PAPER www.rsc.org/njc | New Journal of Chemistry

Synthesis and properties of a tetrathiafulvalene–perylene tetracarboxylic diimide–tetrathiafulvalene dyad

Yu Zhang,[a] Liang-Zhen Cai,[b] Cheng-Yun Wang,*[a] Guo-Qiao Lai[c] and Yong-Jia Shen*[a]

Received (in Durham, UK) 3rd January 2008, Accepted 18th April 2008
First published as an Advance Article on the web 4th June 2008
DOI: 10.1039/b719844b

A donor–acceptor–donor dyad **4** involving 2-sulfur-3-methylthio-6,7-bis(hexylthio)-tetrathiafulvalene (TTF) as a donor attached directly to *N*,*N*′-dibutylperylene-3,4,9,10-tetracarboxylic diimide (PDI) as an acceptor was synthesized by condensation of *N*,*N*′-dibutyl-1,6-dibromo-3,4,9,10-perylenetetracarboxylic diimide and 2-(2-cyanoethylthio-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene. The cyclic voltammetric (CV) data implied significant intramolecular interaction and the absorption spectrum indicated that there was an intramolecular charge transfer (ICT) interaction between TTF and PDI moieties in dyad **4**. Comparing with PDI **13**, the fluorescence emission intensity of dyad **4** was quenched almost quantitatively, which might result from the photo-induced electron transfer (PET) interaction between the PDI and TTF moieties in dyad **4**. The fluorescence intensity of dyad **4** could be reversibly modulated by sequential oxidation and reduction of the TTF unit using chemical methods. Thus dyad **4** can be regarded as a new reversible fluorescence-redox dependent molecular switch.

Introduction

Tetrathiafulvalene (TTF) **1** is well known as a good π-electron donor in the field of organic metals and its numerous derivatives have been widely used as a building block of organic conductors and superconductors.[1] The applications of TTF and its derivatives in materials science have been widely searched, such as molecular shuttles,[2] and chemical sensors.[3] In particular, donor–acceptor (D–A) molecular systems based on TTF and its derivatives are one focus of such intensive investigations,[4] such as TTF–anthrancene,[5] TTF–phthalocyanine,[6] TTF–porphyrin,[7] TTF–perylene-3,4,9,10-tetracarboxylic diimide,[8] TTF–ethynylbipyridine[9] and TTF–dipyridophenazine.[10]

Fine-tuning of the HOMO–LUMO gap for these molecular systems was another concern during the designing process with the aim to construct molecular electronic devices.[8a,11] Most of these molecular systems were designed according to the D–σ-A model in order to realize the charge, energy or electron transfer processes between TTF and acceptor counterparts. Within this typical model, the charge transfer processes from donor to acceptor passed through spacer to form a stable D–σ-A system. The direct connection of donor and acceptor is an important method to obtain a D–A system, in which the charge transfer process was caused by the overlap of the electron orbitals of D and A. For the TTF–PDI dyads reported, TTF and PDI units were all linked by the flexible spacers in the "imide" region to construct dyad **2** (donor–σ-acceptor)[8a,b] or triad **3** (donor–σ-acceptor–σ-donor)[8c] rather than connecting the TTF and PDI units in the "bay" region to gain a donor–acceptor–donor dyad **4** (Scheme 1).

Becher and co-workers[12] have reported a straightforward approach to synthesize the thioalkyl TTF derivatives. Dithione **5** was treated as a key material, and an appropriate electrophile (usually halide) as the realkylation reagent to form the expected TTF derivatives. However, aromatic halides have never been reported as realkylation reagents because of their weak electrophile reactivity. We were very interested in using the aromatic halides as new electrophiles to synthesize dyads consisting of both TTF and perylene moieties. Herein we report the synthesis (Scheme 2), spectroscopic and electrochemical properties of dyad **4**.

Results and discussion

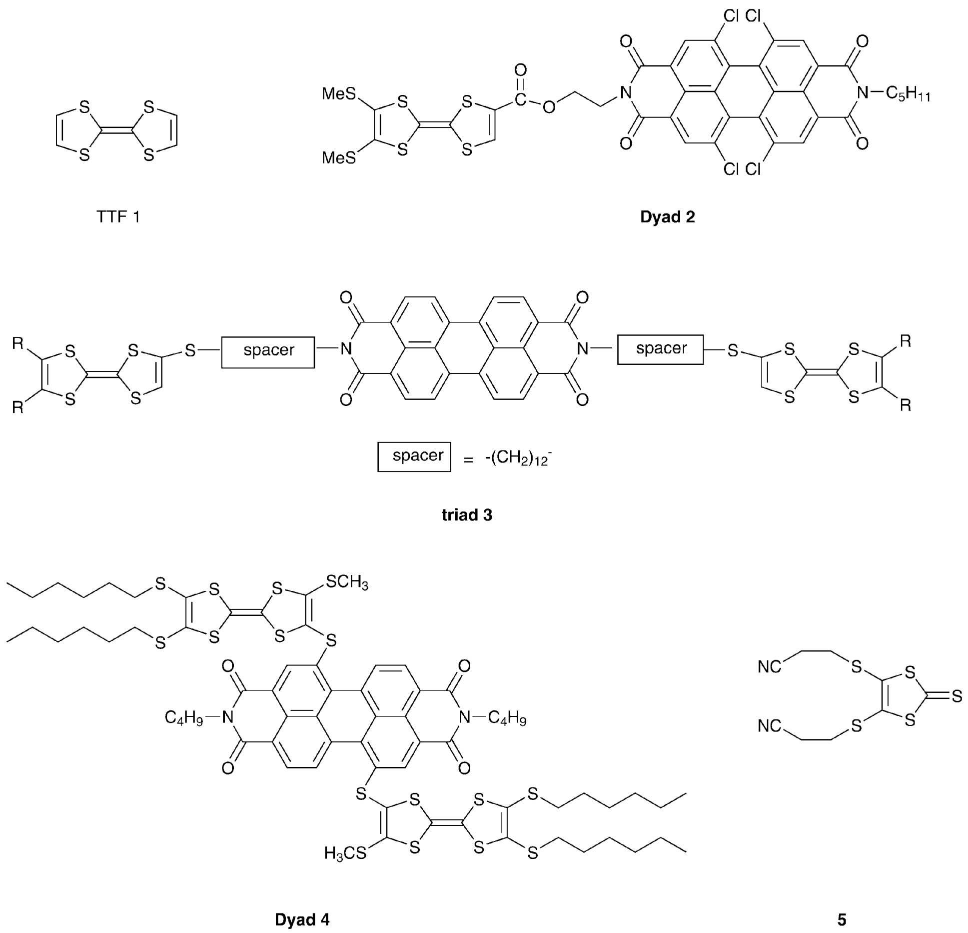
Cyclic voltammetry (CV)

Cyclic voltammetry (Fig. 1, Table 1) of dyad **4** showed two one-electron reversible reduction waves at $E_{\mathrm{red1}} = -0.50$ V and $E_{\mathrm{red2}} = -0.63$ V, respectively, due to the successive formation of the radical anion TTF–PDI$^{\bullet-}$–TTF and dianion TTF–PDI^{2-}–TTF. They are both anodically shifted as compared to the first and second reduction waves of the model PDI **13**, indicating that the LUMO orbital of dyad **4** was located at lower energy than the LUMO orbital of **13**.

Two clear and reversible two-electron TTF oxidation waves were shown in the positive direction, at $E_{\mathrm{ox1}} = 0.70$ V and $E_{\mathrm{ox2}} = 1.01$ V, respectively, corresponding to the radical

---

[a] *Labs for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, 200237, P. R. China. E-mail: yjshen@ecust.edu.cn; cywang@ecust.edu.cn; Fax: +86 21 64252967; Tel: +86 21 64252967*
[b] *Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, P. R. China*
[c] *Key Lab of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou, 310012, P. R. China*



Scheme 1 The structures of TTF **1**, dyads **2–4** and dithione **5**.

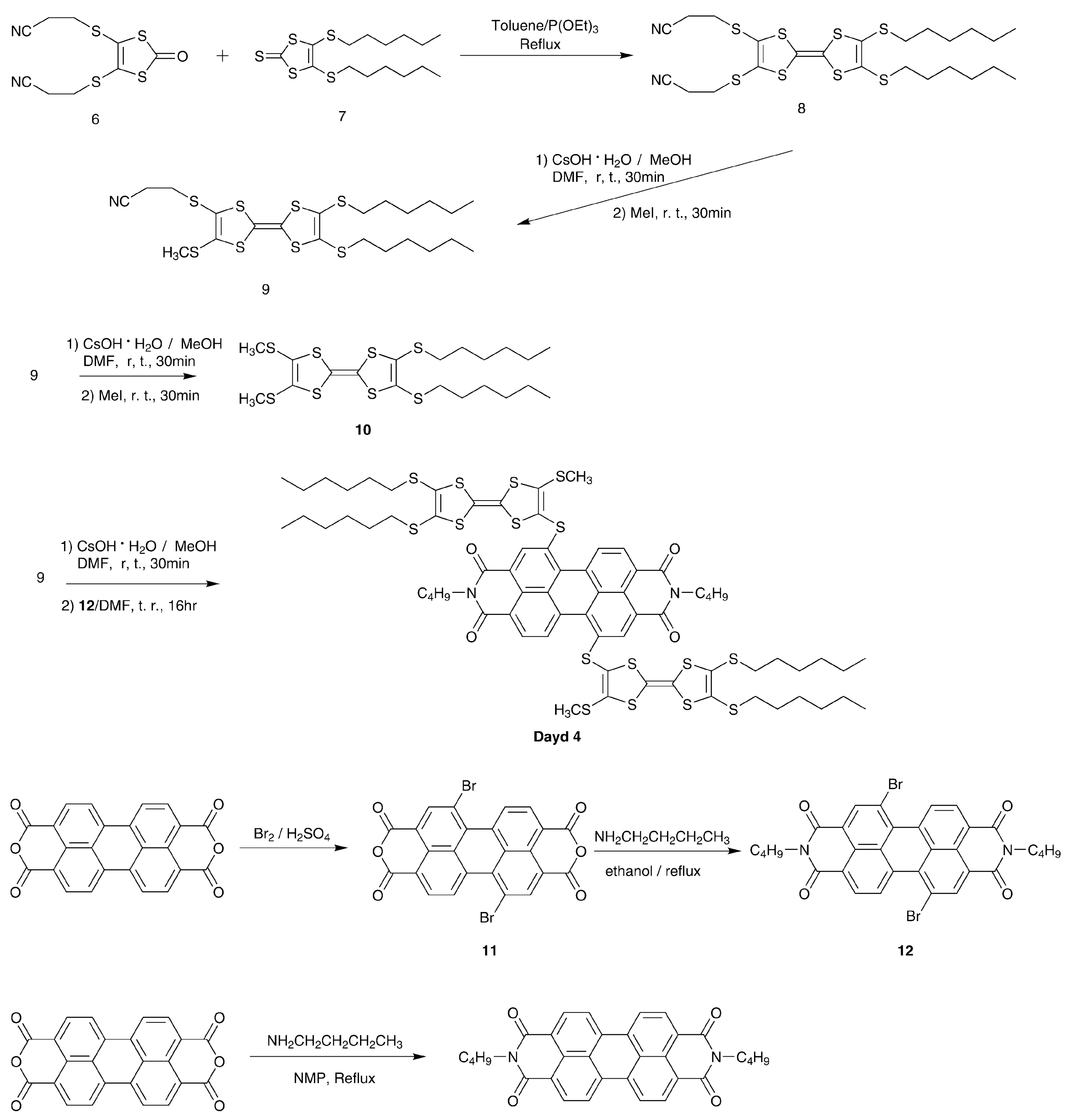
cation $TTF^{\bullet+}$–PDI–$TTF^{\bullet+}$ and dication TTF^{2+}–PDI–TTF^{2+}. The oxidation of the PDI moiety was not observed in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6. Comparing with the model TTF **10**, there was about 100 mV anodic shift for dyad **4** (Table 1). This indicated that dyad **4** was more difficult to be oxidized than TTF **10** and its HOMO orbital was also located at a lower energy ($HOMO_{dyad\,4} = -5.68$ eV) than the energy of HOMO orbital of TTF **10** ($HOMO_{TTF\,10} = -5.58$ eV). This might be caused by the effect of electron withdrawing of the 20 π-electron perylene ring.[7b]

Comparing with dyad **2** and triad **3**,[8] the CV data of dyad **4** implied that there was a significant interaction between its electro-active moieties in the ground state,[8a] as suggested by the anodic shift of position of dyad **4**. However, since the TTF unit in dyad **4** showed the same electrochemical characteristics as a normal TTF molecule, it could be concluded that the π electrons in the sulfur atoms of the linking S–C bond were not included in the delocalization pathway for the 20 π-electron system. The electrochemical investigations indicated that the perylene moiety and the TTF moiety in dyad **4** could show their individual electrochemical characteristics and the interaction between the two components was not very strong.[7b] The energetically minimized conformation of dyad **4** is shown in Fig. 2. It is notable that two TTF groups were exposed to different sides of the PDI plane, which is beneficial for participation in redox processes.[13]

Electronic absorption

The UV-visible absorption spectrum of dyad **4** (bold line) in CH_2Cl_2 showed a wide absorption in the whole range from 300 to 700 nm, with the maximum at $\lambda = 540$ nm (Fig. 3). The absorption spectra of TTF **10** (dash-dot line, $\lambda_{max} = 334$ nm), PDI **13** (solid line, $\lambda_{max} = 524$ nm) and the mixture of these in 2 : 1 molar ratio (dashed line, $\lambda_{max} = 523$ nm) are shown in Fig. 3. The absorption spectrum of the mixture exhibited no charge-transfer band or intermolecular interaction between these two compounds in their ground states.

The absorption curve of dyad **4** indicated no sharp peak but a wide absorption band (Fig. 3). By comparing with the other three absorption curves, there was a 190 and 16 nm red shifting relative to the maximum absorptions of TTF **10** and PDI **13**, respectively. In dyad **4**, the PDI moiety displays a strong electron withdrawing effect and the TTF exhibits a strong electron-donating effect.[14] Since these units are linked directly by a C–S bond the two electro-active moieties can readily interact with each other, which would predictably lead to the existence of an intramolecular charge transfer (ICT) interaction in the ground state. Using the relation $E_g(\mathrm{eV}) = 1240/\lambda_{(\mathrm{nm})}$, ΔE between the LUMO and HOMO orbital of dyad **4** could be calculated as 1.96 eV, and the energy of LUMO orbital of dyad **4** is −3.72 eV. This result also matched the CV behavior of dyad **4** ($LUMO_{PDI\,13} = -3.67$ eV). In



Scheme 2 Synthetic processes for dyad **4** and compounds **8**, **9**, **10**, **11**, **12**, **13**.

addition, there was a weak broad absorption band in the region from 600 and 900 nm (Fig. 3), which resulted from an ICT interaction between the donor TTF and acceptor PDI, according to the previous literature.[8,15]

Fluorescence spectra

The fluorescence spectra of dyad **4**, PDI **13** and a 2 : 1 mixture of TTF **10**–PDI **13** are shown in Fig. 4. The fluorescence intensity of dyad **4** was nearly zero, that is, the fluorescence of PDI moiety in dyad **4** was quenched almost quantitatively. As the fluorescence spectrum of the mixture was almost coincident with the fluorescence spectrum of PDI **13**, this indicated there was an interaction taking place in the excited state of dyad **4**, which was probably the result of a PET process.

The PET interaction between the TTF and PDI moieties in dyad **4** might be caused by three reasons: (1) a PET process is thermodynamically favorable as the calculated free energy (ΔG_{PET}) was estimated to be −1.33 eV (calculated using the Rehm–Weller equation);[16] (2) there was no spectral overlap of the absorption curve of the TTF unit and the fluorescence curve of the PDI unit, so not allowing the energy transfer

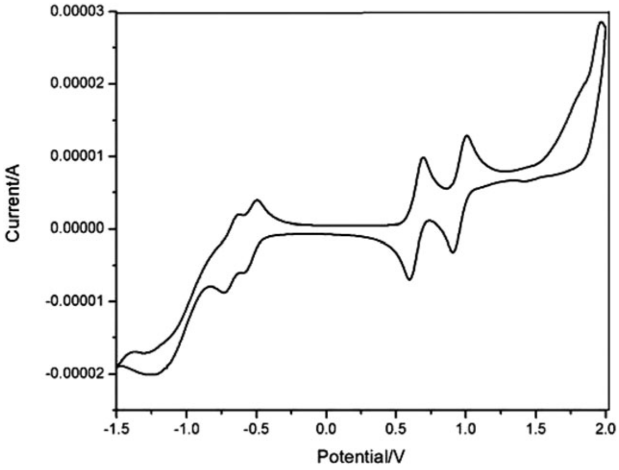


Fig. 1 Cyclic voltammogram of dyad **4** ($c = 10^{-3}$ mol L^{-1}) in CH_2Cl_2 using 0.1 M n-Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as the reference electrode, platinum wires as counter and working electrodes, scan rate: 50 mV s^{-1}, *vs.* AgCl/Ag.

process from PDI to TTF, according to the Förster mechanism;[8c] (3) the photoexcitation of the PDI unit decreased its electron cloud density and electron transfer from the TTF unit to the PDI unit became much easier, leading to thorough quenching of the fluorescence of the PDI unit in dyad **4**.

Chemical oxidation

Chemical oxidation experiments were carried out to measure the potential of dyad **4** as a fluorescence switch by adding an excess of diacetoxyiodobenzene in the presence of triflic acid ($PhI(OAc)_2$–CF_3SO_3H) in CH_2Cl_2 (Fig. 5).[17] The fluorescence emission was recorded without any further addition of oxidising reagent. Consequently, the fluorescence intensity was recorded at the TTF^{2+}–PDI–TTF^{2+} stage. The fluorescence intensity reached a limiting value after 50 min and the value corresponded to around 25% of the intensity of fluorescence intensity of PDI **13** recorded under the same experimental conditions. In the TTF–PDI–TTF triad system reported previously,[8c] no increase of fluorescence emission was noted for the $TTF^{\bullet+}$–PDI–TTF species and no further oxidation to TTF^{2+} was carried out by addition of $Fe(ClO_4)_3$ as oxidation agent. Only in a TTF–PDI dyad system,[8a] was the further oxidation to TTF^{2+} achieved and the fluorescence intensity was recovered in a smaller degree.

The reversible processes of dyad **4** were studied by adding an excess of zinc power to the solution in order to reduce TTF^{2+}–PDI–TTF^{2+} to TTF^0–PDI–TTF^0. Upon reduction, the fluorescence intensity of dyad **4** was quenched again and the initial fluorescence spectra was almost completely recovered. Thus, the chemical oxidation and reduction processes clearly indicated that dyad **4** possessed the potential to act as a reversible fluorescence-redox switch.

Table 1 Electrochemical data for dyad **4**, TTF **10** and PDI **13** in CH_2Cl_2

Compound	E_{red2}/V	E_{red1}/V	E_{ox1}/V	E_{ox2}/V
4	−0.63	−0.50	0.70	1.01
10			0.56	0.91
13	−1.03	−0.60		

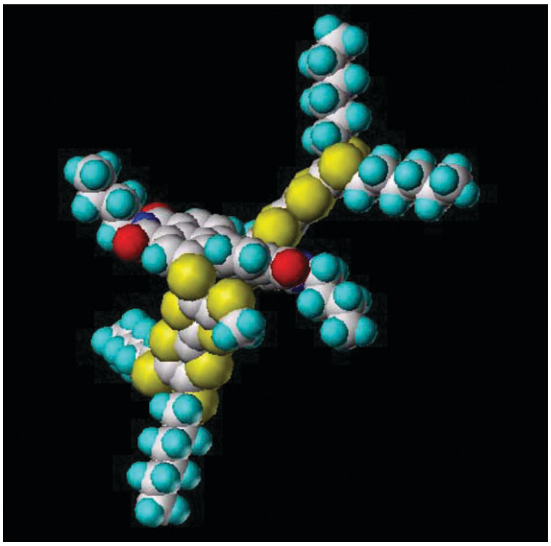


Fig. 2 Energetically minimized structures of dyad **4**, modeled using SYBYL 7.3;[19] white = carbon; cyan = hydrogen; red = oxygen; blue = nitrogen; yellow = sulfur.

Conclusions

A "bay" type donor–acceptor–donor dyad containing both TTF and PDI moieties was synthesized by condensation of N,N'-dibutyl-1,6-dibromo-3,4,9,10-perylenetetracarboxylic diimide and 2-(2-cyanoethylthio-3-methylthio-6,7-bis-(hexylthio)tetrathiafulvalene. Cyclic voltammetry, electronic absorption and fluorescence spectra of the dyad indicated both intramolecular charge transfer interaction and the photo-induced charge transfer process occurred between the TTF and PDI moieties in the dyad. The chemical oxidation experiment indicated the fluorescence intensity was dependent on the

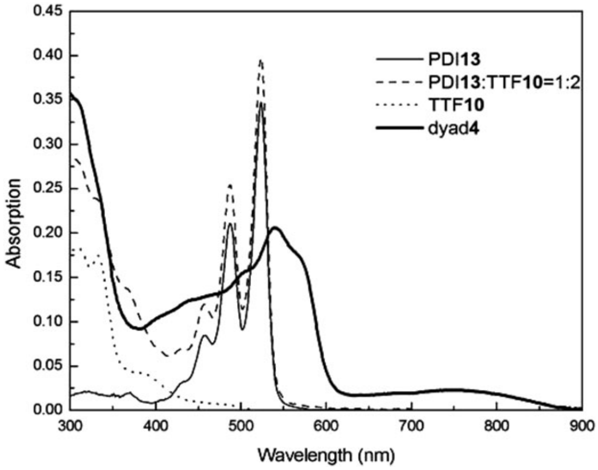


Fig. 3 Absorption spectra of dyad **4** (bold line) and references PDI **13** (solid line), TTF **10** (dotted line) and the mixture PDI **13**–TTF **10** = 1 : 2 (dashed line) in CH_2Cl_2, $c = 1 \times 10^{-5}$ mol L^{-1}.

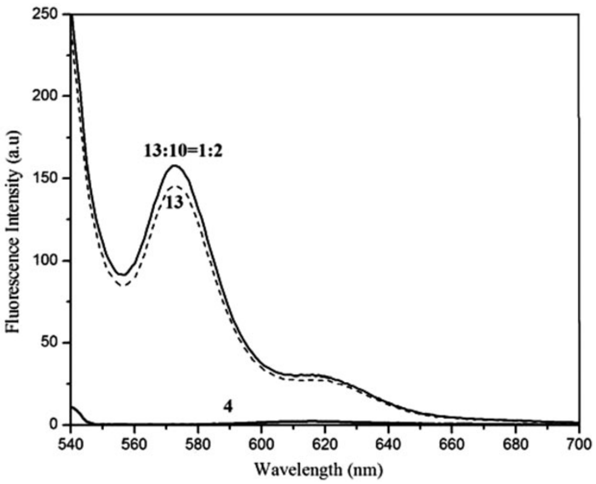


Fig. 4 Fluorescence spectra of dyad **4** (bold line), PDI **13** (dotted line) and a 2 : 1 mixture of TTF **10**–PDI **13** (solid line) in CH_2Cl_2 (λ_{exc} = 540 nm, = 10^{-5} mol L^{-1}).

oxidation state of the TTF units in dyad **4**, which could be considered as a new fluorescence redox molecular switch.

Experimental

Chemicals and instruments

All chemicals were purchased commercially and the solvents dried or distilled when necessary using standard procedures. ^1H and ^{13}C NMR spectra were obtained on a Bruker AVANCE 500 spectrometer operating at 500 MHz: chemical shifts were quoted downfield of TMS. Elemental analyses were obtained from a German elementar vario ELIII C, H, N analyzer. UV-Vis absorption spectra were recorded on a CARY 100 Conc UV-visible spectrophotometer. The fluorescence spectra were recorded on a CARY Eclipse Fluorescence spectrophotometer and were corrected for the spectral response of the machines. All the electrochemical experiments were performed in dichloromethane with n-Bu_4NPF_6 as the supporting electrolyte, platinum as the working and counter electrodes, and AgCl/Ag as the reference electrode. The scan rate was 50 mV s^{-1}.

Synthesis

Compound **5–9** and **11** were synthesized according to the reported procedures.[12,18]

2,3-Bis(methylthio)-6,7-bis(hexylthio)tetrathiafulvalene 10. Compound **9** (284 mg, 0.5 mmol) was dissolved in dried DMF (30 ml) and a solution of $CsOH{\cdot}H_2O$ (84 mg, 0.53 mmol) in dried methanol (5 ml) was added dropwise over a period of 15 min under N_2. After stirring for 30 min, MeI (0.5 ml, 8 mmol) was added and the solution turned from dark-orange to yellow–orange. The reaction mixture was stirred for a further 30 min under N_2. The solvents and excess MeI were removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2–petroleum ether, 1 : 1 v/v) to give the bismethylthio-substituted tetrathiafulvalene **10** (180 mg, 68% yield) as a red–orange oil. ^1H NMR ($CDCl_3$, 500 MHz): δ 2.79 (4H, t, J 6.90 = Hz, SCH_2CH_2), 2.38 (6H, s, SCH_3), 1.57–1.62 (4H, m, SCH_2CH_2), 1.32–1.38 (4H, m, CH_2CH_3), 1.18–1.28 (8H, m, –CH_2–), 0.83 (6H, t, J = 6.96 Hz, –CH_3); m/z (EI): 528.0 (M^+, 100%), 513.0 (3.5), 410.0 (11), 237.9 (9).

***N,N′*-Dibutyl-1,6-dibromo-3,4,9,10-perylenetetracarboxylic diimide 12.** n-Butylamine (2.97 ml, 30 mmol) was added to a solution of 1,6-dibromo-3,4,9,10-perylenetetracarboxylic dianhydride **11** (3.30 g, 6 mmol) in ethanol (100 ml). The reaction mixture was heated to reflux under N_2 for 20 h and cooled to room temperature, poured into 10% HCl (v/v) carefully and the dark brown precipitate was filtered off and washed with water, and purified by column chromatography on silica gel (CH_2Cl_2) to give **12** (2.30 g, 58% yield) as a brown solid; mp >300 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.60 (2H, d, J = 8.36 Hz, Ph), 8.56 (2H, d, J = 8.35 Hz, Ph), 8.34 (2H, s, Ph), 4.16 (4H, t, J = 7.62 Hz, NCH_2), 1.68–1.72 (4H, m, NCH_2CH_2–), 1.41–1.46 (4H, m, –CH_2CH_3), 0.96 (6H, t, J = 7.36 Hz, –CH_3); m/z (EI): 660.02 (M^+, 100%).

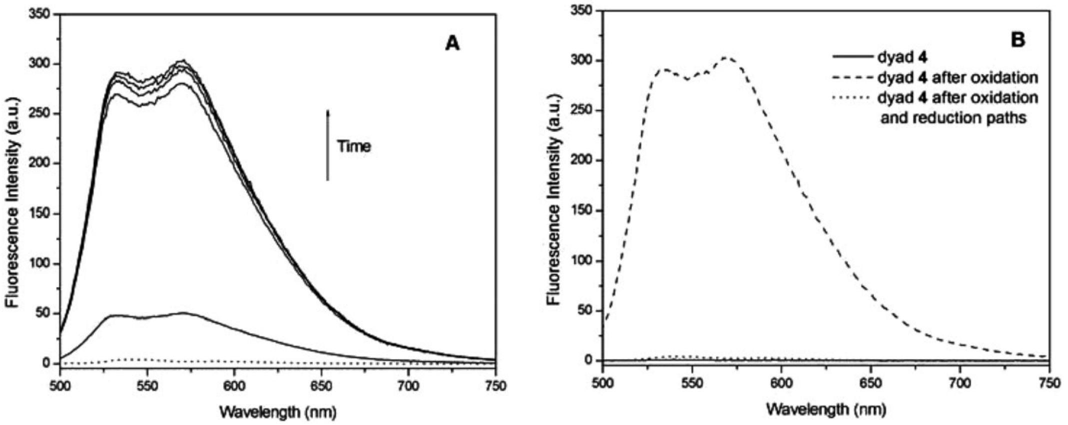


Fig. 5 (A) Fluorescence emission spectra of dyad **4** recorded before (dotted line) and after addition of an excess of diacetoxyiodobenzene in the presence of triflic acid in CH_2Cl_2 (c = 10^{-5} mol L^{-1}, λ_{exc} = 480 nm). (B) Fluorescence emission spectra of dyad **4** (solid line), of dyad **4** after oxidation (dashed line), and of dyad **4** after oxidation and reduction processes (dotted line) (c = 10^{-5} mol L^{-1}, λ_{exc} = 480 nm).

Dyad 4. Compound **9** (567 mg, 1 mmol) was dissolved in dried DMF (60 ml) and a solution of $CsOH\cdot H_2O$ (168 mg, 1.05 mmol) in dried methanol (10 ml) was added dropwise under N_2. After stirring for 30 min, *N*,*N*′-dibutyl-1,6-dibromo-3,4,9,10-perylenetetracarboxylic diimide **11** (330 mg, 0.5 mmol) dispersed in dried DMF (20 ml) was added. The reaction mixture was stirred for 16 h, filtered to give a dark brown solid, and purified by column chromatography on silica gel (CH_2Cl_2–petroleum ether, 2 : 1 v/v) to afford dyad **4** (993 mg, 65% yield) as a dark maroon solid; mp 219–221 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.97–9.12 (1H, br, Ph), 8.70 (1H, s, Ph), 8.59–8.63 (1H, m, Ph), 8.47 (2H, d, J = 8.56 Hz, Ph), 8.13 (1H, d, J = 7.62 Hz, Ph), 4.15 (4H, t, J = 7.62 Hz, NCH_2), 2.55–2.75 (14H, m, SCH_3, SCH_2CH_2), 1.65–1.78 (4H, m, $-CH_2-$), 1.46–1.57 (12H, m, $-CH_2-$), 1.30–1.36 (4H, m, $-CH_2-$), 1.20–1.28 (20H, m, $-CH_2-$), 0.79–0.95 (18H, m, $-CH_3$), ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.48, 162.77, 133.50, 132.16, 131.87, 128.98, 128.77, 128.29, 126.60, 121.53, 40.64, 35.95, 35.76, 31.29, 31.26, 30.19, 29.69, 29.59, 28.24, 28.16, 22.51, 20.48, 19.18, 13.99, 13.85; Found: C, 55.12, H 5.40, N 1.67. $C_{70}H_{82}N_2O_4S_{16}$ requires C, 55.01, H 5.41, N 1.83%; *m*/*z* (ES^+): 1551.1 (100%, M^+ + Na), 1528.2 (26, M^+).

***N*,*N*′-Dibutyl-3,4:9,10,-perylenetetracarboxylic diimide 13.** To a suspension of 3,4,9,10-perylenetetracarboxylic dianhydride (1.96 g, 5 mmol) in NMP (80 ml) were added *n*-butylamine (1.98 ml, 20 mmol). The reaction mixture was heated to reflux under N_2 for 20 h, cooled to room temperature, poured into 10% HCl (v/v) carefully, filtered and washed with water to obtain a dark maroon solid, and purified by column chromatography on silica gel (CH_2Cl_2–ethyl acetate, 10 : 1 v/v) to give **13** (1.91 mg, 76% yield) as a reddish brown solid; mp > 300 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.57 (8H, d, J = 8.12 Hz, Ph), 4.16 (4H, t, J = 8.85 Hz, $-NCH_2-$), 1.58–1.62 (4H, m, $-CH_2-$), 1.17–1.20 (4H, m, $-CH_2-$), 0.94 (6H, t, J = 10.13 Hz, $-CH_3$); *m*/*z* (EI^+): 502.2 (M^+, 100), 390.1 (43), 485.2 (40).

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 20676036) and the Key Project of the Ministry of Education of China (No. 03053).

References

1 (*a*) F. Wudl, G. M. Smith and E. J. Hufnagel, *Chem. Commun.*, 1970, 1453–1454; (*b*) J. L. Segura and N. Martín, *Angew. Chem., Int. Ed.*, 2001, **40**, 1372–1409; (*c*) C. A. Christensen, A. S. Batsanov and M. R. Bryce, *J. Org. Chem.*, 2007, **72**, 1301–1308; (*d*) C. A. Christensen, A. S. Batsanov and M. R. Bryce, *J. Am. Chem. Soc.*, 2006, **128**, 10484–10490.

2 (*a*) C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath and J. F. Stoddart, *J. Am. Chem. Soc.*, 2001, **123**, 12632–12641; (*b*) J. O. Jeppesen, J. Perkins, J. Becher and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2001, **40**, 1216–1221.

3 (*a*) Z. Wang, D. Q. Zhang and D. B. Zhu, *J. Org. Chem.*, 2005, **70**, 5729–5732; (*b*) G. Trippé, E. Levillain, F. Le Derf, A. Gorgues, M. Sallé, J. O. Jeppesen, K. Nielsen and J. Becher, *Org. Lett.*, 2002, **4**, 2461–2464; (*c*) K. A. Nielsen, J. O. Jeppesen, E. Levillain and J. Becher, *Angew. Chem., Int. Ed.*, 2003, **42**, 187–191.

4 M. Bendikov, F. Wuld and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891–4945.

5 G. X. Zhang, D. Q. Zhang, X. F. Guo and D. B. Zhu, *Org. Lett.*, 2004, **6**, 1209–1212.

6 C. Farren, C. A. Christensen, S. FitzGerald, M. R. Bryce and A. Beeby, *J. Org. Chem.*, 2002, **67**, 9130–9139.

7 (*a*) J. Becher, T. Brimert, J. O. Jeppesen, J. Z. Pedersen, R. Zubarev, T. Bjørnholm, N. Reitzel, T. R. Jensen, K. Kjaer and E. Levillain, *Angew. Chem., Int. Ed.*, 2001, **40**, 2497–2500; (*b*) H. C. Li, J. O. Jeppesen, E. Levillain and J. Becher, *Chem. Commun.*, 2003, 846–847.

8 (*a*) S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M.-J. Blesa and P. Hudhomme, *J. Org. Chem.*, 2005, **70**, 6313–6320; (*b*) S. Leroy-Lhez, L. Perrin, J. Baffreau and P. Hudhomme, *C. R. Chim.*, 2006, **9**, 240–246; (*c*) X. F. Guo, D. Q. Zhang, H. J. Zhang, Q. H. Fan, W. Xu, X. C. Ai, L. Z. Fan and D. B. Zhu, *Tetrahedron*, 2003, **59**, 4843–4850.

9 C. Goze, S. X. Liu, C. Leiggener, L. Sanguinet, E. Levillain, A. Hauser and S. Decurtins, *Tetrahedron*, 2008, **64**, 1345–1350.

10 C. Y. Jia, S. X. Liu, C. Tanner, C. Leiggener, A. Neels, L. Sanguinet, E. Levillain, S. Leutwyler, A. Hauser and S. Decurtins, *Chem.–Eur. J.*, 2007, **13**, 3804–3812.

11 D. F. Perepichka and M. R. Bryce, *Angew. Chem., Int. Ed.*, 2005, **44**, 5370–5373.

12 (*a*) K. B. Simonsen, N. Svenstrup, J. Lau, O. Simonsen, P. Mørk, G. J. Kristensen and J. Becher, *Synthesis*, 1996, **3**, 407–418; (*b*) C. A. Christensen, M. R. Bryce and J. Becher, *Synthesis*, 2000, **12**, 1695–1704.

13 M. R. Bryce, W. Devonport, L. M. Goldenberg and C. S. Wang, *Chem. Commun.*, 1998, 945–951.

14 J. Baffreau, L. Perrin, S. Leroy-Lhez and P. Hudhomme, *Tetrahedron Lett.*, 2005, **46**, 4599–4603.

15 M. R. Bryce, *Adv. Mater.*, 1999, **11**, 11–23.

16 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259. For dyad **4**: $\Delta G_{PET} = E_{(ox)} - E_{(red)} - E^{0-0}(\mathbf{13}) - \Delta e$, with $E_{(ox)} = +0.56$ eV, $E_{(red)} = -0.53$ eV, $E^{0-0}(\mathbf{13}) = 2.32$ eV, $\Delta e \approx 0.1$ eV.

17 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.

18 (*a*) N. Svenstrup, K. M. Rasmussen, T. K. Hansen and J. Becher, *Synthesis*, 1994, **8**, 809–812; (*b*) M. J. Ahrens, L. E. Sinks, B. Rybtchinski, W. H. Liu, B. A. Jones, J. M. Giaimo, A. V. Gusev, A. J. Goshe, D. M. Tiede and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2004, **126**, 8284–8294.

19 SYBYL 7.3, Tripos International, St. Louis, MO, USA.