Synthesis, spectroscopic, and electrochemical properties of three tetrathiafulvalenes attached to perylene

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Abstract Three donor-acceptor dyads 1-3 comprising of a tetrathiafulvalene (*TTF*) unit linked with perylene by a simple σ -bond were synthesized and characterized. Spectroscopy and cyclic voltammetry provided an indication that intramolecular charge-transfer interactions in their ground states between *TTF* and perylene for dyads 1-3 are negligible. Compared with the compound perylene, dyads 1-3 exhibited large fluorescence quenching, which might be ascribed to photo-induced electron transfer interaction between *TTF* and perylene units in the excited state.

Keywords Donor–acceptor effects; Fluorescence spectroscopy; UV/Vis spectroscopy; Cyclic voltammetry; Tetrathiafulvalene.

Introduction

Since the discovery of donor and acceptor systems based on *TTF*–*TCNQ* [1] was first reported, tetra-thiafulvalene (*TTF*) and its derivatives have been extensively investigated as excellent electron donors

for the development of building blocks in electrical conductors and superconductors [2]. These molecular systems perform distinctively in their photophysical and electrochemical properties, which allow them to be widely studied on intramolecular charge-transfer interactions and photo-inducing electron-transfer processes. Ongoing research leaves potential applications open in materials science, including chemical sensors, molecular switches, molecular shuttles, organic ferromagnets, molecular rectifiers, molecular transistors, nonlinear optical materials, and photovoltaic materials [3–8].

One of the most interesting properties of TTF is that it can be oxidized successively and reversibly to the radical cation and dication species within a very accessible potential window. Consequently, the possibility of exploiting these multistage redox states $(TTF^{0}, TTF^{+}, TTF^{2+})$ was investigated to construct supramolecular systems that can be controlled by external stimuli [9]. The peculiar electronic properties of TTF were also opportunely applied to architecture molecular systems, especially TTF-based fluorescence-redox switches attaching different acceptors including phthalocyanine [10], porphyrin [11], anthrancene [12], or C_{60} [13], even highly fluorescent acceptor perylene-3,4,9,10-bis(dicarboximide) (PDI) [14]. While PDI involving fluorescence redox switch has been demonstrated in a PDI-TTF-PDI triad or

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Scheme 1

PDI-TTF dyads, it still has the problems in low solubility in most of organic solvents. Considering the difficulty to manipulate such insoluble materials, alkyl perylenes offer alternatives for exhibiting relatively high electron affinity as well. Perylene, which also possesses favorable photochemical properties, such as high fluorescent quantum yield and stability, was widely used in various fields, even including application as a probe by hybridization with a target *DNA* or *RNA* in biochemistry [15]. Considerable interest in perylene applications is now focused on organometallic materials but there are no reports on the *TTF*-perylene system.

In this work, we report the synthesis and electrochemical and spectroscopic properties of dyads 1-3 (Scheme 1), which present potential ability of being a new fluorescent redox dependent molecular system.

Results and discussion

Synthesis

The strategy to synthesize dyads 1-3 was through a deprotection/realkylation process: selective removal of 2-cyanoethyl protecting groups in 4 or 5 with the aid of CsOH \cdot H₂O and subsequent reaction with 3-(bromomethyl)perylene 9 as crucial alkylating agents (Scheme 2).

Cross-coupling reaction of **6** and **8** in the presence of $P(OEt)_3$ led to the precursor 2,3-bis(2-cyanoethylthio)-*TTF* **5** in 50% yield, and afterward it was deprotected by CsOH \cdot H₂O in anhydrate *DMF* and further reacted with *MeI* affording 2-(2-cyanoethylthio)-3-methylthio-*TTF* **4** in 80% yield. The key intermediate compounds **6–8** were synthesized according to reported procedures [16–18].



Reagents: (a) Br(CH₂)₆Br, MeCN; (b) BrCH₂CH₂CN, MeCN; (c) Hg(OAc)₂, CHCl₃/HOAc; (d) P(OEt)₃, toluene; (e) CsOH · H₂O/MeOH, DMF, MeI



Reagents: (f) POCl₃, DMF, o-dichlorobenzene; (g) NaBH₄/MeOH, THF; (h) PBr₃, CCl₄



On the other hand, new bromomethylperylene **9** was synthesized in a modified procedure (Scheme 3).

Formylation of perylene with $POCl_3/DMF$ gave compound **11** [19], which was reduced by sodium borohydride in methanol to afford hydroxymethylperylene **10**. After being treated with PBr₃ and subsequent simple purification, compound **9** was isolated. Because of the instability of **9** [20], it was used immediately to carry out the deprotection/realkylation procedure mentioned above to obtain target dyads **1–3**.

UV/Vis absorption

The absorption spectra of dyads **1–3** showed compared to compounds **9** and **4** in CH₂Cl₂ a wide absorption between 300–550 nm with the absorption maximum at $\lambda_{max} = 421$, 447, 397, 333 nm (Fig. 1). The *TTF* moiety absorbed strongly around 330 nm, and the perylene moiety showed strong absorption bands at 420 and 450 nm with a shoulder at 390 nm. These UV/Vis absorption spectra matched the profile offered by summation of the spectra of donor 4 and acceptor 9, and no new intramolecular charge-transfer absorption bands or unique shoulders were observed in the whole wavelength range. The results also indicated that no significant interactions between *TTF* and perylene units in the 300–550 nm range were arrested in the ground state.

Steady-state fluorescene

The fluorescence spectra were compared with the perylene, which is more suitable as reference than **9** due to its higher stability and higher fluorescence quantum yield. A mass quantitative quenching (*ca.* 80%) of the perylene moiety fluorescence emission was observed in dyad **1** (Fig. 2 and Table 1). Moreover, on comparison with dyad **1**, dyads **2** and **3** showed much weaker fluorescence intensities, but slight discrepancy in the shape. The fluorescence



Fig. 1 UV/Vis absorption spectra of dyads 1–3, reference compounds 4, 9, and perylene ($c = 1 \times 10^{-5} M$) in CH₂Cl₂



Fig. 2 Fluorescene spectra of dyads 1-3 ($c = 3 \times 10^{-6} M$), compounds 4, 9, and reference compound perylene ($c = 3 \times 10^{-6} M$) in CH₂Cl₂ excited at $\lambda_{exc} = 400$ nm

Table 1 Fluorescence quantum yield of 1–3, compound 9, and the reference compound perylene ($c = 1.0 \times 10^{-6} M$) in CH₂Cl₂ at rt

Reference	Quantum yield	
perylene	0.21 ± 0.02	
perylene	0.33 ± 0.02	
perylene	0.22 ± 0.03	
perylene	0.28 ± 0.01	
perylene	1	
	Reference perylene perylene perylene perylene perylene	

spectra of the three dyads with two bands around $\lambda_{\text{max}} = 450$ and 477 nm were indeed the mirror images of UV/Vis absorption spectrum of compound 9. No band was observed in the fluorescence spectrum of compound 4. These phenomena implied that the fluorescence spectra of dyads 1-3 were ascribed to their perylene unit. The reduction of fluorescence intensities of dyads 1-3 was the result of an intramolecular process because of slight change in either shape or intensity in the fluorescence spectrum of 9 by inducing a mixture of 4 and 9 (in 1:1 stoichiometry). In addition, a photo-induced electron transfer (PET) reaction between TTF and perylene moieties in dyads 1-3 might be one reason for fluorescence waning. And from Fig. 2, the low fluorescence intensity and low quantum yield of compound 9 were due to the bromine atom quenching effect.

Cyclic voltametry

The cyclic voltammograms of dyads 1-3 are shown in Fig. 3. The redox potentials of dyads 1-3, *TTF* 4-5, compound 9 are listed in Table 1.

TTF is well-known in respect of electrochemistry. Cyclic voltametry of dyad **1** showed two manifest and reversible one-electron *TTF* oxidation waves $(E_{1/2} = 0.63 \text{ and } 1.01 \text{ V})$. Three irreversible oneelectron waves from the perylene core (one oxida-



Fig. 3 Cyclic voltammogram of dyads 1-3 ($c = 1 \times 10^{-3} M$) using $n-Bu_4$ NPF₆ in CH₂Cl₂ as a supporting electrolyte, platinum wires as working and counter electrodes Ag/AgCl wire as a reference electrode, and a scan rate of 100 mV/sec

tion around 1.32 V, two reductions around -1.89 and -1.50 V) were detected. Comparing with compounds **4** and **9**, the oxidation peaks maintained at 0.63 and 1.01 V pertain to the *TTF* unit oxidized to the radical cation *TTF*⁺-perylene and dication *TTF*²⁺-perylene, while the irreversible oxidation peak was attributed to the oxidation of the perylene unit. Moreover, the irreversible reduction waves (-1.89 and -1.50 V) in dyad **1** were due to the reduction of the perylene unit. Dyads **2** and **3** have a similar electrochemistry character. The reversible reduction waves were ambiguous as some might occur above -2.0 V, which is the limit potential in our experimental condition.

TTF is an outstanding electron donor, which generates radical cation or dication species by removing one or two electrons. Its oxidation potentials lie lower than that of perylene, hence it should be possible to selectively oxidize the *TTF* preventing it (when it comes to oxidation) from acting as an electron donor and quenching perylene emission.

Table 2 Redox potentials of 1-3, TTF 4-5, and compound 9

Compound	$E_{1/2 \text{ red1}}/\mathrm{V}$	$E_{1/2 \text{ red2}}/\mathrm{V}$	$E_{1/2 \text{ ox}1}/\mathrm{V}$	$E_{1/2 \text{ ox} 2}/\mathrm{V}$	$E_{1/2 \text{ ox} 3}/\text{V}$
Dyad 1	-1.89	-1.50	0.63	1.01	1.32
Dyad 2	-1.79	-1.35	0.57	0.94	1.34
Dyad 3	-1.76	-1.58	0.61	1.00	1.49
4	_	_	0.64	1.02	_
5	_	_	0.60	0.99	_
9	-2.43	-1.96	_	-	_

Condition: Potentials vs. Ag/AgCl, scan rate of 100 mV/s, working electrode Pt, supporting electrolyte n-Bu₄NPF₆ in CH₂Cl₂

Properties of three tetrathiafulvalene attached to perylene

Experiment

¹H NMR spectra were obtained with a Bruker AM 500 spectrometer with tetramethylsilane as internal standard. Elemental analyses were performed on a Vario EL III (Elemental) instrument; their results agreed favourably with the calculated values. Mass spectra were obtained with an MA1212 instrument, MALDI-TOF spectra were recorded on a 4700-Propeotics analyzer, and UV/Vis spectra on a Varian Cary 500 spectrophotometer (1 cm quartz cell) at 25°C. Fluorescence emission spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell) at 25°C. Melting points were determined with a Fisher-Johns melting point apparatus. Cyclic voltammetry experiments were carried out with a computer-controlled BAS CV50W potentiostat at a scan rate of 100 mV/s in CH₂Cl₂ using BuNPF₆ as electrolyte, platinum as counter and work electrodes, and Ag/AgCl as reference electrode.

All solvents and chemicals were purchased from Shanghai reagent company and distilled over appropriate drying agents prior to use.

3-Formylperylene (11)

Perylene (2.52 g, 10 mmol) was added to a stirred mixture of 5 cm^3 anhydrous *o*-dichlorobenzene and 4.75 g anhydrous *DMF* (65 mmol), the reaction mixture was heated to 100°C, 3.07 g POCl₃ (20 mmol) were steadily added through a dropping funnel over a period of 30 min, and then stirred for an additional 2 h at the same temperature. The reaction mixture was cooled, and neutralized to Congo red by pouring into dilute aqueous sodium acetate and standing at 0°C for 3 h. The precipitate was filtered off, washed with $3 \times 30 \text{ cm}^3$ H₂O, and purified by column chromatography on silica gel with CHCl₃ as eluent. Compound **11** was obtained as orange-crystals (1.76 g, 62.8%), mp 233–235°C (Ref. [19] 236°C).

3-Hydroxymethylperylene (10)

A solution of sodium 0.074 g borohydride (2 mmol) in 5 cm³ absolute methanol was added dropwise to a stirred solution of 0.52 g 3-formylperylene **11** (1.86 mmol) in 100 cm³ anhydrous degassed THF at room temperature over a period of 2 h, then stirred for an additional 4 h. The solvent was evaporated under reduced pressure. The residue was dissolved in 100 cm³ CHCl₃ and washed with 3×50 cm³ H₂O. After drying (MgSO₄), the solvent was evaporated under reduced pressure, and the residue was subjected to silica column chromatography (CH₂Cl₂ as eluent) to afford yellow powder **10** (0.28 g, 53.5%), mp 204–207°C (Ref. [20] 208–210°C).

3-Bromomethylperylene (9, C₂₁H₁₃Br)

To a suspension of 0.42 g **10** (1.5 mmol) in 50 cm³ CCl₄ were added 0.49 g PBr₃ (1.8 mmol) at room temperature. The reaction mixture was heated to reflux for 2 h, the solution was evaporated under reduced pressured at room temperature, the residue was stirred with 40 cm³ absolute *Me*OH, whereupon the bromide precipitated. The mixture was filtered, and washed with 3×10 cm³ *Me*OH to obtain 0.37 g orange crystals (72.5%). MS(EI): m/z = 345; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.28 - 8.13$ (m, 4H, *Ar*-H), 7.90 (d, 1H, J = 7.9 Hz, *Ar*-

H), 7.74 (d, 2H, *J* = 8.0 Hz, *Ar*-H), 7.64 (t, 1H, *J* = 7.9 Hz, *Ar*-H), 7.56 (d, 1H, *J* = 7.6 Hz, *Ar*-H), 7.51 (m, 2H, *Ar*-H), 4.95 (s, 2H, alkyl–H) ppm.

2,3-Bis(2-cyanoethylthio)-6,7-bis(hexylthio)tetrathiafulvalene (5, $C_{24}H_{34}N_2S_8$)

Synthetic procedure in analogy to Ref. [16]. MS(EI): m/z = 606; ¹H NMR (500 MHz, CDCl₃): $\delta = 3.04$ (t, 4H, J = 7.8 Hz, S–CH₂–CH₂–CN), 2.81 (t, 4H, J = 7.3 Hz, S–CH₂–), 2.74 (2H, t, J = 7.4 Hz, S–CH₂–CH₂–CN), 1.72–1.58 (m, 4H, alkyl–H), 1.46–1.42 (m, 4H, alkyl–H), 1.30–1.25 (m, 8H, alkyl–H), 0.88 (t, 6H, J = 6.8 Hz, alkyl–CH₃) ppm.

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (4, C₂₂H₃₃NS₈)

Synthetic procedure in analogy to Ref. [15]. MS(EI): m/z = 567; ¹H NMR (500 MHz, CDCl₃): $\delta = 3.03$ (2H, t, J = 7.5 Hz, S–CH₂–CH₂–CN), 2.82 (4H, t, J = 7.3 Hz, S–CH₂–), 2.71 (2H, t, J = 7.1 Hz, S–CH₂–CN), 2.46 (s, 3H, S–CH₃), 1.72–1.58 (m, 4H, alkyl-H), 1.46–1.42 (m, 4H, alkyl–H), 1.30–1.25 (m, 8H, alkyl–H), 0.88 (6H, t, J = 6.7 Hz, alkyl–CH₃) ppm.

6,7-Bis(hexylthio)-3-methylthio-2-(3-perylenylmethylthio)-tetrathiafulvalene (1, $C_{40}H_{42}S_8$)

To a solution of 0.567 g 4 (1 mmol) in 50 cm^3 anhydrous degassed DMF was added a solution of $0.168 \text{ g CsOH} \cdot \text{H}_2\text{O}$ (1 mmol) in 5 cm^3 absolute degassed MeOH over a period of 30 min. The mixture was stirred for an additional 30 min, whereupon 0.345 g 3-bromomethylperylene (9) (1 mmol) in $20 \,\mathrm{cm}^3$ anhydrous *DMF* were introduced and orange solid started to precipitate. The mixture was stirred for an additional 6 h, stood for 4 h, and precipitate was filtered off, washed with $3 \times 10 \text{ cm}^3$ MeOH, and dried. Purification by column chromatography on silica gel with CH_2Cl_2 /petroleum ether (60–90°C) (1/1, v/v) as eluent, provided 0.23 g orange powder (29.6%), mp 107–110°C. MS(EI): m/z = 778; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.28 - 8.13$ (m, 4H, Ar-H), 7.96 (d, 1H, J = 7.8 Hz, Ar-H), 7.71 (d, 2H, J = 8.2 Hz, Ar-H), 7.64 (t, 1H, J = 7.9 Hz, Ar-H), 7.56 (d, 1H, J = 7.6 Hz, Ar-H), 7.51 (m, 2H, Ar-H), 4.95 (s, 2H, alkyl–H), 2.82 (4H, t, J=7.3 Hz, S-CH2-), 2.46 (s, 3H, S-CH3), 1.72-1.58 (m, 4H, alkyl-H), 1.46-1.42 (m, 4H, alkyl-H), 1.30-1.25 (m, 8H, alkyl-H), 0.88 (6H, t, J = 6.2 Hz, alkyl–CH₃) ppm.

6,7-Bis(hexylthio)-2,3-bis(3-perylenylmethylthio)-

tetrathiafulvalene ($\mathbf{2}, C_{60}H_{52}S_8$)

To a solution of 0.303 g **5** (1 mmol) in 30 cm³ anhydrous degassed *DMF* was added a solution of 0.235 g CsOH \cdot H₂O (1.4 mmol) in 5 cm³ absolute degassed *Me*OH over a period of 30 min. The mixture was stirred for an additional 30 min, whereupon 0.690 g 3-bromomethylperylene (**9**) (2 mmol) in 20 cm³ anhydrous *DMF* were introduced and an orange solid started to precipitate. After standing for 10 h, the precipitate was filtered off, washed with 3×10 cm³ *Me*OH, and dried. Purification by column chromatography on silica gel with CH₂Cl₂/petroleum ether (60–90°C) (1/1, v/v) as elu-

ent, gave 0.078 g orange powder (15.2%), mp 134–138°C. MS(EI): m/z = 1028; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.28-8.13$ (m, 4H, Ar-H), 7.96 (d, 1H, J = 7.8 Hz, Ar-H), 7.71 (d, 2H, J = 8.2 Hz, Ar-H), 7.64 (t, 1H, J = 7.9 Hz, Ar-H), 7.56 (d, 1H, J = 7.6 Hz, Ar-H), 7.51 (m, 2H, Ar-H), 4.95 (s, 2H, alkyl-H), 2.82 (4H, t, J = 7.3 Hz, S-CH₂-), 1.72–1.58 (m, 4H, alkyl-H), 1.46–1.42 (m, 4H, alkyl-H), 1.30–1.25 (m, 8H, alkyl-H), 0.88 (6H, t, J = 6.2 Hz, alkyl-CH₃) ppm.

3-(2-Cyanoethylthio)-6,7-bis(hexylthio)-2-(3-perylenylmethylthio)tetrathiafulvalene (**3**, C₄₂H₄₃NS₈)

The synthesis procedure was the same as that of **2** described above, just the molar ratio of **5** and **9** was 1:1. The product is an orange powder, yield: 17.1%, mp 162–164°C. MS(EI): m/z = 817; ¹H NMR (500 MHz, CDCl₃): $\delta = 8.28 - 8.13$ (m, 4H, Ar-H), 7.96 (d, 1H, J = 7.8 Hz, Ar-H), 7.71 (d, 2H, J = 8.2 Hz, Ar-H), 7.64 (t, 1H, J = 7.9 Hz, Ar-H), 7.56 (d, 1H, J = 7.6 Hz, Ar-H), 7.51 (m, 2H, Ar-H), 4.95 (s, 2H, alkyl-H), 2.81 (4H, t, J = 7.3 Hz, S-CH₂-), 2.74 (2H, t, J = 7.4 Hz, S-CH₂-CH₂-CN), 1.72-1.58 (m, 4H, alkyl-H), 1.46-1.42 (m, 4H, alkyl-H), 1.30-1.25 (m, 8H, alkyl-H), 0.88 (6H, t, J = 6.2 Hz, alkyl-CH₃) ppm.

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