

This article is published as part of a themed issue of ***Photochemical & Photobiological Sciences*** in honour of

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Guest edited by **Cornelia Bohne** and **Tadashi Mori**

Published in [issue 9, 2011](#)

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Supramolecular architecture of tetrathiafulvalene-bridged bis(β -cyclodextrin) with porphyrin and its electron transfer behaviors†‡

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Received 19th July 2010, Accepted 13th September 2010

DOI: 10.1039/c0pp00224k

A bridged bis(β -cyclodextrin) **3** with a tetrathiafulvalene (TTF) linker was synthesized by an electrophilic reaction of mono-6-deoxy-6-iodo- β -cyclodextrin **1** with 6,7-bis(methylsulfanyl)-2,3-bis(2-cyanoethylsulfanyl)tetrathiafulvalene **2** under the alkaline condition. Benefiting from the good solubilizing ability of the β -cyclodextrin unit, the solubility limit of **3** in water could reach 1.0×10^{-3} M, *i.e.* 0.4 mg mL⁻¹ calculated as TTF residue. The conformational changes during the inclusion complexation process of **3** with 5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin **4** were investigated by UV/Vis and 2D NMR spectroscopy. Significantly, the photo-induced electron transfer (PET) process between the TTF moiety in **3** and the porphyrin unit in **4** would take place within the **3/4** supramolecular complex under the light irradiation, leading to the highly efficient quenching of the fluorescence of **4**, and could then be recovered by the formation of TTF cations in the presence of H₂O₂. Furthermore, taking advantage of the high affinity between **3** and **4**, the linear nanoarchitectures were achieved and comprehensively characterized by using transmission electron microscopy (TEM) and atomic force microscopy (AFM). These observations indicated that the strong complexation was a crucial and basic factor to achieve the PET process in the non-covalently constructed assemblies.

Introduction

The construction of supramolecular donor–acceptor systems for photo-induced energy and electron transfer processes has attracted considerable interest in the last few years. Non-covalent interactions, such as hydrogen bonding, aromatic π -stacking, hydrophobic interactions, and labile metal–ligand coordination, have been widely used to construct multi-component photo-active complexes.¹ Moreover, the use of molecular recognition strategy and supramolecular nanotechnology also offers the great promise for the assembly of many structurally sophisticated systems which would not be accessible by the covalent synthetic methodology.² Among the wide variety of organic molecules used to construct the donor–acceptor systems, tetrathiafulvalene (TTF) as an electron-rich moiety is one of the most attractive and promising candidates in the light of the photo-induced intramolecular electron transfer function. As an interesting class of electroactive materials, TTF is a good electron donor forming the charge transfer complexes (or the radical ion salts) with the various electron acceptors, such as pyridine,³ anthracene,⁴ biphenyls,⁵ porphyrin,⁶ phthalocyanine,⁷ C₆₀,⁸ viologen,⁹ carbon nanotubes,¹⁰ and diimide derivatives.¹¹ However, most of the works on the TTF-based donor–acceptor systems were focused on the covalently linked ones in non-aqueous media. The studies on the construction and application of the TTF-based noncovalent

donor–acceptor systems in water phase,¹² especially those in nanometre scale,¹³ are still rare due to the poor water solubility of TTF. On the other hand, cyclodextrins (CDs), a class of cyclic oligosaccharides with 6–8 D-glucose units linked by α -1,4-glucose bonds, are one kind of ideal water-soluble host molecules and well known to encapsulate various organic guests within their cavities and thus widely used in the construction of artificial enzymes, drug delivery systems, and molecular machines.¹⁴ In addition, the good biocompatibility of CDs also enables its applications to mimicking the biological photosynthesis in aqueous solution by means of hydrophobic interactions.¹⁵ Recently, we reported the investigation on the photo-induced electron transfer (PET) between a fullerene-bridged bis(permethyl- β -CD) and porphyrin derivatives in ethanol-aqueous media by the fluorescence decay and nanosecond transient spectroscopy,¹⁶ which showed the efficient fluorescent quenching and charged separation in a non-covalently constructed supramolecular assembly. Herein, we synthesized a non-covalent donor–acceptor dyad composed of a TTF-bridged bis(β -CD) as the donor moiety and a water soluble porphyrin derivative as the acceptor moiety (Scheme 1). Its complexation mode, photo-induced electron transfer behavior in water, and morphological feature were investigated by UV/Vis spectroscopy, fluorescence spectroscopy, cyclic voltammetry, transmission electron microscopy (TEM) and atomic force microscopy (AFM). These studies will help us deeply understand this important, but less investigated, area of supramolecular chemistry.

Results and discussion

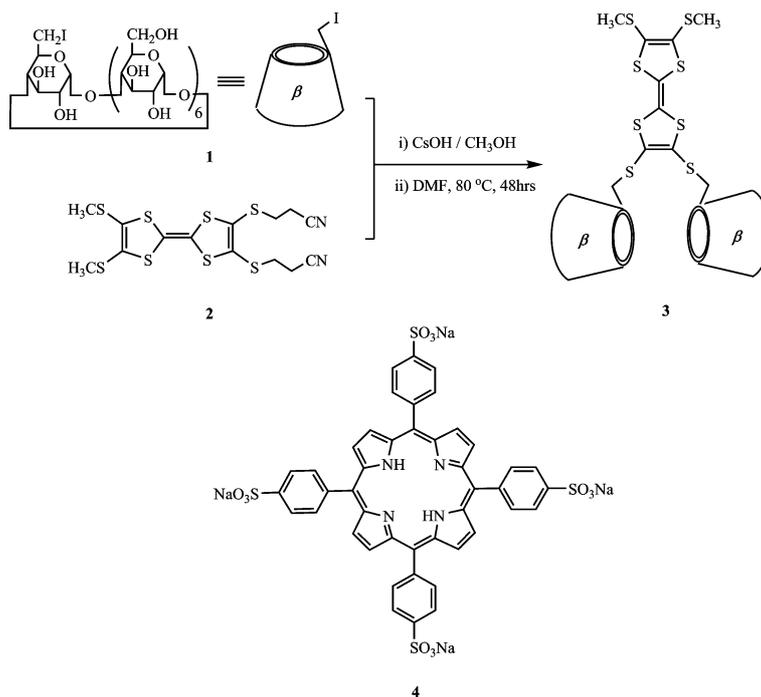
Synthesis and conformation analysis of **3**

Compound **2** was prepared according to the reported procedure,¹⁷ in which the tetrathiafulvalene derivatives were generated from tetraethylammonium bis(2-thioxo-1,3-dithiole-4,5-dithio) zincate

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† This article is published as part of a themed issue in honour of Yoshihisa Inoue's research accomplishments on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Characterization of **3**, 2D NMR spectra of **3** and **3/4** complex, Job's plot of **3/4** system, as well as AFM and TEM images of the linear assembly. See DOI: 10.1039/c0pp00224k



Scheme 1 Molecular structures of 1–4.

salt with iodomethane and the selective protection with 3-bromopropionitrile. Then, **2** reacted with mono-6-deoxy-6-iodo- β -CD¹⁸ **1** under a strong basic condition to yield TTF-bridged bis(β -CD) **3** in 20% yield. Considering the steric hindrance of **1**, the electrophilic reaction was carried out at a higher temperature for 2 days in DMF. Since the caesium salts of the tetrathiafulvalenethiolates are unstable and normally decompose rapidly in air, an atmosphere of N₂ and a gradual heating were necessary to get the target product. Interestingly, it was found that the ¹H NMR signals of the methylsulfanyl groups (–SCH₃) of **3** were split into two peaks at 2.27 and 2.29 ppm (Fig. S1, ESI[†]). The possible reasons of the splitting of –SCH₃ protons could be the partial self-inclusion of the TTF group into the β -CD cavity. To study the original conformation of **3** in aqueous solution, the NOESY experiment was performed in D₂O at 25 °C. In the NOESY spectrum of **3** (Fig. S4, ESI), the NOE correlations between the –SCH₃ protons and the interior protons (H3/H5) of β -CD cavity were clearly observed. These NOE correlations indicated that the TTF moiety was self-included in the β -CD cavity.¹⁹ As discerned in Fig. S5, there was no significant variation of the ¹H-NMR spectra of **3** with its concentration, indicating that the self-inclusion complexation of **3** should be intramolecular.²⁰ Benefiting from the introduction of β -CD unit as the solubilizer, the solubility limit of **3** in water was up to 1.0×10^{-3} M, *i.e.* 0.4 mg mL⁻¹ calculated as TTF residue.

UV/Vis spectroscopy

The UV/Vis spectrum of **3** (Fig. 1, inset) showed a broad absorption band in the range of 220 to 360 nm accompanied by three peaks at 260, 310, and 330 nm assigned to the TTF moiety. This information, along with the NMR, MS, and elemental analysis results, confirmed the incorporation of TTF with the β -CD. As seen in Fig. 1, the titration of UV-Vis spectroscopy

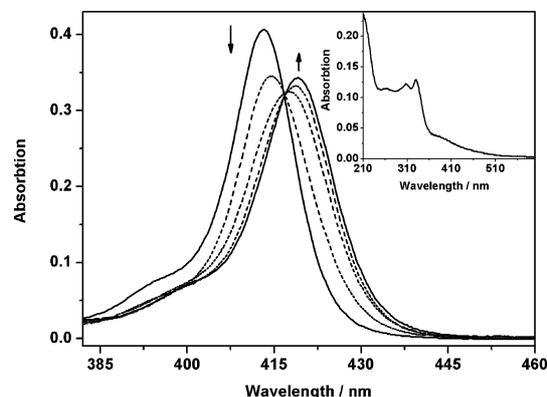


Fig. 1 UV-Vis titration spectra of **4** (1.0×10^{-6} M) upon addition of **3** (0 – 1.0×10^{-5} M) in NaH₂PO₄–Na₂HPO₄ buffer solution (pH 7.2), where a solution of **3** in the same concentration (0 – 1.0×10^{-5} M) was used as a reference. Inset: UV/Vis spectrum of free **3** (1.0×10^{-5} M).

showed that the Soret band intensity of **4** changes gradually by continuous addition of **3**, accompanied by the bathochromic shift of the absorption maximum from 413 nm to 419 nm with an isosbestic point appearing at 417 nm, which jointly indicated the change in the polarity around porphyrin and the simple one-step transformation from the free **3** to the **4**-associated species.²¹

Fluorescence spectroscopy

The quantitative investigation of the inclusion complexation behavior of **3** with **4** was examined by means of the fluorescence spectroscopy titration method. As illustrated in Fig. 2, the fluorescence intensity of **4** gradually decreased *ca.* 93% with the stepwise addition of **3**. Meanwhile, the emission peak of **4** showed a bathochromic shift from 643 nm to 648 nm. In the

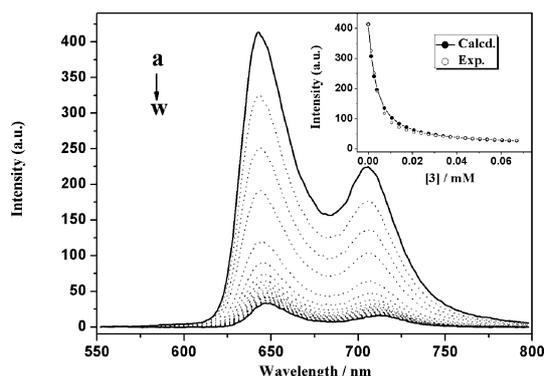


Fig. 2 Fluorescence changes of **4** (1.0×10^{-6} M) upon addition of **3** ($0-6.7 \times 10^{-5}$ M, from a to w) in $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ buffer solution (pH 7.2) at 25°C ($\lambda_{\text{ex}} = 422$ nm). Inset: The nonlinear least squares analysis of the fluorescence intensity (at 643 nm) to calculate the complex stability constant (K_s).

comparative experiment, the fluorescence intensity of porphyrin derivative in the aqueous solution was slightly enhanced with an increasing concentration of native $\beta\text{-CD}$,²² indicating that the quenching process was attributed to PET process between TTF moiety of **3** and **4** included in the $\beta\text{-CD}$ cavity. Furthermore, the Job's plot of the **3/4** system in $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ buffer solution showed a maximum peak at a molar fraction of 0.5, corresponding to a 1:1 **3/4** complex (Fig. S6, ESI[†]). After validating the 1:1 binding stoichiometry, the binding constant (K_s) between **3** and **4** was estimated to be $3.50 \times 10^5 \text{ M}^{-1}$ by analyzing the sequential changes in fluorescence intensity (ΔF) of **4** at varying concentrations of **3** using a nonlinear least-square curve-fitting method (Fig. 2, inset).²³ In the repeated measurements, the K_s values were reproducible within an error of $\pm 5\%$. These observations indicated that **4** had a high affinity with the $\beta\text{-CD}$ cavity of **3**, and there should be an efficient intermolecular photo-induced electron transfer process between the porphyrin unit of **4** and the TTF moiety in **3**.

When a TTF unit, as a strong electron donor, was connected to an electron acceptor moiety, the PET process between TTF and the acceptor group would occur and thus result in the fluorescence quenching. The fluorescence would then be recovered by the electrochemical or chemical oxidation of the TTF moiety. This mechanism has already been employed to construct the redox-fluorescence switches.^{4,6,24} For instance, Stoddart *et al.* reported a redox-switchable $\alpha\text{-cyclodextrin}$ -based [2]rotaxanes using spectroscopic probe in 30% $\text{D}_2\text{O}_2/\text{D}_2\text{O}$ solution.²⁵ In our case, the hydrogen peroxide (H_2O_2) was chosen as a substitute for other inorganic oxidants, such as Fe^{3+} and Hg^{2+} , to eliminate the influence of metal ion on the porphyrin core and to achieve the fluorescence recovery experiment successfully.²⁶ As seen in Fig. 3, the fluorescence intensity of **3/4/H}_2\text{O}_2 system obviously increased compared to that of the free **4** after 24 h, while the fluorescence of both **4/H}_2\text{O}_2 and **3/4** system quenched under the same conditions. In this case, the enhancement of emission intensity in **3/4/H}_2\text{O}_2 system was attributed to the hydrophobic nature of CD cavity and the changes in the solvent-solute dipole interactions to decrease the collisional quenching and reduce the exposure of free porphyrins to aqueous media when **4** was included into the cavity of **3**.²² This phenomenon indicated that the PET******

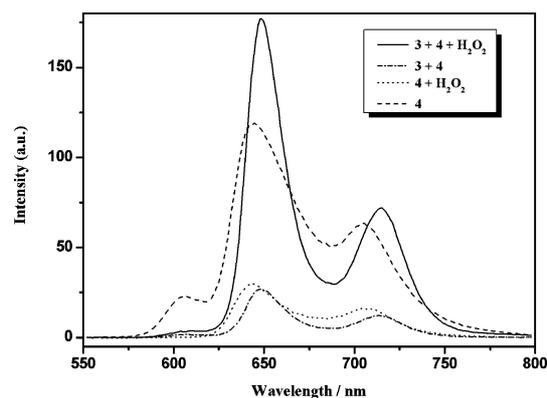
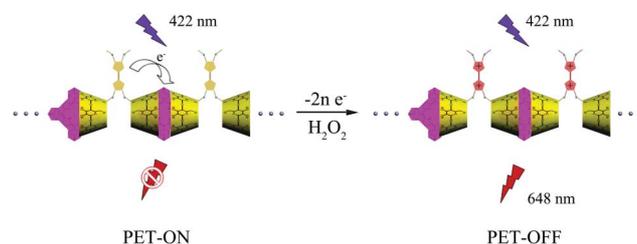


Fig. 3 Fluorescence recovery of **3/4/H}_2\text{O}_2 system in $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ buffer solution (pH 7.2) after 24 h. $[\mathbf{3}] = 2.4 \times 10^{-5}$ M, $[\mathbf{4}] = 1.0 \times 10^{-6}$ M, $[\text{H}_2\text{O}_2] = 2.0 \times 10^{-3}$ M. ($\lambda_{\text{ex}} = 422$ nm).**

process from the TTF moiety of **3** to the porphyrin unit of **4** could be inhibited to some extent through the formation of TTF cations in the presence of H_2O_2 , because the electron-donating ability of the cationic TTF unit was much lower than that of the neutral one and, as a result, the corresponding PET process would become less favorable (Scheme 2).



Scheme 2 Schematic representation of the fluorescence recovery process via supramolecular complexes formed by **3** and **4** in the presence of H_2O_2 .

Electrochemical studies

To shed more light on the PET process between TTF and porphyrin units, the electrochemical behaviors of **3**, **4**, and **3/4** complex were investigated in aqueous solution with NaCl as the supporting electrolyte.^{16,27} The cyclic voltammetry (CV) experiment was performed with a wide potential window in order to obtain a thorough characterization of the redox process. It has been well-known that TTF derivatives can undergo two successive reversible one-electron redox to the TTF^{2+} and TTF^{+} species, respectively. In our case, however, the reversibility was less favorable mainly due to the aqueous media and the steric hindrance of CDs. As shown in Fig. 4, the CV curve of **3** showed two oxidation and only one reduction peaks at 645, 886, and 490 mV, respectively, and the CV curve of **4** displayed one clear oxidation peak at 1013 mV. Interestingly, in comparison to **3** and **4**, the CV curve of the **3/4** complex displayed three oxidation peaks at 601, 720, and 1087 mV, and one reduction peak at 541 mV. These observations should be reasonable, because the association of CD cavity with **4** enabled both the close location and the consequent strong electronic communication between the donor (TTF unit) and the acceptor (porphyrin unit). As a result, the electron transfer from the TTF unit to the porphyrin moiety

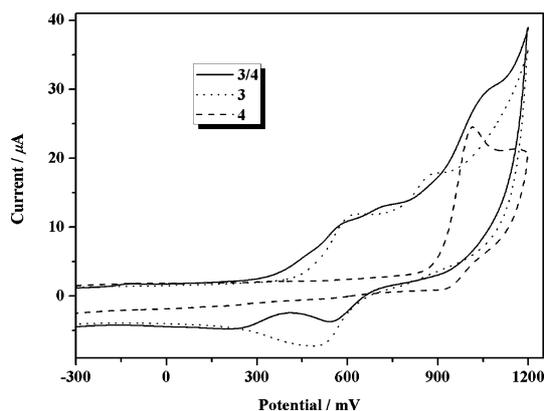


Fig. 4 Cyclic voltammetric spectra of **3** (1×10^{-3} M), **4** (1×10^{-3} M), and **3/4** system ($[3] = [4] = 1 \times 10^{-3}$ M) in aqueous solution at 200 mV s^{-1} containing 0.1 M NaCl as the supporting electrolyte.

decreased the electron density of TTF. Furthermore, Rehm–Weller eqn (1) was introduced to estimate the Gibbs free energy ΔG_{PET} of an electron-transfer reaction between **3** and **4**.

$$\Delta G_{\text{PET}} = E_{\text{ox}} - E_{\text{red}} - E_{00} - e^2/\epsilon d \quad (1)$$

where E_{00} is the excited singlet energy of **4**, which could be calculated from the maximum emission wavelength of **4** (643 nm, 1.93 eV), e is the electron charge in Coulomb, d is the distance between the electron donor and the acceptor, and ϵ is the dielectric constant of the buffer solution. Considering that the ϵ value of water was a large value and that of e^2 was small, the last term in eqn (1) could be neglected in the estimation. The E_{ox} and E_{red} values were the oxidation potentials of **3** and the reduction potentials of **4**²⁸ ($E_{\text{ox},3} = 0.65 \text{ V}$, $E_{\text{red},4} = -1.06 \text{ V}$). Therefore, ΔG_{PET} could be calculated as $\Delta G_{\text{PET},3 \cdot 4} = -0.22 \text{ eV}$. The negative ΔG_{PET} value indicated that the PET process could occur in a thermodynamically favorable way. It should be noted that because the electrochemical data were non-reversible, there would be errors in the calculation of free energy changes.

TEM and AFM images

The ROESY spectrum of a stoichiometric 1 : 1 mixture of **3** and **4** in D_2O (Fig. S7, ESI[†]) exhibited the obvious NOE cross-peaks between the H3 protons of the β -CD cavity in **3** with those of the pyrrole and phenyl moieties in **4**, which clearly indicated that the pyrrole and phenyl groups of **4** were located near the secondary side of β -CD cavity. On the other hand, no obvious NOE correlations between the protons of $-\text{SCH}_3$ and the interior

protons of β -CD cavity could be found in the 2D NMR spectrum of **3/4** complex, indicating that the self-included substituent of **3** was excluded from the β -CD cavity after the association with **4**. This conformational change of **3** upon associating with **4** was favorable to the formation of a linear supramolecular assembly. Transmission electron microscopy (TEM) and atomic force microscope (AFM) experiments gave the direct information about the shape and size of the nanoarchitecture. The TEM image of the **3/4** system displayed several 1D linear morphology consisted of fiberlike nanowires with a same width of 2.0 nm (Fig. 5a and Fig. S8a[†]). Additionally, the AFM images examined at a fairly dilute concentration displayed a fine structure of the **3/4** system as an ordered single-lined array (Fig. 5b and Fig. S8b). Cross-section analysis showed that the measured average height of the linear structure was around 2.2 nm, which was basically consistent with the outer diameter of β -CD cavity (1.6 nm),²⁹ and the length of the linear structure was around $1.0 \mu\text{m}$. However, there was no evidence to support the PET process in the 1D linear aggregation.

Conclusion

A novel tetrathiafulvalene-bridged bis(β -CD) **3** was synthesized by an electrophilic reaction and fully characterized. The introduction of the CD unit efficiently increased the water solubility of the TTF group. As a result of the PET process between the TTF and porphyrin moieties, the fluorescence of **4** dramatically quenched with the addition of **3**, but could be recovered in the presence of H_2O_2 through the oxidation of TTF moiety to the corresponding cations. Furthermore, benefiting from the strong complexation between the host and the guest, a linear nanoarchitecture was constructed and its morphology was fully characterized. These findings suggest that the supramolecular approach clearly offers the immense scope for the assembly of high-nuclearity, multi-component complexes and enables us to rationally construct and develop the nanoscale systems with the controlled photoactive functions.

Experimental

Materials

All the chemicals were used as reagent grade unless noted. DMF was stirring in CaH_2 for three days and then distilled under reduced pressure prior to use. Native β -CD was recrystallized twice from water and dried *in vacuo* at $90 \text{ }^\circ\text{C}$

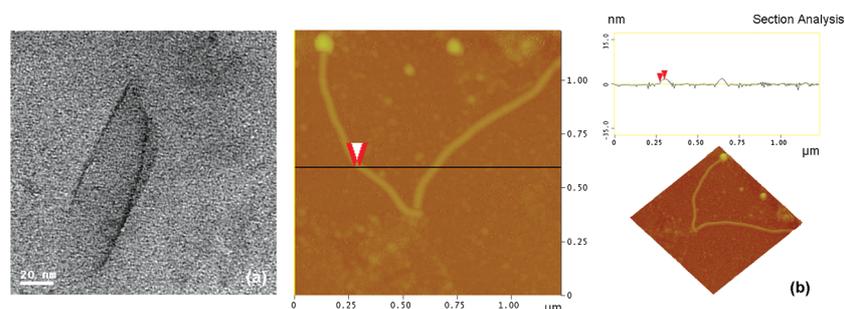


Fig. 5 Typical TEM (a) and AFM (b) images of the linear assembly formed by **3** and **4**.

for 24 h. 2,3-Bis(2-cyanoethylsulfanyl)-6,7-bis(methylsulfanyl)-tetrathiafulvalene was prepared according to the reported procedures.¹⁷ 5,10,15,20-Tetrakis(4-sulfonatophenyl)-porphyrin **4** was purchased from commercial resource and used as received.

Measurements

The water solubility of tetrathiafulvalene-bridged bis(β -cyclodextrin) **3** was assessed by the preparation of its saturated solution.³⁰ Excess amount of **3** was dispersed in 1 mL of deionized water and the resultant yellow suspension was further sonicated for 1 h. Insoluble precipitates were removed by filtration, and the filtrates were evaporated *in vacuo* to dryness and the residue was dosed by weighing method. UV-Vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a Shimadzu UV-2401PC spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C. The determination of K_s value and the fluorescence recovery experiments were recorded in a conventional quartz cell (10 mm \times 10 mm \times 45 mm) at 25 °C on VARIAN CARY Eclipse with the excitation and emission slits of 5 nm width. NMR spectra were recorded on Varian Mercury Plus 400 instrument. Elemental analyses were performed on a Perkin-Elmer-2400C instrument. The cyclic voltammetry (CV) measurements were carried out on a BAS Epsilon electrochemical analyzer with C3 cell stand. At the beginning of the electrochemistry experiment, the aqueous solution was deoxygenated by purging with dry nitrogen for at least 15 min. All the solutions were prepared in deionized water at 298 K containing 0.1 M NaCl as a supporting electrolyte. The glassy carbon working electrode was polished with 0.05 μ m BAS alumina suspension on a brown Texmet polishing pad, sonicated in distilled water for a few minutes to remove any residual alumina particles and then rinsed with ethanol before use. A platinum wire was used as the counter electrode. The measured potentials were recorded with respect to an Ag/AgCl (immersed in a solution containing 3 M sodium chloride) reference electrode. Transmission electron microscopy (TEM) experiments were performed using a Philips Tacnai G² 20 S-TWIN microscope operating at 200 kV. TEM samples (1.0×10^{-6} M) were prepared by depositing a drop of the suspension onto a holey carbon grid or by placing a drop of the solution onto a carbon coated copper grid. For AFM measurements, a drop of sample solution (1.0×10^{-6} M) was dropped onto newly clipped mica and then air-dried. The samples were examined using an AFM (Veeco Company, Multimode, Nano IIIa) in tapping mode in the air at room temperature.

Synthesis

2,3-Bis(6-deoxy- β -cyclodextrin-6-yl)-6,7-bis(methylsulfanyl)-tetrathiafulvalene (3). 2,3-Bis(2-cyanoethylsulfanyl)-6,7-bis(methylsulfanyl)tetrathiafulvalene¹⁷ (0.5 mmol, 233 mg) was dissolved in dry DMF (15 mL) and degassed with N₂ for 30 min. A solution of caesium hydroxide monohydrate (1.3 mmol, 218 mg) in dry methanol (6 mL) was added dropwise to the mixture, and the colour of the solution became darker. After stirring for an additional 20 min, mono-6-deoxy-6-iodo- β -CD¹⁸ (2 mmol, 2.49 g) dissolved in DMF (10 mL) was added dropwise to the solution mentioned above. The mixture was stirring at room temperature for about 2 h and then heated at 80 °C for 2 days. After cooling

to room temperature, the stirring was kept overnight, and the brown–yellow solution was concentrated *in vacuo*. The residue was dissolved in a small amount of water, and washed with 300 mL of acetone for at least three times. The crude product was subjected to a medium-pressure liquid chromatography (MPLC) system (Yamazen Co. Japan) using a gradient elution system of distilled water and ethanol gradient with ethanol from 5 to 20% ethanol at a flow rate of 10 mL min⁻¹. The detector wavelength was set at 300 nm. After drying under vacuum, the target compound was obtained as a yellow solid in 20% yield (260 mg, 0.1 mmol). ¹H NMR (400 MHz, D₂O, ppm) δ 2.27–2.29 (m, 6H, –SCH₃ of TTF), 3.08–4.09 (m, 84H, H of C-3, C-5, C-6, C-2, C-4 of β -CD), 4.75–5.06 (m, 14H, H of C-1 of β -CD). ¹³C NMR (100 MHz, DMSO-d₆, ppm): δ 18.5, 37.3, 56.0, 59.9, 60.2, 69.6, 72.0, 72.2, 72.3, 72.6, 72.7, 73.0, 80.9, 81.4, 81.5, 84.1, 101.6, 101.9, 102.4, 107.3, 109.7, 110.8, 114.6, 126.1, 126.8. Anal. calcd for C₉₂H₁₄₄O₆₈S₈·25H₂O: C, 36.29; H, 6.42; found: C, 36.12; H, 6.48. MS (MALDI-TOF): *m/z* 2592.714 (M⁺). λ_{\max} (lge, H₂O) 331 (4.14), 308 (4.12), and 262 nm (4.11).

Acknowledgements

We thank the 973 program (2006CB932900) and National Natural Science Foundation of China (20932004, 20721062 and 20772062), and Tianjin Natural Science Foundation (07QTPTJC29600) for financial support.

References

- 1 M. D. Ward, Photo-induced Electron and Energy Transfer in Non-covalently Bonded Supramolecular Assemblies, *Chem. Soc. Rev.*, 1997, **26**, 365–375; P. Piotrowiak, Photoinduced Electron Transfer in Molecular Systems: Recent Developments, *Chem. Soc. Rev.*, 1999, **28**, 143–150.
- 2 L. Sánchez, N. Martín and D. M. Guldi, Hydrogen-Bonding Motifs in Fullerene Chemistry, *Angew. Chem., Int. Ed.*, 2005, **44**, 5374–5382; D.-S. Guo, K. Chen, H.-Q. Zhang and Y. Liu, Nano-Supramolecular Assemblies Constructed from Water-soluble Bis(calix[5]arenes) with Porphyrins and Their Photoinduced Electron Transfer Properties, *Chem.–Asian J.*, 2009, **4**, 436–445.
- 3 Y.-P. Zhao, L.-Z. Wu, G. Si, Y. Liu, H. Xue, L.-P. Zhang and C.-H. Tung, Synthesis, Spectroscopic, Electrochemical and Pb²⁺-Binding Studies of Tetrathiafulvalene Acetylene Derivatives, *J. Org. Chem.*, 2007, **72**, 3632–3639.
- 4 G. Zhang, D. Zhang, X. Guo, D. Zhu and A. New, Redox-Fluorescence Switch Based on a Triad with Tetrathiafulvalene and Anthracene Units, *Org. Lett.*, 2004, **6**, 1209–1212.
- 5 G. Delogu, D. Fabbri, M. A. Dettori, M. Sallé, F. Le Derf, M. J. Blesa and M. Allain, Electroactive C₂ Symmetry Receptors Based on the Biphenyl Scaffold and Tetrathiafulvalene Units, *J. Org. Chem.*, 2006, **71**, 9096–9103.
- 6 H. Li, J. O. Jeppesen, E. Levillain and J. Becher, A Mono-TTF-annulated Porphyrin as a Fluorescence Switch, *Chem. Commun.*, 2003, 846–847.
- 7 C. A. Donder, S. X. Liu, C. Loosli, L. Sanguinet, A. Neels and S. Decurtins, Synthesis of Tetrathiafulvalene-annulated Phthalocyanines, *Tetrahedron*, 2006, **62**, 3543–3549; C. Loosli, C. Jia, S.-X. Liu, M. Haas, M. Dias, E. Levillain, A. Neels, G. Labat, A. Hauser and S. Decurtins, Synthesis and Electrochemical and Photophysical Studies of Tetrathiafulvalene-Annulated Phthalocyanines, *J. Org. Chem.*, 2005, **70**, 4988–4992.
- 8 M. M. Alam, A. Watanabe and O. Ito, Efficient Photoinduced Electron Transfer between C₆₀ and Tetrathiafulvalenes Studied by Nanosecond Laser Photolysis, *J. Photochem. Photobiol., A*, 1997, **104**, 59–64; J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell and C. Rovira, The First Diels–Alder Adduct of [60]Fullerene with a Tetrathiafulvalene, *Chem. Commun.*, 1997, 659–660; C. Boule, J.

- M. Rabreau, P. Hudhomme, M. Cariou, M. Jubault, A. Gorgues, J. Orduna and J. Garin, The *Bis*-linking of Tetrathiafulvalene (TTF) to C_{60} : Towards the Control of Electron Transfer Between π -Donors and C_{60} , *Tetrahedron Lett.*, 1997, **38**, 3909–3910; J. Baffreau, F. Dumur and P. Hudhomme, New Versatile Building Block for the Construction of Tetrathiafulvalene-Based Donor–Acceptor Systems, *Org. Lett.*, 2006, **8**, 1307–1310; N. Martín, L. Sánchez, M. Á. Herranz, B. Illescas and D. M. Guldi, Electronic Communication in Tetrathiafulvalene (TTF)/ C_{60} Systems: Toward Molecular Solar Energy Conversion Materials?, *Acc. Chem. Res.*, 2007, **40**, 1015–1024.
- 9 M. B. Nielsen, C. Lomholt and J. Becher, Tetrathiafulvalenes as Building Blocks in Supramolecular Chemistry II, *Chem. Soc. Rev.*, 2000, **29**, 153–164.
- 10 M. Á. Herranz, N. Martín, S. Campidelli, M. Prato, G. Brehm and D. M. Guldi, Control over Electron Transfer in Tetrathiafulvalene-Modified Single-Walled Carbon Nanotubes, *Angew. Chem., Int. Ed.*, 2006, **45**, 4478–4482.
- 11 X. Guo, Z. Gan, H. Luo, Y. Araki, D. Zhang, D. Zhu and O. Ito, Photoinduced Electron-Transfer Processes of Tetrathiafulvalene-(Spacer)-(Naphthalenediimide)-(Spacer)-Tetrathiafulvalene Triads in Solution, *J. Phys. Chem. A*, 2003, **107**, 9747–9753.
- 12 G. Cooke, P. Woisel, F. Delattre, M. Bria, J. F. Garety, S. G. Hewage and G. Rabani, An Electrochemically Tuneable Cyclodextrin-Based Molecular Adapter, *Tetrahedron Lett.*, 2006, **47**, 6449–6452; M. Bria, G. Cooke, A. Cooper, F. Delattre, S. G. Hewage, G. Rabani, M. Nutleyb and P. Woisel, An Investigation of the Complexation of a TTF Derivative with α -, β - and γ -Cyclodextrins in Aqueous Media, *Tetrahedron Lett.*, 2007, **48**, 8430–8433; I. Hwang, A. Y. Ziganshina, Y. H. Ko, G. Yun and K. Kim, A New Three-way Supramolecular Switch Based on Redox-controlled Interconversion of Hetero- and Homo-Guest-Pair Inclusion inside a Host Molecule, *Chem. Commun.*, 2009, 416–418.
- 13 T. D. Nguyen, Y. Liu, S. Saha, K. C.-F. Leung, J. F. Stoddart and J. I. Zink, Design and Optimization of Molecular Nanovalves Based on Redox-Switchable Bistable Rotaxanes, *J. Am. Chem. Soc.*, 2007, **129**, 626–634; G. Fernández, E. M. Pérez, L. Sánchez and N. Martín, Self-Organization of Electroactive Materials: A Head-to-Tail Donor–Acceptor Supramolecular Polymer, *Angew. Chem., Int. Ed.*, 2008, **47**, 1094–1097; G. Fernández, E. M. Pérez, L. Sánchez and N. Martín, An Electroactive Dynamically Polydisperse Supramolecular Dendrimer, *J. Am. Chem. Soc.*, 2008, **130**, 2410–2411; E. M. Pérez, B. M. Illescas, M. Á. Herranza and N. Martín, Supramolecular Chemistry of π -Extended Analogues of TTF and Carbon Nanostructures, *New J. Chem.*, 2009, **33**, 228–234.
- 14 M. E. Brewster and T. Loftsson, Cyclodextrins as Pharmaceutical Solubilizers, *Adv. Drug Delivery Rev.*, 2007, **59**, 645–666; Y. Chen and Y. Liu, Cyclodextrin-Based Bioactive Supramolecular Assemblies, *Chem. Soc. Rev.*, 2010, **39**, 495–505.
- 15 Y.-H. Wang, H.-M. Zhang, L. Liu, Z.-X. Liang, Q.-X. Guo, C.-H. Tung, Y. Inoue and Y.-C. Liu, Photoinduced Electron Transfer in a Supramolecular Species Building of Mono-6-*p*-nitrobenzoyl- β -cyclodextrin with Naphthalene Derivatives, *J. Org. Chem.*, 2002, **67**, 2429–2434; Q.-H. Wu, M.-Z. Zhu, S.-J. Wei, K.-S. Song, L. Liu and Q.-X. Guo, Photoinduced Electron Transfer in Host–Guest Complexes of α - and β -Substituted Naphthalene Derivatives with Mono-6-*O*-m-Nitrobenzoyl- β -Cyclodextrin, *J. Inclusion Phenom. Macrocyclic Chem.*, 2005, **52**, 93–100; B. Balan and K. R. Gopidas, Photoinduced Electron Transfer in α -Cyclodextrin-Based Supramolecular Dyads: A Free-Energy-Dependence Study, *Chem.–Eur. J.*, 2006, **12**, 6701–6710; J. A. Faiz, R. M. Williams, M. J. J. Pereira Silva, L. De Cola and Z. Pikramenou, A Unidirectional Energy Transfer Cascade Process in a Ruthenium Junction Self-Assembled by α - and β -Cyclodextrins, *J. Am. Chem. Soc.*, 2006, **128**, 4520–4521; B. Balan and K. R. Gopidas, An Anthracene-Appended β -Cyclodextrin-Based Dyad: Study of Self-Assembly and Photoinduced Electron-Transfer Processes, *Chem.–Eur. J.*, 2007, **13**, 5173–5185; J. A. Faiz, L. E. P. Kyllonen, P. Contreras-Carballada, R. M. Williams, L. De Cola and Z. Pikramenou, Photoinduced Energy Transfer across Non-covalent Bonds in the Nanoscale: Cyclodextrin Hosts with Enhanced Luminescent Properties for Guest Communication, *Dalton Trans.*, 2009, 3980–3987.
- 16 Y.-M. Zhang, Y. Chen, Y. Yang, P. Liu and Y. Liu, Supramolecular Architecture by Fullerene-Bridged Bis(permethyl- β -cyclodextrin)s with Porphyrins, *Chem.–Eur. J.*, 2009, **15**, 11333–11340.
- 17 N. Svenstrup, K. M. Rasmussen, T. K. Hansen and J. Becher, The Chemistry of TTF-TTF; 1: New Efficient Synthesis and Reactions of Tetrathiafulvalene-2,3,6,7-tetrathiolate (TTF-TTF): An Important Building Block in TTF-Syntheses, *Synthesis*, 1994, 809–812.
- 18 R. P. Bonomo, V. Cucinatta, F. D’Alessandro, G. Impellizzeri, G. Maccarrone, G. Vecchio and E. Rizzarelli, Conformational Features and Coordination Properties of Functionalized Cyclodextrins. Formation, Stability, and Structure of Proton and Copper(II) Complexes of Histamine-bearing β -Cyclodextrin in Aqueous Solution, *Inorg. Chem.*, 1991, **30**, 2708–2713.
- 19 Y. Liu, Z. Fan, H.-Y. Zhang, Y.-W. Yang, F. Ding, S.-X. Liu, X. Wu, T. Wada and Y. Inoue, Supramolecular Self-Assemblies of β -Cyclodextrins with Aromatic Tethers: Factors Governing the Helical Columnar versus Linear Channel Superstructures, *J. Org. Chem.*, 2003, **68**, 8345–8352.
- 20 J. W. Park, S. Y. Lee, H. J. Song and K. K. Park, Self-Inclusion Behavior and Circular Dichroism of Aliphatic Chain-Linked α -Cyclodextrin-Viologen Compounds and Their Reduced Forms Depending on the Side of Modification, *J. Org. Chem.*, 2005, **70**, 9505–9513.
- 21 K. Kano, R. Nishiyabu, T. Asada and Y. Kuroda, Static and Dynamic Behavior of 2:1 Inclusion Complexes of Cyclodextrins and Charged Porphyrins in Aqueous Organic Media, *J. Am. Chem. Soc.*, 2002, **124**, 9937–9944; W. Deng, T. Onji, H. Yamaguchi, N. Ikeda and A. Harada, Competitive Photoinduced Electron Transfer by the Complex Formation of Porphyrin with Cyclodextrin Bearing Viologen, *Chem. Commun.*, 2006, 4212–4214.
- 22 S. Hamai and T. Ohshida, Inclusion Complexes of Cyclodextrins with Tetrakis(4-carboxyphenyl)porphyrin and Tetrakis(4-sulfonatophenyl)porphyrin in Aqueous Solutions, *J. Inclusion Phenom. Macrocyclic Chem.*, 2004, **50**, 209–217.
- 23 Y. Liu and Y. Chen, Cooperative Binding and Multiple Recognition by Bridged Bis(β -cyclodextrin)s with Functional Linkers, *Acc. Chem. Res.*, 2006, **39**, 681–691.
- 24 X. Xiao, W. Xu, D. Zhang, H. Xu, L. Liu and D. Zhu, Novel Redox-fluorescence Switch Based on a Triad Containing Tetrathiafulvalene and Pyrene Units with Tunable Monomer and Excimer Emissions, *New J. Chem.*, 2005, **29**, 1291–1294; D. Canevet, M. Sallé, G. Zhang, D. Zhang and D. Zhu, Tetrathiafulvalene (TTF) Derivatives: Key Building-blocks for Switchable Processes, *Chem. Commun.*, 2009, 2245–2269.
- 25 Y.-L. Zhao, W. R. Dichtel, A. Trabolsi, S. Saha, I. Aprahamian and J. F. Stoddart, A Redox-Switchable α -Cyclodextrin-Based [2]Rotaxane, *J. Am. Chem. Soc.*, 2008, **130**, 11294–11296.
- 26 G. Zhang, X. Li, H. Ma, D. Zhang, J. Li and D. Zhu, A Selective and Sensitive Chemiluminescence Reaction of 4,4′(5′)-Bis[2-(9-anthryloxy)ethylthio]-tetrathiafulvalene with Singlet Oxygen, *Chem. Commun.*, 2004, 2072–2073.
- 27 P. Liang, H.-Y. Zhang, Z.-L. Yu and Y. Liu, Solvent-Controlled Photoinduced Electron Transfer between Porphyrin and Carbon Nanotubes, *J. Org. Chem.*, 2008, **73**, 2163–2168.
- 28 K. Kalyanasundaram and M. Neumann-Spallart, Photophysical and Redox Properties of Water-soluble Porphyrins in Aqueous Media, *J. Phys. Chem.*, 1982, **86**, 5163–5169.
- 29 Y. Liu, P. Liang, Y. Chen, Y.-M. Zhang, J.-Y. Zheng and H. Yue, Interlocked Bis(polyrotaxane) of Cyclodextrin-Porphyrin Systems Mediated by Fullerenes, *Macromolecules*, 2005, **38**, 9095–9099.
- 30 P. Montassier, D. Duchêne and M.-C. Poelman, Inclusion Complex of Tretinoin with Cyclodextrins, *Int. J. Pharm.*, 1997, **153**, 199–209; Y. Liu, G.-S. Chen, Y. Chen and J. Lin, Inclusion Complexes of Azadirachtin with Native and Methylated Cyclodextrins: Solubilization and Binding Ability, *Bioorg. Med. Chem.*, 2005, **13**, 4037–4042.