

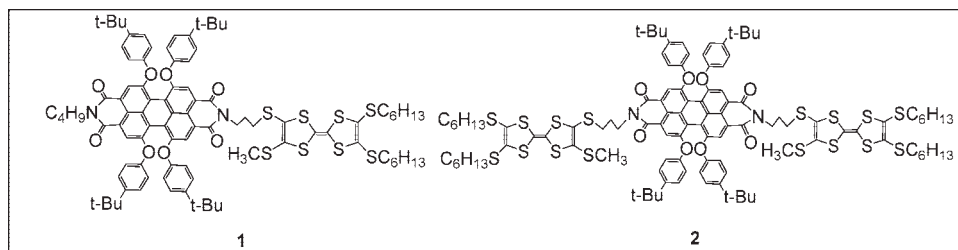
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Two highly soluble donor- σ -acceptor and donor- σ -acceptor- σ -donor type fluorescence switches consisting tetrathiafulvalene (TTF) and 3,4,9,10-perylene tetracarboxylic diimides (PDI) were synthesized. The structure of the dyad and triad as well as their intermediates was characterized by ^1H NMR, ^{13}C NMR MS, elemental analysis. Their fluorescence behavior could be modulated by oxidation and reduction of the TTF unit using either chemical or electrochemical method.

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INTRODUCTION

Perylene diimide (PDI) [1–7] has been used in donor-acceptor supramolecules due to their optical, redox, and stability properties. Tetrathiafulvalene (TTF) and its derivatives [8–11] are well known for their π -electron-donor properties. They have been extensively investigated as building blocks in electrical conductors and superconductors [12]. Some electron donor-acceptor supramolecules with TTF units have been prepared for studies related to intramolecular photoinduced electron transfer processes, intramolecular charge-transfer (ICT) interactions and construction of molecular rectifiers [13–16].

However, the research of PDI-TTF type donor-acceptor system was confined because of the poor solubility of perylene diimide (PDI). Thus, we interested in the introduction of tetra-substituent tetra-butylphenoxy group to the bay region of PDIs to improve its solubility. In this article, electron donor- σ -acceptor dyad **1** and donor- σ -acceptor- σ -donor triad **2** containing PDI and TTF unit were synthesized and characterized (Scheme 1). The TTF unit is linked to PDI unit and the PDI unit is modified by *tert*-butylphenol to increase its solubility. TTF-type compounds are able to exist in three different stable redox states (TTF, TTF $^{\bullet+}$, TTF $^{2+}$). Therefore, the donating ability of TTF could be tuned by either chemical or electrochemical reversible redox reactions. And the optical absorption, fluorescent spec-

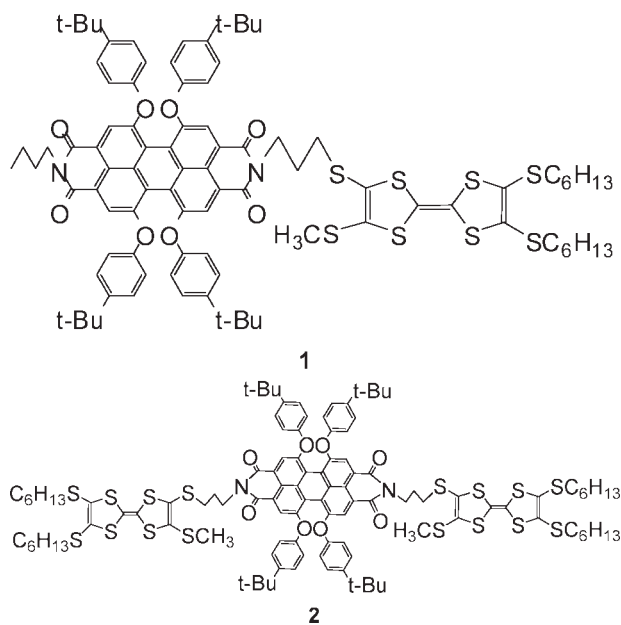
tra, chemical, and electrochemical methods shows that two novel fluorescence switches were established.

RESULTS AND DISCUSSION

The target compound **1** and **2** were synthesized starting from *N*-hexyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylicimide (**4**) and 1,6,7,12-tetrakis(4-*tert*-butylphenoxy)-3,4,9,10-perylene-tetracarboxy-anhydride (**5**) (Scheme 2).

Compounds **4**, **5**, and **6** were prepared by method previously reported [17–20]. The amino TTF **7** was synthesized through ammonization of TTF **6** with the presence of LiAlH_4 in THF. The reaction of compound **4** and amino TTF **7** led to dyad **1** (yield, 45%). The way to get compound **2** was just like the reaction to get compound **1**. Amino TTF **7**, compound **6** together with imidazole were heated to 175–180°C for 48 h, and compound **2** was finally achieved with a yield of 40% after column chromatography on silica gel (CH_2Cl_2 : ethyl acetate = 1:1).

With tetrasubstitutions of *p*-*t*-butylphenoxy at the bay region, compound **1** and **2** were highly soluble in common organic solvents like CH_2Cl_2 , CHCl_3 , ethyl acetate, acetone, DMF, toluene, pyridine, and acetonitrile, slightly soluble in methanol, and insoluble in hexane and petroleum ether. The UV-vis spectra of dyad **1** and triad **2** were measured in CH_2Cl_2 (1.0×10^{-5} M) with CARY 100 Conc UV-vis spectrophotometer (Fig. 1).

Scheme 1. Structure of dyad **1** and triad **2**.

For comparison, the UV-vis spectra of model compound **3** and **8** (1.0×10^{-5} M in CH_2Cl_2) were also given. Their spectral data were listed in Table 1.

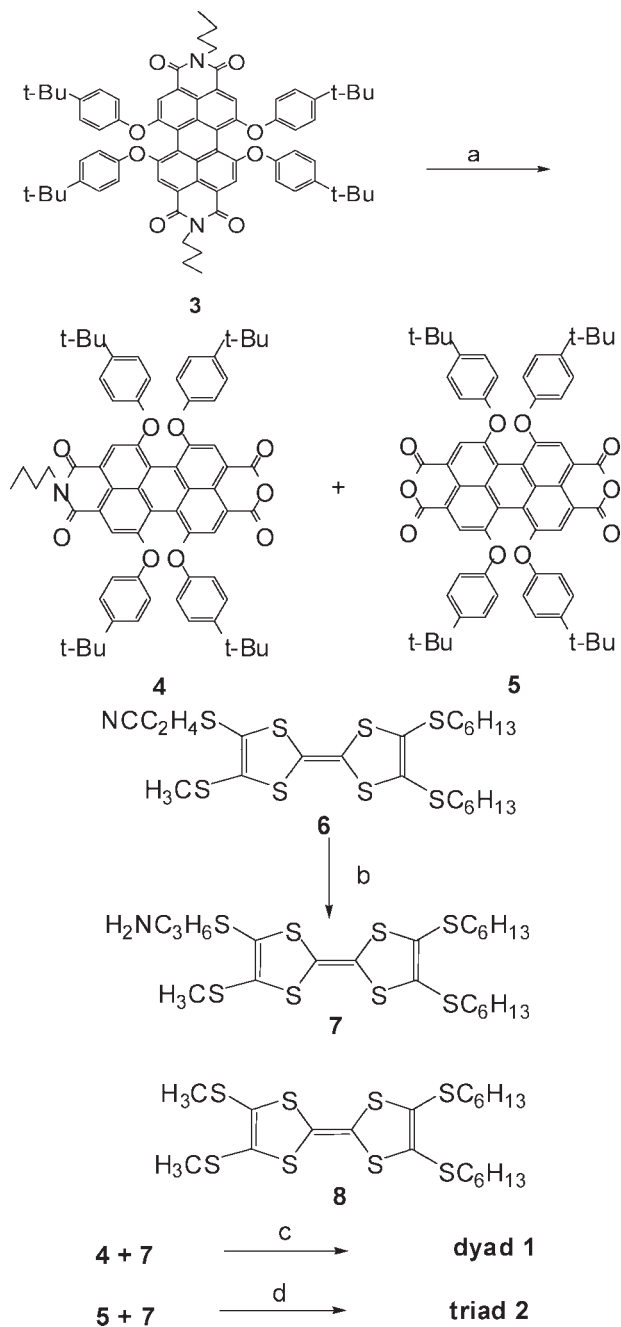
The absorption spectra of **1**, **2**, **3** showed a wide absorption between 300 and 650 nm with identical absorption maximum at about 451, 537, 577 nm. Compared with PDI **3**, compound **1** and **2** have a new band at about 331 nm which is coincide with the absorption of TTF **8**. The UV-vis absorption spectra of **1** and **2** were almost summation of the spectra of donor **8** and acceptor **3** and no new band or unique spectroscopic shoulder was observed, this implying neglectable ground state electronic interaction between perylene diimide and TTF unit.

The electrochemical characterization of **1**, **2** and reference compounds **3**, **8** were tested by cyclic voltammetry (CV) and their voltammetric data were listed in Table 2. All the experiments were performed in dichloromethane, using $n\text{-Bu}_4\text{NPF}_6$ (10^{-1} M) as the supporting electrolyte, platinum as the working and counter electrodes, and Ag/AgCl as the reference electrode; the scan rate was 50 mV s^{-1} . Dyad **1** and triad **2** show almost the same reduction potentials at about -0.90 and -0.60 V, which were ascribed to the successive formation of the anion radical $\text{PDI}^{\cdot-}$ and dianion PDI^{2-} . In positive direction, **1** and **2** exhibited two one-electron reversible oxidation waves at about $+0.58$, $+0.91$, and $+1.37$ V, corresponding to the successive generation of the cation radical $\text{TTF}^{\cdot+}$, dication TTF^{2+} and cation radical $\text{PDI}^{\cdot+}$. Comparison of different values for dyad **1** and triad **2** with reference compounds **3** and **8** suggested that no significant interaction takes place between both electroactive

moieties in the ground state. This result was coincident with that of the UV-vis absorption.

Fluorescence spectra of **1**, **2**, and **3** were carried out with a CARY Eclipse Fluorescence Spectrophotometer in a 1 cm quartz cell (Fig. 2). Compared to compound **3**, dyad **1** and triad **2** show a rather weak fluorescence. The fluorescence quantum yield ϕ_f ($\lambda_{\text{exc}} = 540 \text{ nm}$) of

Scheme 2. Synthetic procedure for compound **1** and **2**: (a) KOH, isopropanol/ H_2O , N_2 , reflux; (b) LiAlH_4 , THF, N_2 ; (c) imidazole, reflux in *m*-cresol for 24 h, yield: **6**, 45%; **7**, 10%; (d) imidazole, reflux in *m*-cresol for 48 h, yield 40%.



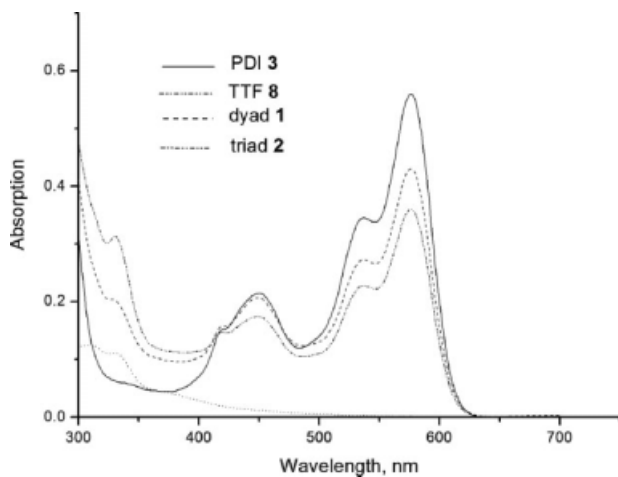


Figure 1. Absorption spectrum of compounds **1**, **2**, **3**, and **8** (1.0×10^{-5} M in CH_2Cl_2).

1 and **2** was 0.172 and 0.087 compared to PDI **3** ($\phi_f = 1$). This weakly fluorescence emission of **1** and **2** could be attributed to a photoinduced electron transfer (PET) reaction between PDI and TTF unit in the dyad and triad for two major reasons: (1) ΔG values of **1** and **2** calculated using the Rehm-Weller equation [21] for the photoinduced electron transfer reactions were -1.03 and -1.04 eV, thus these reactions are thermodynamically favorable; (2) there was no spectral overlap between the absorption spectrum of TTF unit and Fluorescence spectrum of PDI unit. Hence, the energy transfer process was prohibited according to Förster mechanism [4].

Figure 3 was fluorescence spectra of **1** and **2** after addition of different amount of Fe^{3+} and further reduction by $\text{Na}_2\text{S}_2\text{O}_3$ (1.0×10^{-5} M in CH_2Cl_2 , $\lambda_{\text{ex}} = 540$ nm). It is known that TTF and its analogues can be oxidized stoichiometrically by Fe^{3+} . As TTF being oxidized to corresponding cation radical and dication species, the fluorescence of compound **1** and **2** both increased gradually after Fe^{3+} was added. The maximum fluorescent intensity of dyad **1** increased by 245% after reaction with 1.0 equiv of Fe^{3+} and the maximum fluorescent intensity of triad **2** increased by 663% after 2.0 equiv of Fe^{3+} was added. As expected, after react with excess sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the former

Table 1
The absorption data of compounds **1**, **2**, **3**, and **8**
(1.0×10^{-5} M in CH_2Cl_2).

Compound	Absorption nm, $\epsilon \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$
1	329(0.20), 448(0.21), 537(0.27), 577(0.43)
2	331(0.31), 449(0.17), 536(0.23), 577(0.37)
3	451(0.21), 537(0.34), 578(0.56)
8	312(0.12), 332(0.11)

Table 2

Oxidation potentials of compounds **1**, **2**, **3**, and **8** in dichloromethane (1.0×10^{-3} M).

Compound	$E_{1/2}$ (V)				
	PDI ²⁻	PDI ⁻	TTF ^{*+}	TTF ²⁺	PDI ⁺
3	-0.91	-0.60			1.37
8			0.54	0.91	
1	-0.90	-0.60	0.58	0.93	1.38
2	-0.89	-0.61	0.56	0.92	1.40

chemically oxidized solution, both absorption and fluorescence spectrum of compound **1** and **2** restored (see Fig. 3). This is because the radical cation of TTF unit (TTF^{2+}) of compound **1** and **2** transferred into neutral unit after adding of $\text{Na}_2\text{S}_2\text{O}_3$. This indicates that the fluorescence of dyad **1** and triad **2** could be modulated by reversible chemical oxidation and reduction of TTF unit.

The fluorescence of dyad **1** and triad **2** could also be modulated by reversible electrochemical oxidation and reduction of TTF unit (see Fig. 4). Oxidation of compound **1** and **2** (1.0×10^{-5} M) containing $n\text{-Bu}_4\text{NPF}_6$ (1.0×10^{-1} M) was performed by applying an oxidation potential of 0.60 V (vs. Ag wire) to the solution. Figure 4 show that the oxidation led to the increase at 600 nm. This is similar to the fluorescence spectral variation observed after chemical oxidation which is discussed above. The application of a reduction potential of 0.1 V (vs. Ag wire) to former electrochemically oxidized solution for 5 min also led to the transformation of TTF^{2+} into neutral unit. Consequently, the fluorescence of dyad **1** and triad **2** restored (Fig. 4). As a result, electrochemically oxidization and reduction could also modulate the fluorescence of both dyad **1** and triad **2**.

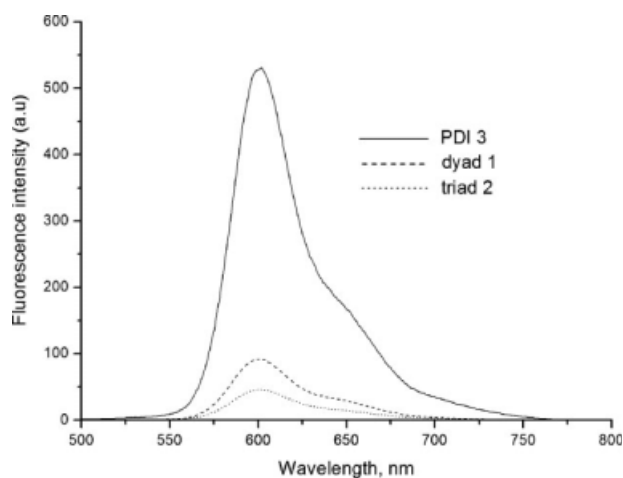


Figure 2. Fluorescence spectrum of compounds **1**, **2**, and **3** (1.0×10^{-5} M in CH_2Cl_2 , $\lambda_{\text{ex}} = 540$ nm).

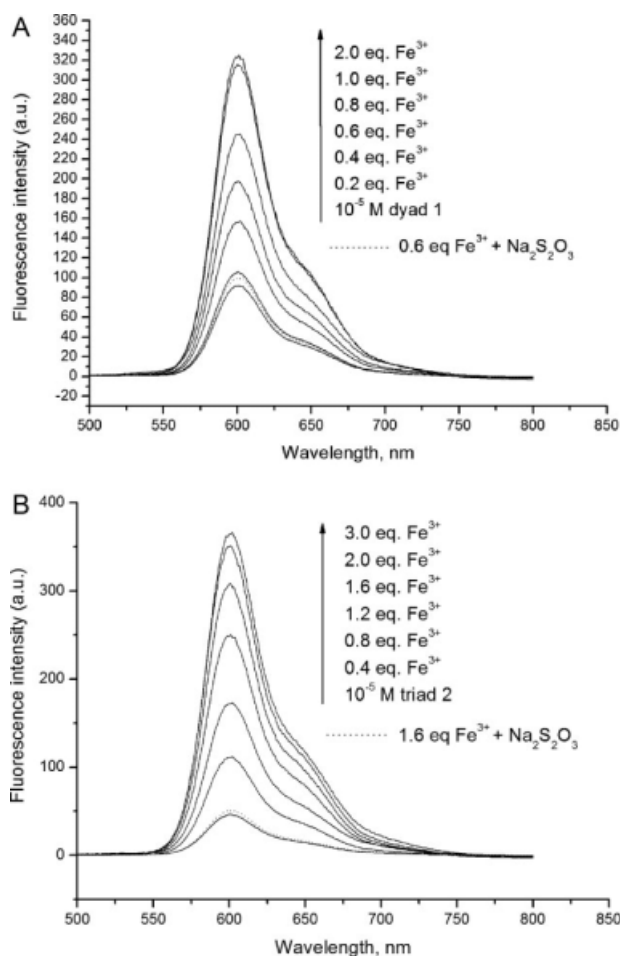


Figure 3. Fluorescence spectrum of dyad **1** (A) and triad **2** (B) (1.0×10^{-5} M in CH_2Cl_2 , $\lambda_{\text{ex}} = 540$ nm) in the presence of different amounts of $\text{Fe}(\text{ClO}_4)_3$ and further reduction by $\text{Na}_2\text{S}_2\text{O}_3$.

CONCLUSIONS

We have designed and synthesized a new donor- σ -accepter (D- σ -A) type molecular fluorescence switches dyad **1** and a new donor- σ -accepter- σ -donor (D- σ -A- σ -D) type molecular fluorescence switch triad **2** containing PDI and TTF units. Compound **1** and **2** both have excellent solubility in most organic solvents because of the tetra-substituted *p*-*t*-butylphenoxy at the bay region. What's more, their fluorescent behavior could be modulated by reversible oxidation and reduction of TTF unit either chemically or electrochemically.

EXPERIMENTAL

N-Hexyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylicimide (**4**) and 1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylicbis-anhydride (**5**). *N,N'*-Dihexyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylicdiimide (2.2 g, 2.0

mmol) with KOH (6 g, 10 mmol) in isopropylalcohol (60 mL) and H_2O (6 mL) were heated to reflux temperature under argon for 10 h, followed by acidic work up and thorough washing and drying, yielded a mixture (1.0 g) of perylenemonoocetyl-imide (**4**) and perylenebis-anhydride (**5**) in a ratio of about 7:3. Compound **4** and **5** were separated by column chromatography on a silica gel with CH_2Cl_2 /petroleum ether (1:1). Compound (**4**): mp > 300°C; ^1H NMR (CDCl_3 , 500 MHz): δ 8.25 (s, 4H, H_{per}), 7.25 (d, $J = 8.45$ Hz, 8H, H_{ar}), 6.85 (d, $J = 8.84$ Hz, 8H, H_{ar}), 4.15 (t, $J = 7.6$ Hz, 2H, N- CH_2), 1.65 (m, 4H), 1.3 (s, 36H, 4- $\text{C}(\text{CH}_3)_3$), 0.85 (t, $J = 6.4$ Hz, 3H, $-\text{CH}_3$). Compound (**5**): mp > 300°C; ^1H NMR (CDCl_3 , 500 MHz): δ 8.28 (s, 4H, H_{per}), 7.25 (d, $J = 8.46$ Hz, 8H, H_{ar}), 6.85 (d, $J = 8.76$ Hz, 8H, H_{ar}), 1.3 (s, 36H, 4- $\text{C}(\text{CH}_3)_3$).

4-Methyl-5-aminopropyl-4,5-bis-hexylenetetra-thiafulvalene (**7**). LiAlH_4 (21 mg, 0.55 mmol) which is dissolved in 5 mL anhydrous degassed THF was added dropwise to a stirred solution of compound **6** (114 mg, 0.2 mmol) in anhydrous degassed THF (20 mL) under N_2 . The mixture was refluxed for 2 h. After cooling, THF was evaporated *in vacuo* and

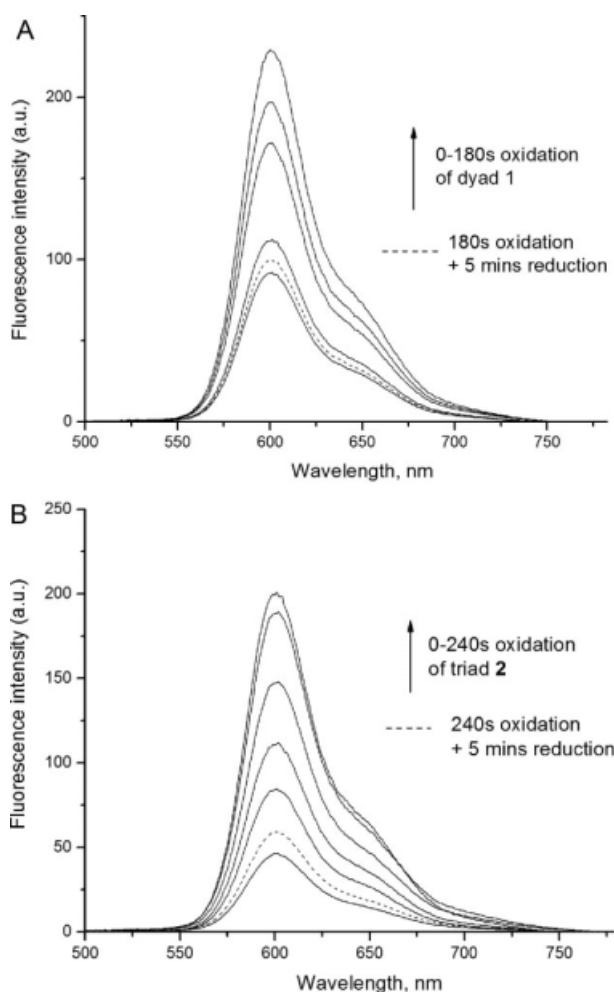


Figure 4. Fluorescence spectrum of dyad **1** (A) and triad **2** (B) (10^{-5} M in CH_2Cl_2 , $\lambda_{\text{ex}} = 540$ nm, containing 10^{-1} M *n*- Bu_4NPF_6) after oxidation of 0.60 V (vs. Ag wire) for different period and further reduction of 0.1 V (vs. Ag wire) for 5 min (scan rate was 50 mV s^{-1}).

CH₂Cl₂ (20 mL) and H₂O (10 mL) was added. The two phases were separated and the organic phase was washed with H₂O. Column chromatography (silica gel, CH₂Cl₂: MeOH = 4:1) after drying (MgSO₄) give compound **7** (67mg). Yield: 60%. ¹H NMR (CDCl₃): δ 2.82 (m, 6H, —SCH₂—), 2.68 (m, 2H, —CH₂N), 2.40 (s, 3H, —SCH₃), 2.08 (s, 2H, NH₂) 2.01 (m, 2H, —CH₂—), 1.85 (m, 4H, —CH₂—), 1.42 (m, 4H, —CH₂—), 1.20–1.30 (m, 8H, —CH₂—), 0.86 (t, *J* = 6.8 Hz, 6H, —CH₃).

Perylene-TTF dyad 1. *N*-Hexyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylicimide (**4**) (208mg, 0.2 mmol), amino-TTF **7** (110mg, 0.2 mmol) and imidazole (0.5 g) are added to 30 mL of *m*-cresol. The reaction mixture was heated to 175–180°C under dry nitrogen for 48 h with stirring. After the reaction mixture was cooled to room temperature, it was evaporated *in vacuo* to remove *m*-cresol. The residue was washed by methanol to remove excess *m*-cresol and TTF **7**. Then the residue was washed with hot 1% NaOH solution and hot water three times, respectively. After drying, the residue was purified by chromatography on silica gel using a mixture of dichloromethane-petroleum ether (1:1) as eluent, to give a purple solid of dyad **1** (yield: 45%, 144 mg). mp > 300°C; ¹H NMR (CDCl₃, 500 MHz): δ 8.20 (s, 4H, H_{per}), 7.22 (d, *J* = 8.45 Hz, 8H, H_{ar}), 6.80 (d, *J* = 8.84 Hz, 8H, H_{ar}), 4.20–4.28 (m, 4H, N—CH₂), 2.75 (m, 6H, S—CH₂—), 2.71 (m, 2H) 2.38 (s, 3H, —SCH₃), 2.05 (m, 4H, —CH₂), 1.70 (m, 4H), 1.45 (m, 4H, CH₂), 1.28–1.35 (m, 44H), 0.88 (t, *J* = 6.4 Hz, 6H, —CH₃). 0.82 (t, *J* = 6.4 Hz, 3H, —CH₃). ¹³C NMR (CDCl₃, 100 MHz): δ 160.9, 155.7, 152.5, 147.2, 131.5, 127.4, 126.5, 122.3, 120.5, 119.7, 119.2, 110.1, 39.3, 36.7, 34.4, 31.6, 29.8, 29.3, 28.2, 27.7, 27.1, 22.5, 21.7, 19.4, 14.2, 13.8; MS(MALDI-TOF): *m/z* 1592.3 [M]⁺ (calcd for C₉₀H₁₀₀N₂O₈S₈ 1592.5); Anal. Calcd (%) for C₉₀H₁₀₀N₂O₈S₈: C 67.80, H 6.32, N 1.76; Found C 67.71, H 6.38, N 1.72

TTF-Perylene-TTF triad 2. 1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylicbis-anhydride **5** (100 mg, 0.1 mmol), amino-TTF **7** (230 mg, 0.4 mmol) and imidazole (0.5 g) are added to 30 mL of *m*-cresol. The reaction mixture was heated to 175–180°C under dry nitrogen for 48 h with stirring. After the reaction mixture was cooled to room temperature, it was evaporated *in vacuo* to remove *m*-cresol. The residue was washed by methanol to remove excess *m*-cresol and TTF **7**. Then the residue was washed by hot 1% NaOH solution and hot water three times, respectively. After drying, the residue was purified by chromatography on silica gel using a mixture of dichloromethane-ethyl acetate (1:1) as eluent, to give a purple solid of triad **2** (yield: 40%, 84 mg). mp > 300°C; ¹H NMR (CDCl₃, 500 MHz): δ 8.28 (s, 4H, H_{per}), 7.23 (d, *J* = 8.38 Hz, 8H, H_{ar}), 6.85 (d, *J* = 8.62 Hz, 8H, H_{ar}), 4.20–4.25 (m, 4H, N—CH₂), 2.94 (m, 8H, S—CH₂—), 2.59 (s, 6H, —SCH₃), 2.01 (m, 8H, —CH₂), 1.65 (m, 8H), 1.45 (m, 8H, CH₂), 1.28–1.35 (m, 52H), 0.85 (t, *J* = 6.4 Hz, 12H, —CH₃). ¹³C NMR (CDCl₃, 100MHz): δ 163.3, 156.2, 152.9, 147.2, 131.3, 127.6, 126.8, 122.1, 120.6, 119.8, 119.1, 110.5, 39.2, 34.4, 31.7, 29.9, 28.3, 27.6, 27.2, 22.5,

19.6, 14.1; MS (MALDI-TOF): *m/z* 2090.2 [M]⁺ (calcd for C₁₀₈H₁₂₆N₂O₈S₁₆ 2090.5); Anal. Calcd (%) for C₁₀₈H₁₂₆N₂O₈S₁₆: C 61.97, H 6.07, N 1.34; Found C 61.91, H 6.02, N 1.38.

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- [21] (a) Rehm, D.; Weller, A. *Isr J Chem* 1970, 8, 259; (b) For dyad **1**: $\Delta G_{PET} = -E_{ex} + E_{ox} - E_{red} - e^2/\epsilon r$, $E_{ox} = +0.58$ eV, $E_{red} = -0.60$ eV, $\lambda_{ex} = 540$, $e^2/\epsilon r = -0.1$ eV; For triad **2**: $E_{ox} = +0.56$ eV, $E_{red} = -0.61$ eV, $\lambda_{ex} = 540$, $e^2/\epsilon r = -0.1$ eV.