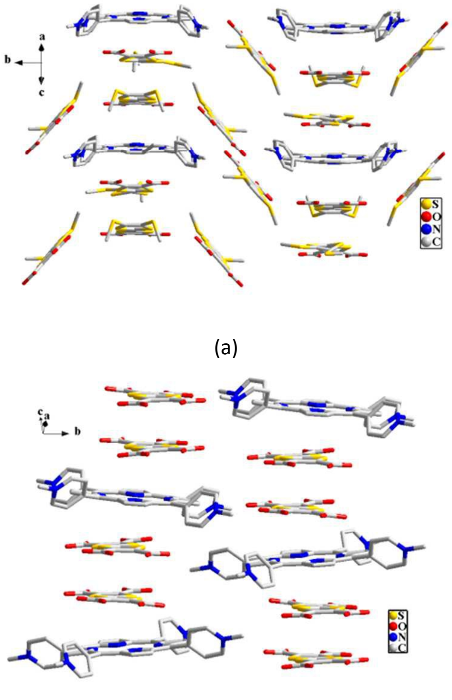
Single crystal X-ray diffractometry shows that compound **1** crystallized in the monoclinic $P2_1/m$ space group. The asymmetric unit is composed of one TMPyP cation, four HL^1 anions, and three co-crystallized water molecules (Fig. 1a). Although the proton of the carboxylate group cannot be located in the Fourier maps, considering the planar arrangement of two carboxylate groups and the charge balance rule, the bicarboxylate moiety of L^1 should be monoprotonated.[27] Compound **2** crystallized in the monoclinic $C2/c$ space group. The asymmetric unit is composed of one TMPyP cation, two H_2L^2 anions, and five co-crystallized water molecules



(a)

(b)

Fig. 1 Molecular structures of compounds **1** (a) and **2** (b).

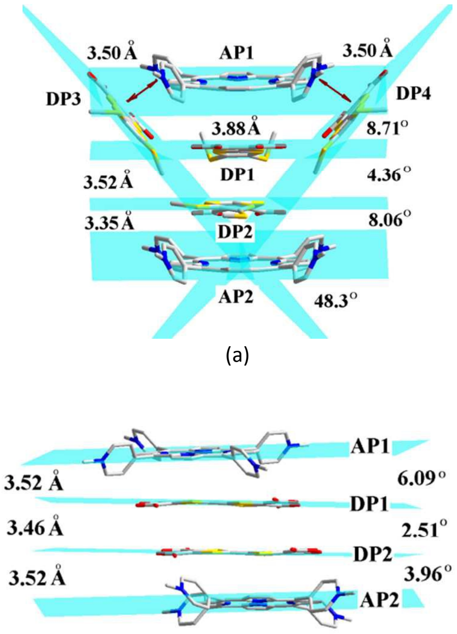


(a)

(b)

Fig. 2 1D column D–D–A–D–D–A structures of compounds **1** (a) and **2** (b). Co-crystallized water molecules and all hydrogen atoms except those of O–H and N–H are omitted for clarity.

(Fig. 1b). Both compounds 1 and 2 exhibit D–D–A–D–D–A column structures. (Fig. 2a and 2b) by virtue of intermolecular π···π interaction between porphyrin core and TTF moiety as well as S···C face-to-face short contacts between TTF moieties. Molecular planes of the cation and anion are calculated and their plane to plane distances and some angles are displayed in Fig. 3 [DP and AP represent donor (TTF) plane and acceptor (porphyrin core) plane, respectively]. As shown in Fig. 3, it should be noticed that the stacking of TTF and porphyrin cores in **2** is better than that in **1**, because the symmetrical H_2L^2 anion has good planarity. The layered packing in **2** is closer and more regular than those in **1**, and hence the anion–cation interaction in **2** should be stronger than that in **1** (see plane to plane distances and angles in Fig. 3). The regular D-A stacking assembly in these two compounds are different from the host-guest structures reported for the neutral TTF-porphyrin compound.[8d] In concentrated solution, the anion–cation interactions can act through the ion assembly in similar manner to those in solid state.



(a)

(b)

Fig. 3 Molecular planes of the cation and anion and plane to plane distances and some angles of (a) **1** and (b) **2**.

Anion-cation charge transfer property

Solid state electronic spectra of **1** and **2** together with the starting materials TMPyP, Na_2L^1, Na_4L^2 as used for comparison were measured at room temperature using $BaSO_4$ as a standard reference (Fig. 4). By comparing with the absorption curve of TMPyP, the Q-bands at 511, 547, 585, and 636 nm of TMPyP are red-shifted about 15 nm for **1** and **2**, while the shifts of Soret bands at about 440 nm of TMPyP cannot be judged because of the overlapping with the band of TTF moiety. It can be deduced from the red-shift of TMPyP Q-bands that the TTF moiety appears to have a substantial perturbation of electronic transition states centered on the TMPyP core. In the visible and near-infrared range, the spectra of **1** and **2** show a broad absorption ranging from 750 to 1200 nm for **1**, and from 750 to 1010 nm for **2**. The new broad lowest energy band could be attributed to anion-cation charge-transfer (ACCT) transition from the TTF anion to the TMPyP cation, which is enhanced by the cation and anion electrostatic interaction. Based on the results of structural analysis (discussed above), it is certain that the ACCT bands of **1** and **2** result from the π···π interaction, and short contacts between TMPyP and TTF moieties.

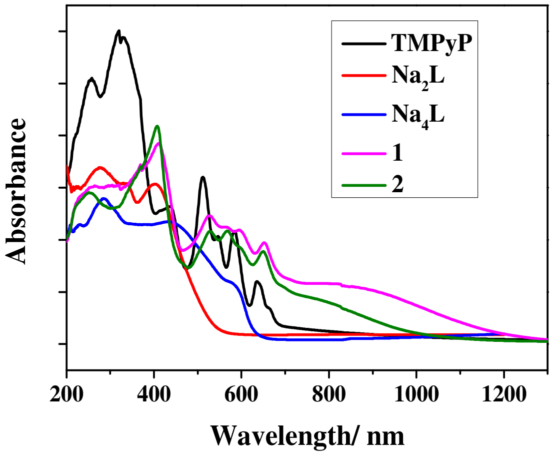


Fig. 4 Electronic spectra of **1** and **2** along with the starting materials TMPyP, Na_2L^1, and Na_4L^2 in the solid state.

Theoretical calculations of **2** show that the electronic density distributions of the highest occupied molecular orbitals (HOMO, HOMO–1) are mainly localized on the TTF unit of L^2 and the lowest unoccupied frontier molecular orbitals (LUMO, LUMO+1) are mainly localized on the TMPyP (Fig. S1). These theoretical results strongly support the occurrence of ACCT from the TTF unit to the porphyrin unit. The calculated energy gap Δ*E* is in the range of 1.04–1.17 eV (1192–1058 nm) ($E_{\text{LUMO+1}}$ - $E_{\text{HOMO-1}}$ = 1.17 eV, E_{LUMO} - E_{HOMO} = 1.04 eV) (Table S2), which reasonably agrees with the experimental charge-transfer absorption band.

Solution spectra of crystals **1** and **2** in different concentrations were measured (Fig. S2). The appearance of the broad ACCT absorption shoulder at about 700 nm for **1** indicates that the anion-cation interaction (partial charge transfer) exists even in solution and increases with the increasing of the concentration. The results further suggest that there are anion-cation aggregates or ensembles in concentrated solution. Comparing with that of **1**, the increasing of ACCT band of **2** is not so obvious and only the platform is raised. The ACCT interactions were also investigated by ^{1}H NMR spectroscopy. Fig. 5 shows a comparison of the partial ^{1}H NMR spectra of TMPyP, **1** and **2** in *d*6-DMSO. The chemical shift of the resonance of H–C=C–H of the pyrrol ring (denoted as c) of TMPyP located at 9.24 ppm.[17] Upon formation of the ionic CT compound, distinct upfield shift occurred (Δδ = 0.14 for **1** and 0.09 for **2**) suggesting that the pyrrol ring of TMPyP is shielded by TTF moiety. The difference of the shifts between **1** and **2** indicated that the CT interaction in solution between anion and cation of **1** is stronger than that of **2**. In order to verify the effect of cation-anion interaction on charge-transfer, a control experiment is carried out using neutral TTF derivative TTF($CONH_2$)$_2$ (chart S1). No obvious shifts can be seen when adding 4eq. TTF($CONH_2$)$_2$ into the solution of TMPyP (Fig. S3). The results show that the cation-anion interaction enhances the charge-transfer.

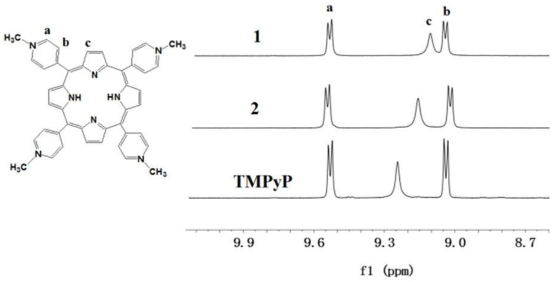


Fig. 5 Partial ^{1}H NMR spectra of TMPyP, **1** and **2** in *d*6-DMSO (4×10^{-3} mol·L^{-1}).

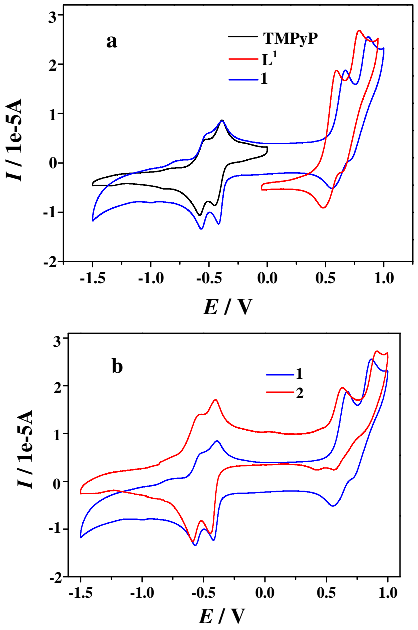


Fig. 6 Cyclic voltammogram under an argon atmosphere in DMF solution (1.0×10^{-3} mol·L^{-1}) (0.1 mol·L^{-1} Bu_4NClO_4, 100 mV s^{-1})of (a) **1** along with the starting materials TMPyP and Na_2L^1 and (b) **1** and **2**.

The electrochemical potentials of **1** and **2** together with those of the starting compounds TMPyP, Na_2L^1, Na_4L^2 were measured by cyclic voltammetric (CV) analyses under an argon atmosphere in DMF solution containing 0.1 mol·L^{-1} tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) as the supporting electrolyte. In the electrochemistry window of DMF (-1.5–1.0 V), unlike other porphyrin derivatives, only two sets of negative signals of TMPyP are observed (Fig. 6a), and the two positive signals of TMPyP do not appear at this window for their more positive potentials. This indicates a relatively electron deficient nature of the TMPyP due to the influence of four methylated pyridine entities possessing a total of four positive charges, which is in favour of charge-transfer as a strong electron-acceptor in D–A system. Comparative studies with TMPyP and Na_2L^1 (Fig. 6a) indicate that two redox waves in the anodic direction of **1** ($E_{1/2}^1$ = 0.615 V, $E_{1/2}^2$ = 0.796 V) correspond to the TTF/TTF$^{\cdot+}$ and TTF$^{\cdot+}$/ TTF^{2+} redox couples, while the redox waves in the cathodic direction ($E_{1/2}^3$ = –0.406 V, $E_{1/2}^4$ = –0.552 V) are ascribed to the porphyrin unit. About 30 mV positive shifts for TTF redox waves of **1** occurs in comparison with those of L^1, which indicates the charge transfer from TTF to TMPyP, while no distinguishable shift of the TMPyP peaks is observed that might be due to the limited CV sensitivity for the charge increase on the TMPyP cation. The CV of **2** is shown in Fig. 6b along with that of **1**. Similar to that of **1**, four redox waves appear, two of which are ascribed to TTF unit ($E_{1/2}^1$ = 0.600 V, $E_{1/2}^2$ = 0.838 V) and the other two correspond to the porphyrin moiety ($E_{1/2}^3$ = –0.418 V, $E_{1/2}^4$ = –0.559 V).

To further investigate whether an efficient anion-cation charge transfer or partial electron transfer has happened, electron spin resonance (ESR) studies were carried out at 110 K (Fig. 7). The solid state ESR spectra of **1** and **2** show signals at g = 2.0006 and 2.0003, respectively, correspondence with the characteristic of free radical signal (S=1/2),[29] which indicates that partial electron transfer in the ground state via the anion-cation interaction. The signal split of **1** might be an effect of axial field, which is in accordance with the result of the crystal structural analysis. There are two sets of TTF anions coupling with the TMPyP cation in **1**, but only one set of TTF stacking with the TMPyP cation in **2** (Fig. 2).

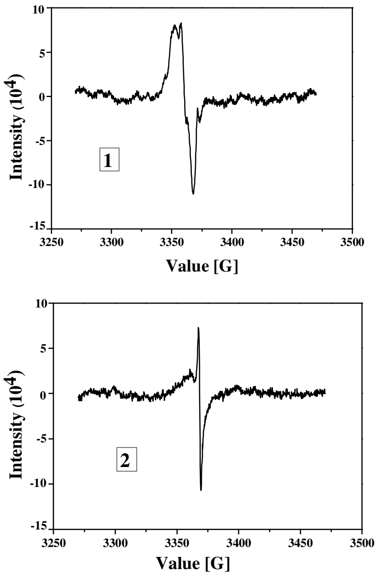


Fig. 7 ESR spectra of **1** and **2** recorded at 110 K.

Charge transfer induced fluorescence quenching

It is well-known that diamagnetic porphyrins display a strong fluorescence-emission feature in the range of 570–800 nm spectral region,[30] and electron transfer from TTF to acceptor that fluoresces intrinsically would result in fluorescence quenching.[31] Therefore, the anion-cation charge-transfer property of **1** and **2** can be studied quantitatively by comparing their fluorescence spectra with that of TMPyP. The fluorescence spectra of **1**, **2** and TMPyP at selected concentrations in DMF at room temperature were recorded (Fig. 8a and Fig. S4). Upon photoexcitation, the overall fluorescence of **1** and **2** is significantly quenched compared with that of TMPyP, which means the fluorescence quenching not only happened in the TTF-annulated porphyrin,[14g] but also in solution of ionic TTF-porphyrin assembly. The quenching is increased along with the increased concentration (Fig. S5). Addition of $Fe(ClO_4)_3$ to the solution of **1** or **2** led to fluorescence recovery, and the fluorescence intensity increased with the increasing amounts of $Fe(ClO_4)_3$ (Fig. 8b) (CAUTION: All metal perchlorates must be regarded as potentially explosive. Only a small amount of compound should be prepared, and it should be handled with caution), because the electron-donating ability of TTF unit is lowered upon the TTF being oxidized to $TTF^{\bullet+}$.[32] Thus a new fluorescence switch based on noncovalently linked TTF-porphyrin ionic supramolecular dyad is established.

It is worth noting that, in electronic spectra, the anion-cation charge transfer (ACCT) band of **1** extends to the lower energy region and the band intensity of **1** is stronger than that of **2** as shown in Fig. 4. The result suggests that the ACCT intensity between bicarboxylate and TMPyP (L^1-TMPyP) in **1** is stronger than that between tetracarboxylate and TMPyP (L^2-TMPyP) in **2**. As a more convinced evidence for the conclusion, the fluorescence intensity of **1** is quantitatively weaker than that of **2** at the same molar concentrations (Fig. 9) due to the charge transfer induced fluorescence quenching of **1** being stronger than that of **2**. Similar result was observed for solid state fluorescence spectra of crystals **1** and **2** (Fig. S6).

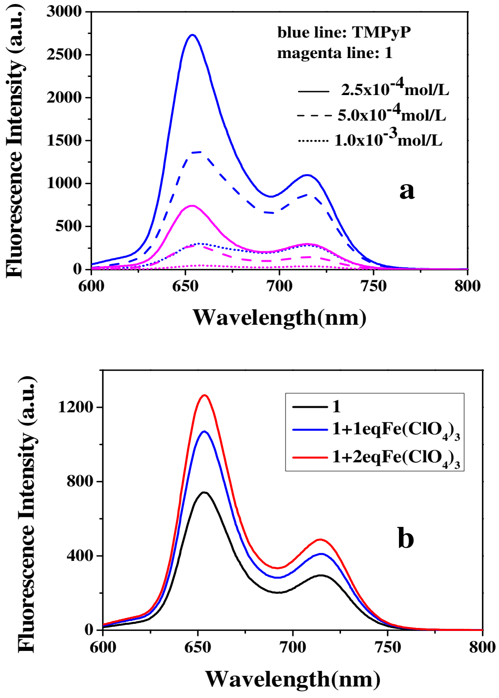


Fig. 8 Changes of the fluorescence spectra in DMF at room temperature of (a) **1** (λex = 576 nm) and TMPyP (λex = 470 nm), recorded at different concentrations from 1.0×10^{-3} to 5.0×10^{-4} $mol \cdot L^{-1}$, and (b) **1** (2.5×10^{-4} $mol \cdot L^{-1}$) upon addition of increasing amounts of the oxidant $Fe(ClO_4)_3 \cdot 6H_2O$ in DMF.

The negative charge on TTF-bicarboxylate is a half as that on TTF-tetracarboxylate, and better donor property (higher electron density on TTF moiety) is expected for the latter. Moreover, the inter-planar layer interaction in **2** is more effective than those in **1** as discussed in the structural analysis. Whereas, all the spectra experimental results suggest the charge transfer in **1** is stronger than that in **2**. To be more cautious, fluorescence spectra of TMPyP are recorded upon quantitative titration of neutral $TTF(CONH_2)_2$, L^1 and L^2 and the results are given in Fig. 10, Fig. S7 and Fig. S8. Upon adding 4 eq. of $TTF(CONH_2)_2$, the fluorescence decrease is only 700 (Fig. S7), while the same value of fluorescence decrease is achieved when adding only 0.5eq. L^1 or 0.25 eq. L^2 (Fig. S8), which shows the effect of neutral $TTF(CONH_2)_2$ on the fluorescence quenching is greatly weaker than that of ionic L^1 and L^2. When added two eq. of L into the TMPyP solution (2.0×10^{-5} $mol \cdot L^{-1}$), the fluorescence quenching for L^2 (from 6172 to 1837) is clearly more effective than that for L^1 (from 6172 to 2778). The fluorescence quenching platform appeared at the concentration 3.5 eq. for L^1 and 2.25 eq. for L^2. Therefore, TTF-tetracarboxylate is convinced to be a stronger donor than TTF-bicarboxylate. However, in compounds, the high TTF / TMPyP mole ratio in **1** (4:1) in comparison with that in **2** (2:1), resulted from the variation of the negative charges between L^1 and L^2, should be responsible for the experimental results that **1** is a stronger ACCT system. That is to say, the salt type of TTF-TMPyP dyads is also related to the property of charge transfer and fluorescence quenching.

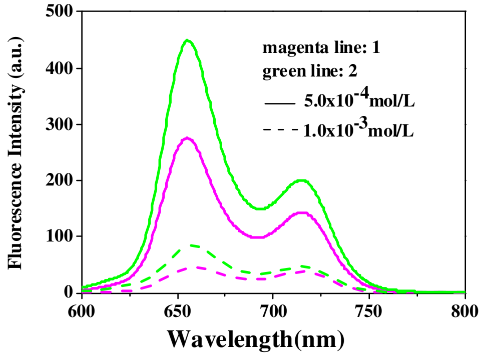


Fig. 9 Comparison of the fluorescence spectra of **1** with that of **2** at the same molar concentrations (solid line: 5.0×10^{-4} $mol \cdot L^{-1}$, dashed line: 1×10^{-3} $mol \cdot L^{-1}$).

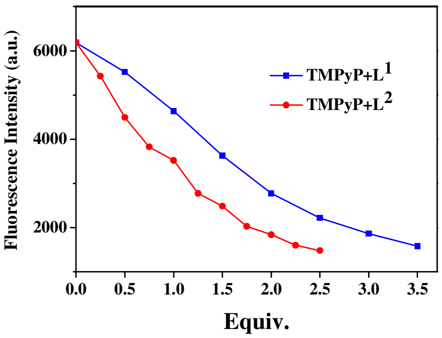
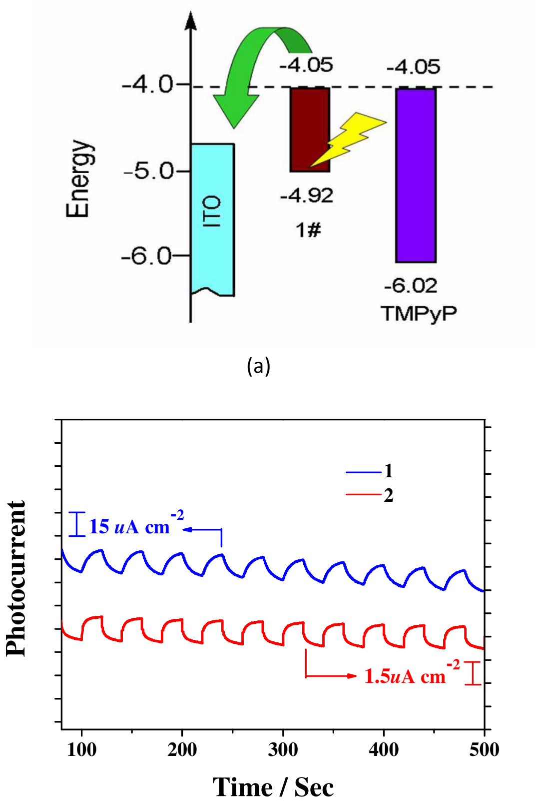


Fig. 10 Changes of the peak at 652 nm of fluorescence spectra of TMPyP (2.0×10^{-5} mol·L^{-1}) in DMF at room temperature, upon quantitative titration of L^1 and L^2.

Energy levels and charge transfer related photocurrent response

As theoretical calculations, the HOMOs are mainly localized on the TTF unit and the LUMOs are mainly localized on the TMPyP (Fig. S1). The results strongly support the CV results that the first reduction potentials (LUMO) of **1** and **2** are related to the TMPyP and their first oxidation potentials (HOMO) are based on the TTF. An energy diagram of **1** and TMPyP is shown in Fig. 11a based on the spectra and CV data along with the potential of ITO glass electrode. The formation of charge-transfer ionic dyad significantly decreases the energy gap from 1.97 to 0.83 eV. It has been discussed in introduction that electron donor–acceptor (D–A) compounds involving porphyrin are of great significance due to their applications in photoinduced physical and chemical events[1-4] and TTFs as electron donors paired with suitable acceptors have been used as light harvesting materials.[13] The CT compounds **1** and **2** with narrow energy gaps should be promising materials for photocurrent conversion. Since the estimated conducting level of ITO is -4.7 eV[33] that is lower than -4.05 eV of the LUMO of the dyad, CT-compounds (poly crystals) modified ITO/**1**/**2** photoelectrodes were designed and prepared to study the photocurrent response property.

The experiments of the electrode were carried out in a three electrode photoelectrochemical cell (a more detailed description is given in the experimental section). As shown in Fig. 11b, upon repetitive irradiation with xenon light on and off, a clear photocurrent response was observed (blue line for **1** and red line for **2**). The photocurrent intensity of **1** is stronger than that of **2** under the same experimental conditions. The data are comparable with those of a similar charge transfer system of L^2 and methyl viologen dication.[34] The results can be explained by the effective photoinduced electron transfer process. The irradiation induces the charge transition of the CT compounds to electron transition (Figure 11a) and then the photogenerated electrons on TMPyP* (LUMO) transfer to the ITO electrode to generate anodic current. Photocurrent responses of a neutral TTF and porphyrin supramolecular architecture were reported that exhibited single crystal photoresponse upon photoirradiation in nA scale.[9e] However it cannot be simply compared due to the different measurement methods.



(a)

(b)

Fig. 11 (a) Energy diagram of **1** and TMPyP along with the ITO glass electrode; (b) Photocurrent responses of crystals **1** and **2** in the presence of a 0.1 mol·L^{-1} Na_2SO_4 aqueous solution.

Conclusions

In summary, selecting methylated tetra(4-pyridyl) porphyrin as the cation, and TTF-carboxylates as anions, two TTF-porphyrin cation-anion ionic dyad were prepared. Their crystal structures were characterized by single-crystal X-ray diffraction. The TTF anions are self paired and mixed-stacked regularly with TMPyP cations through π···π and S···C interactions. The strong ionic interaction enhances the charge-transfer between the anions and cations, which are investigated comprehensively by spectral, electrochemical and theoretical studies. A redox fluorescence switch based on noncovalently linked TTF-porphyrin supramolecular ionic dyad is established. The studies on variation in properties between L^1 and L^2 is of great advantage in understanding the influence factors for charge-transfer. Not only the entity of the donor or acceptor, but also the cation-anion ratio in the salt relate to the extent of CT property that shows great advantage of ionic dyad in design and modulating of new charge-transfer systems.

Acknowledgements

We gratefully acknowledge financial support by the NSF of China (21171127 and 21571136), the Priority Academic Program Development of Jiangsu Higher Education Institutions and by State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials.

Notes and references

1 (a) M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, **256**,2601–2627; (b) A. Uetomo, M. Kozaki, S. Suzuki, K.Yamanaka, O. Ito and K. Okada, *J. Am. Chem. Soc.*, 2011, **133**, 13276–13279; (c) N. Aratani, D. Kim and A. Osuka, *Acc. Chem. Res.*, 2009, **42**, 1922–1934; (d) M. Kozaki, A. Uetomo, S. Suzuki and K. Okada, *Org. Lett.*, 2008, **10**, 4477–4480; (e) M. Choi, T. Aida, T. Yamazaki and I. Yamazaki, *Angew. Chem. Int. Ed.*, 2001, **40**, 3194–3198; (f) A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki and Y. Nishimura, *Angew. Chem. Int. Ed.*, 1998, **37**, 3023–3027.

2 T. K. Khana, M. Broringb, S. Mathura and M. Ravikanthc, *Coord. Chem. Rev.*, 2013, **257**,2348–2387.

3 For example: (a) C. A. Wijesinghe, M. E. El-Khouly, M. E. Zandler, S. Fukuzumi, and F. D'Souza, *Chem. Eur. J.*, 2013, **19**, 9629– 9638; (b) M. E. El-Khouly, C. A. Wijesinghe, V. N. Nesterov, M. E. Zandler, S. Fukuzumi and F. D'Souza, *Chem. Eur. J.*, 2012, **18**, 13844–13853; (c) A. Takai, M. Chkounda, A. Eggenspiller, C. P. Gros, M. Lachkar, J.-M. Barbe and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, **132**, 4477–4489; (d) J.-Y. Liu, M. E. El-Khouly, S. Fukuzumi and D. K. P. Ng, *Chem. Eur. J.*, 2011, **17**, 1605–1613.

4 For example: (a)L.-L. Li and E. W.-G. Diau, *Chem. Soc. Rev.*, 2013, **42**, 291–304; (b)D. Wrobel and A. Graja, *Coord. Chem. Rev* 2011, **255**, *2555–2577;* (c) M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, **256**, 2601–2627; (d) H. Imahori, S. Hayashi, H. Hayashi, A. Oguro, S. Eu, T. Umeyama and Y. Matano, *J. Phys. Chem. C*, 2009, **113**, 18406–18413; (e) Y.-J. Cho, T. K. Ahn, H. Song, K. S. Kim, C. Y. Lee, W. S. Seo, K. Lee, S. K. Kim, D. Kim and J. T. Park *J. Am. Chem. Soc.*, 2005, **127**, 2380–2381; (f) S. Eu, S. Hayashi, T. Umeyama, A. Oguro, M. Kawasaki, N. Kadota, Y. Matano and H. Imahori *J. Phys. Chem. C*, 2007, **111**, 3528–3537; (g) B. Chen, L. Sun and Y.-S. Xie, *Chinese Chemical Letters* 2015, **26**, 899–904. (h) J. Liu, B. Liu, Y. Tang, W. Zhang, W. Wu, Y. Xie and W.H. Zhu, *J. Mater. Chem. C*, 2015, DOI: 10.1039/C5TC02522B.

5 L. Zhang and J. M. Cole, *ACS Appl. Mater. Interfaces*, 2015, **7**, 3427–3455.

6 (a) C. A. Bignozzi, R. Argazzi and C. J. Kleverlaan, *Chem. Soc. Rev.*, 2000, **29**, 87–96; (b) M. Buchalska, J. Kuncewicz and E. Swietek, *Cood. Chem. Rev.*, 2013, **257**, 767–775.

7 (a) N. K. Subbaiyan, C. A. Wijesinghe and F. D'Souza, *J. Am. Chem. Soc.*, 2009, **131**, 14646–14647; (b) J. C. Wang, I. A. Murphy and K. Hanson, *J. Phys. Chem. C*, 2015, **119**, 3502–3508.

8 (a) T. Kojima, T. Nakanishi, R. Harada, K. Ohkubo, S. Yamauchi and S. Fukuzumi, *Chem.-Eur. J.*, 2007, **13**, 8714–8725; (b) R. Harada and T. Kojima, *Chem. Commun.*, 2005, 716–718; (c) T. Kojima, T. Nakanishi, T. Honda and S. Fukuzumi, *J. Porphyrins Phthalocyanines*, 2009; (d)T. Nakanishi, T. Kojima, K.Ohkubo, T. Hasobe, K. Nakayama and S. Fukuzumi, *Chem. Mater.* 2008**, 20**, 7492–7500.

9 (a) F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227–232; (b) M. Giffard, G. Mabon, E. Leclair, N. Mercier, M. Allain, A. Gorgues, P. Molinié, O. Neilands, P. Krief and V. Khodorkovsky, *J. Am. Chem. Soc.*, 2001, **123**, 3852–3853; (c) G. Zhang, D. Zhang, X. Guo and D. Zhu, *Org. Lett.*, 2004, **6**, 1209–1212; (d) M. Yoshizawa, K. Kumazawa and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127***,* 13456–13457; (e) X. Shao, Y. Nakano, M. Sakata, H. Yamochi, Y. Yoshida, M. Maesato, M. Uruichi, K. Yakushi, T. Murata, A. Otsuka, G. Saito, S. Koshihara and K. Tanaka, *Chem. Mater.*, 2008, **20** 7551–7562; (f) X. Shao, Y. Yoshida, Y. Nakano, H. Yamochi, M. Sakata, M. Maesato, A. Otsuka, G. Saito and S. Koshihara, *Chem. Mater.*, 2009, **21**, 1085–1095.

10 F. G. Brunetti, C. Romero-Nieto, , J. López-Andarias, C. Atienza, J. L. López, D. M. Guldi and N Martín,. *Angew. Chem. Int. Ed.*, 2013, **52**, 2180–2184.

11 K. A. Nielsen, G. H. Sarova, L. Martın-Gomis, F. Fernandez-Lazaro, P. C. Stein, L. Sanguinet, E. Levillain, J. L. Sessler, D. M. Guldi, Á. Sastre-Santos and J. Jeppesen, O. *J. Am. Chem. Soc.*, 2008, **130**, 460–462.

12 Y. Matsuo, M. Maruyama, S. S. Gayathri, T. Uchida, D. Guldi, H. Kishida, A. Nakamura and E. Nakamura, *J. Am. Chem. Soc.*, 2009, **131**, 12643–12649.

13 C. Romero-Nieto, A. Medina, A. Molina-Ontoria, C. G. Claessens, L. Echegoyen, N. Martín, T. Torres and D. M. Guldi, *Chem. Commun.*, 2012, **48**, 4953–4955.

14 (a) J. Becher, T. Brimert, J. O. Jeppesen, J. Z. Pedersen, R. Zubarev, T. Bjùrnholm, N. Reitzel, T. R. Jensen, K. Kjaer, and Eric Levillain, *Angew. Chem. Int. Ed.*, 2001, **40**, 2497–2500; (b) G. Kodis, P. A. Liddell, L. de la Garza, A. L. Moore, T. A. Moore and D. Gust, *J. Mater. Chem.*, 2002, **12**, 2100–2108; (c) H. Li, J. O. Jeppesen, E. Levillain and J. Becher, *Chem. Commun.*, 2003, 846–847; (d) S. Saha, E. Johansson, A. H. Flood, H.-R. Tseng, J. I. Zink and J. F. Stoddart, *Chem. Eur. J.*, 2005, **11**, 6846–6858; (e) K. A. Nielsen, E. Levillain, V. M. Lynch, J. L. Sessler and J. O. Jeppesen, *Chem. Eur. J.*, 2009, **15**, 506–516; (f) S. Fukuzumi, K. Ohkubo, Y. Kawashima, D. S. Kim, J. S. Park, A. Jana, V. M. Lynch, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2011, **133**, 15938–15941; (g) Z.. Wan, C. Jia, J. Zhang, X. Yao and Y. Shi, *Dyes and Pigments*, 2012, **93**, 1456–1462; (h) A. Jana, M. Ishida, K. Kwak, Y. M. Sung, D. S. Kim, V. M. Lynch, D. Lee, D. Kim and J. L. Sessler, *Chem. Eur. J.*, 2013, **19**, 338–349; (i) C. M. Davis, Y. Kawashima, K. Ohkubo, J. M. Lim, D. Kim, S. Fukuzumi and J. L. Sessler, *J. Phys. Chem. C*, 2014, **118**, 13503–13513; (j) A. Jana, H. B. Gobeze, M. Ishida, T. Mori, K. Ariga, J. P. Hill and F. D'Souza, *Dalton Trans.*, 2015, **44**, 359–367; (k) R. Bolligarla, M. Ishida, V. S. Shetti, K. Yamasumi, H. Furutab and C.-H. Lee, *Phys. Chem. Chem. Phys.,* 2015, **17**, 8699–8705.

15 (a) J. L. Sessler, B. Wang, S. L. Springs and C. T. Brown, in *Comprehensive Supramolecular Chemistry*, Vol. 4, ed. Y. Murakami, Elsevier, Oxford, UK, 1996, p. 311; (b) F. D'Souza and O. Ito, *Coord. Chem. Rev.*, 2005, **249**, 1410–1422; (c) F. D'Souza, G. R. Deviprasad, M. E. Zandler, T. V. Hoang, A. Klykov, M. Van Stipdonk, A. Perera, M. E. El-Khouly, M. Fujitsuka and O. Ito, *J. Phys. Chem. A*, 2002, **106**, 3243–3252; (d) F. D'Souza, G. R. Deviprasad, M. E. El-Khouly, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 5277–5284; (e) T. Da Ros, M. Prato, D. M. Guldi, M. Ruzzi and L. Pasimeni, *Chem. Eur. J.*, 2001, **7**, 816–827; (f)A. Das and S. Ghosh, *Angew. Chem. Int. Ed.*, 2014, **53**, 2038–2054; (g)M. Kumar, K. V. Rao and S. J. George, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1300–1313.

16 (a) P. K. Poddutoori, N. Zarrabi, A. G. Moiseev, R. Gumbau-Brisa, S. Vassiliev and A. van der Est, *Chem.- Eur. J.*, 2013, **19**, 3148–3161; (b) P. K. Poddutoori, L. P. Bregles, G. N. Lim, P. Boland, R. G. Kerr and F. D'Souza, *Inorg. Chem.* 2015, **54**, 8482–8494; (c) X. Xiao, W. Xu, D. Zhang, H. Xu, H. Lu and D. Zhu, *J. Mater. Chem.*, 2005, **15**, 2557–2561.

17 Y. Liu, H.-J. Zhang, Y.-Q. Cai, H.-H. Wu, X.-L. Liu and Y. Lu, *Chem. Lett.*, 2007, **36**, 848–849.

18 (a) H.-H. Lin, Z.-M. Yan, J. Dai, D.-Q. Zhang, J.-L. Zuo, Q.-Y. Zhu and D.-X. Jia, *New J. Chem.*, 2005, 509–513; (b) P. Hudhomme, S. L. Moustarder, C. Durand, N. Gallego-Planas, N. Mercier, P. Blanchard, E. Levillain, M. Allain, A. Gorgues and A. Riou, *Chem. Eur. J.*, 2001, **7**, 5070–5083; (c) R. D. McCullough, M. A. Petruska and J. A. Belot, *Tetrahedron*, 1999, **55**, 9979–9998.

19 Y.-R. Qin, Q.-Y. Zhu, L.-B. Huo, Z. Shi, G.-Q. Bian, J. Dai, *Inorg. Chem.* 2010, **49**, 7372–7381.

20 Rigaku Corporation, 1999; CrystalClear Software User's Guide, Molecular Structure Corporation. 2000; J. W. Pflugrath, *Acta Crystallogr. Sect. D*. 1999, **55**, 1718–1725.

21 G. M. Sheldrick, SHELXS-97, Program for structure solution, Universität of Göttingen, Germany. 1999.

22 G. M. Sheldrick, SHELXL-97, Program for structure refinement, Universität of Göttingen, Germany. 1997.

23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.1, Gaussian Inc., Wallingford, CT, 2009.

24 (a) A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, 38, 3098; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, 37, 785.

25 (a) K.-J. Lin, *Angew. Chem. Int. Ed.*, 1999, **38**, 2730–2732; (b) L. Pan, S. Kelly, X. Huang and J. Li, *Chem.Commun.*, 2002, 2334–2335; (c) L. Carlucci, G. Ciani, D. M. Proserpio and F. Porta, *Angew. Chem. Int. Ed.,* 2003, **42**, 317–322; (d) D. V. Konarev, A. L. Litvinov, I. S. Neretin, N .V. Drichko, Y. L. Slovokhotov, R. N. Lyubovskaya, J. A. K. Howard and D. S. Yufit, *Cryst. Growth Des.*, 2004, **4**, 643–646; (e) A. L. Litvinov, D. V. Konarev, A. Y. Kovalevsky, I. S. Neretin, P. Coppens and R. N. Lyubovskaya, *Cryst. Growth Des.*, 2005, **5**, 1807–1819; (f) H. Kon, K. Tsuge, T. Imamura, Y. Sasaki, S. Ishizaka and N. Kitamura, *Inorg.Chem.,* 2006, **45**, 6875–6883; (g) S. Lipstman and I. Goldberg, *Cryst. Growth Des.*, 2010, **10**, 1823–1832; (h) L. D. DeVries, P. M. Barron, E. P. Hurley, C. Hu and W. Choe *J. Am. Chem. Soc.*, 2011, **133**, 14848–14851; (i) M.-H. Xie, X.-L. Yang, C. Zou and C.-D. Wu, *Inorg. Chem.*, 2011, **50**, 5318–5320.

26 R. De Zorzi, N. Guidolin, L. Randaccio, R. Purrello and S. Geremia, *J. Am. Chem. Soc.*, 2009, **131**, 2487–2489.

27 P. Huo, J.-P. Wang, M.-Y. Shao, Y.-G. Sun, S.-F. Ji, Q.-Y. Zhu and J. Dai, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16229–16235.

28 Z.-P. Lv, B. Chen, H.-Y. Wang, Y. Wu and J.-L. Zuo, *small***,** 2015, **11**, 3597–3605.

29 (a) R. Berridge, P. J. Skabara, C. Pozo-Gonzalo, A. Kanibolotsky, J. Lohr, J. J. W. McDouall, E. J. L. McInnes, J. Wolowska, C. Winder, N. S. Sariciftci, R. W. Harrington and W. Clegg, *J. Phys. Chem. B*, 2006, **110**, 3140–3152; (b) E. Gomar-Nadal, L. Mugica, J. Vidal-Gancedo, J. Casado, J. T. L. Navarrete, J. Veciana, C. Rovira and D. B. Amabilino, *Macromolecules*, 2007, **40**, 7521–7531.

30 K. Kadish, K. Smith and R. Guilard, *The porphyrin handbook*. San Diego: Academic Press; 2000.

31 X. Xiao, W. Xu, D. Zhang, H. Xu, L. Liu and D. Zhu, *New J. Chem.*, 2005, **29**, 1291–1294.

32 (a) Q.-Y. Zhu, L.-B. Huo, Y.-R. Qin, Y.-P. Zhang, Z.-J. Lu, J.-P. Wang and J. Dai, *J. Phys. Chem. B*, 2010, **114**, 361–367; (b) M. Asakawa, P. R. Ashton, V. Balzani, A. Credi, C. Hamers, G. Mattersteig, M. Montalti, A. N. Shipway, N. Spencer, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White and D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 333–337; (c) V. Balzani, A. Credi, G. Mattersteig, O. A. Matthews, F. M. Raymo, J. F. Stoddart, M. Venturi, A. J. P. White and D. J. Williams, *J. Org. Chem.*, 2000, **65**, 1924–1936; (d) M. Asakawa, M. Higuchi, G. Mattersteig, T. Nakamura, A. R. Pease, F. M. Raymo, T. Shimizu and J. F. Stoddart, *Ad*V. *Mater.*, 2000, **12**, 1099–1102; (e) H.-R. Tseng, S. A. Vignon, P. C. Celestre, J. Perkins, J. O. Jeppesen, A. D. Fabio, R. Ballardini, M. T. Gandolfi, M. Venturi, V. Balzani and J. F. Stoddart, *Chem. Eur. J.*, 2004, **10**, 155–172.

33 (a) Y. L. Zhong, A. Midya, Z. Ng, Z.-K. Chen, M. Daenen, M. Nesladek and K. P. Loh, *J. Am. Chem. Soc.*, 2008, **130**, 17218–17219; (b) K.-H. Hyung, J. Noh, W. Lee and S.-H. Han, *J. Phys. Chem. C*, 2008**, 112**, 18178–18182.

34 Y.-D. Huang, P. Huo, M.-Y. Shao, J.-X. Yin, W.-C. Shen, Q.-Y. Zhu and J. Da, *Inorg. Chem.,* 2014, **53**, 3480−3487.