Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 4843–4850

TETRAHEDRON

Donor–acceptor–donor triads incorporating tetrathiafulvalene and perylene diimide units: synthesis, electrochemical and spectroscopic studies

Xuefeng Guo,[a,b] Deqing Zhang,[a,*] Huijuan Zhang,[a] Qinghua Fan,[a] Wei Xu,[a] Xicheng Ai,[a] Louzheng Fan[c] and Daoben Zhu[a,*]

[a]*Laboratory of Organic Solids, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b]*Graduate School, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[c]*Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China*

Received 3 January 2003; revised 2 April 2003; accepted 28 April 2003

Abstract—Three donor–acceptor–donor triads **1–3** consisting of tetrathiafulvalene units attached to perylene diimides by flexible and rigid spacers were synthesized and characterized. UV/vis spectroscopic and cyclic voltammetric results indicate that they all show negligible intramolecular charge transfer interaction in their ground states. As compared to the reference compound **21**, triads **1–3** display reduced fluorescence and their fluorescence lifetimes are shortened, which is probably owing to the photoinduced electron transfer interactions between the PI units and TTF units. The different photophysical behaviors between **1** and **2** (and **3**) might be due to their difference in the spatial separation of TTF and PI units. It is preliminarily found that the steric hindrance of the groups attached to TTF units can affect their photostability. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Tetrathiafulvalene (TTF) and its derivatives have been extensively investigated as components of organic conductors and superconductors.[1] Meanwhile, on account of their reversible redox properties, TTF derivatives have also been used to construct supramolecules for studies of molecular-based devices, especially in recent years.[2–4] Many electron donor–acceptor supramolecules with TTF units have been prepared for studies related to intramolecular photoinduced electron transfer processes, intramolecular charge-transfer interactions and construction of molecular rectifiers.[5] Various electron acceptor groups have been covalently attached to TTF: fullerene,[6–8] pyromellitic diimide,[9,10] quinones,[6,11,12] tetracyanoanthraquinodimethane,[6] thioindigo,[13] polynitrofluorene,[15] viologen and related ones.[6,9,14] Perylene diimide (PI) as a moderate two-electron acceptor has been also employed in donor–acceptor supramolecules, because of the characteristic absorption bands of its radical ions. For instance, Wasielewski et al. once reported a light intensity-dependent molecular switch on a picosecond time scale based on an electron donor–acceptor–donor triad consisting of two porphyrin donors and one PI unit.[16] Thus, it would be interesting to study electron–donor–acceptor supramolecules containing both TTF and PI units. For this purpose, electron donor–acceptor–donor triads **1–3** (Scheme 1) containing two TTF and one PI units were synthesized. The two TTF units are linked to the PI unit by a flexible spacer [$-(CH_2)_{12}-$] in **1**, while a more rigid spacer [$-CH_2CH(CH_2CH_2)_2CHCH_2-$] is used to connect two TTF units and PI unit in **2** and **3**. Different end groups are attached to two TTF units: *n*-hexyl group for **1**, 2-ethylbutyl group for **2** and G2 dendritic group for **3**.[17] Herein we describe the synthesis, electrochemical and spectroscopic studies of triads **1–3**.

2. Results and discussions

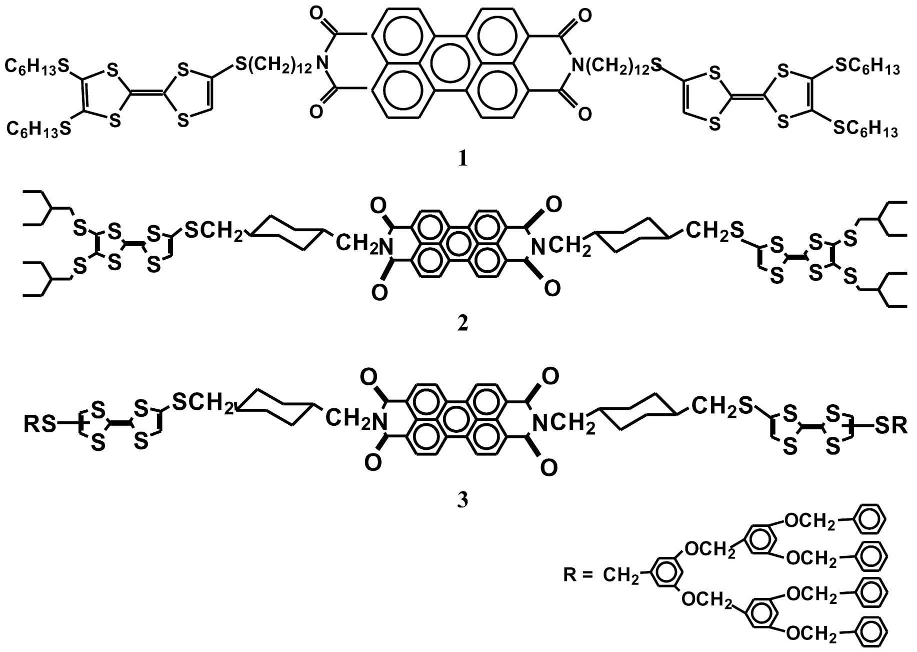
2.1. Synthesis

The usual approach to perylene diimide derivatives is by the reaction of primary amines with perylene tetracarboxylic acid bisanhydride. This strategy requires the preparation of TTF derivatives with primary-amine groups (TTF-amines). Becher et al once reported the preparation of TTF-amines using the classic Gabriel transformation.[10] Here we present a new facile route to TTF-amines by using the unusual reaction of $TBA_2[Zn(DMIT)_2]$ reported recently by us.[18]

Keywords: donor–acceptor systems; tetrathiafulvalene; perylene diimide; photoinduced electron transfer.

* Corresponding authors. Tel.: +86-10-62639355; fax: +86-10-62559373; e-mail: dqzhang@iccas.ac.cn

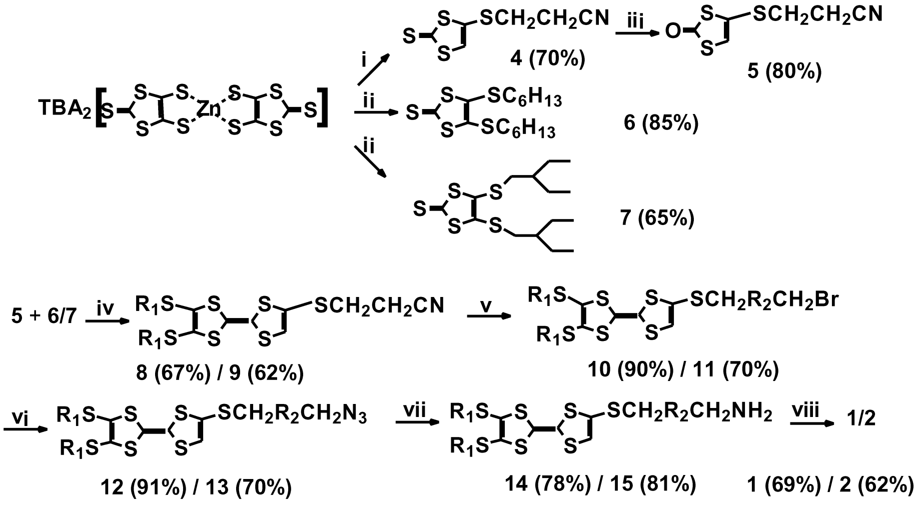
doi:10.1016/S0040-4020(03)00700-2



Scheme 1.

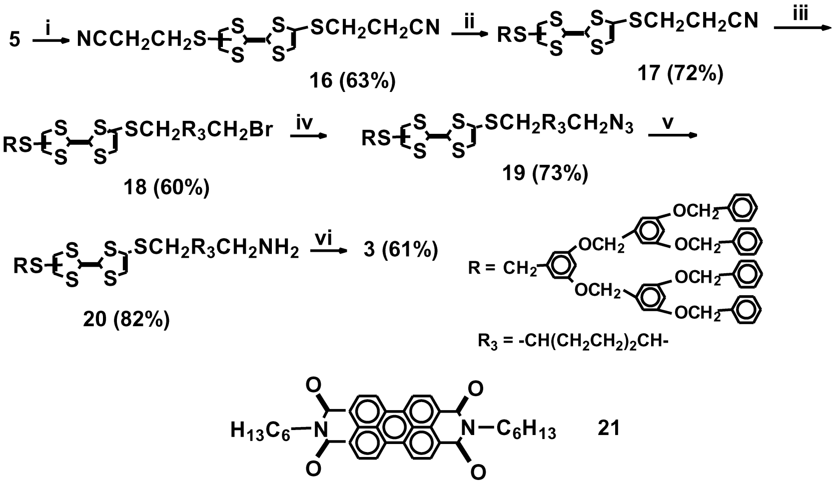
The key intermediate compound 4-(2-cyanoethyl)thio-1,3-dithiole-2-thione (**4**) was easily synthesized starting from $TBA_2[Zn(DMIT)_2]$ and 3-bromopropionitrile in the presence of pyridine hydrogen chloride.[18] Compound **4** was converted to **5** using conventional methods in high yield (Scheme 2). Cross-coupling of **5** with **6** and **7**, which can be easily accessible from $TBA_2[Zn(DMIT)_2]$,[19] in the presence of tri(isopropyl)phosphite, led to compounds **8** and **9** in yields of 67 and 62%, respectively. After removal of 2-cyanoethyl groups from **8** and **9**, followed by the reaction with dibromoelectrophiles, which were used in large excess, compounds **10** and **11** were obtained in yields of 70 and 91%, respectively. Direct reaction of **10** and **11** with large excess of NaN_3 in dry DMF afforded **12** and **13** respectively in high yield. Reduction of compounds **12** and **13** in THF with PPh_3 gave the TTF-amines **14** and **15**, which were purified by column chromatography, followed by recrystallization from CH_2Cl_2/petroleum ether. Triads **1** and **2** were obtained by the reaction of perylene tetracarboxylic acid bisanhydride with compounds **14** and **15**, respectively, catalyzed by $Zn(Ac)_2{\cdot}2H_2O$ in quinoline under an atmosphere of dry N_2 at 160°C.

Triad **3** was prepared in a slightly different way as shown in Scheme 3. Self-coupling of compound **5** in the presence of tri(isopropyl)phosphite gave compound **16** with *cis*/*trans* isomers. Deprotection of one cyanoethyl group from **16** by controlling the reaction conditions and further reaction with



8,10,12,14: $R_1 = -C_6H_{13}$, $R_2 = -(CH_2)_{10}-$
9,11,13,15: $R_1 = -CH_2CH(CH_2CH_3)_2$, $R_2 = -CH(CH_2CH_2)_2CH-$

Scheme 2. *Reagents*: (i) $BrCH_2CH_2CN$, pyridinehydrochloride/CH_3CN; (ii) $C_6H_{13}Br$ or $BrCH_2CH(CH_2CH_3)_2/CH_3CN$; (iii) $Hg(OAc)_2$, CH_2Cl_2; (iv) tri(*i*-propyl)phosphite, 120°C; (v) $CsOH{\cdot}H_2O$, THF, $Br(CH_2)_{12}Br/BrCH_2CH(CH_2CH_2)_2CHCH_2Br$; (vi) DMF, NaN_3; (vii) PPh_3/H_2O, THF; (viii) perylene tetracarboxylic acid dianhydride, $Zn(Ac)_2{\cdot}2H_2O$, quinoline, N_2, 160°C.



Scheme 3. *Reagents*: (i) tri(*i*-propyl)phosphite, toluene, 120°C; (ii) $CsOH\cdot H_2O$, THF, G2-bromodendrimer; (iii) $CsOH\cdot H_2O$, THF, $BrCH_2CH(CH_2CH_2)_2$-CH_2Br; (iv) DMF, NaN_3; (v) PPh_3/H_2O, THF; (vi) perylene tetracarboxylic acid dianhydride, DMF, N_2, 120°C.

one G2-dendrimer featuring benzyl bromide group afforded compound **17**. Starting from compound **17**, the TTF-amine compound **20** was obtained following the same approaches as for compounds **14** and **15**. The condensation reaction between **20** and perylene tetracarboxylic acid bisanhydride, however, failed to give triad **3** by using the same condition as for triads **1** and **2**. Fortunately, direct reaction of **20** with perylene tetracarboxylic acid bisanhydride in dry DMF without any catalyst at 120°C overnight yielded the target triad **3**[20] in moderate yield after careful purification by column chromatography.

For comparative studies, reference compound *N*,*N*-dihexyl perylene diimide **21** was prepared and characterized with similar approaches.

2.2. UV/vis absorption spectra and cyclic voltammetric studies

Figure 1 shows the absorption spectra of triads **1**–**3** together with those of the reference compounds **8** and **21** for comparison.[21] No new absorption bands or distinctive spectroscopic shoulders were detected in the UV/vis spectra of triads **1**–**3** as compared to the corresponding spectra of the reference compounds **8** and **21**. This fact indicates that intramolecular charge-transfer interactions for triads **1**–**3** in their ground states are negligible. The mixture of reference compounds **8** and **21** in solution (in a molar ratio of 1:1; 2.1×10^{-3} M for both **8** and **21**) shows a characteristic charge-transfer absorption band with a maximum at 615 nm. As expected, such an intermolecular charge-transfer absorption is strongly affected by the concentrations of the reference compounds **8** and **21**. Therefore, it might be concluded that the spatial separation of electron donor and acceptor units is the main reason for the negligible charge-transfer interaction in triads **1**–**3**.[22]

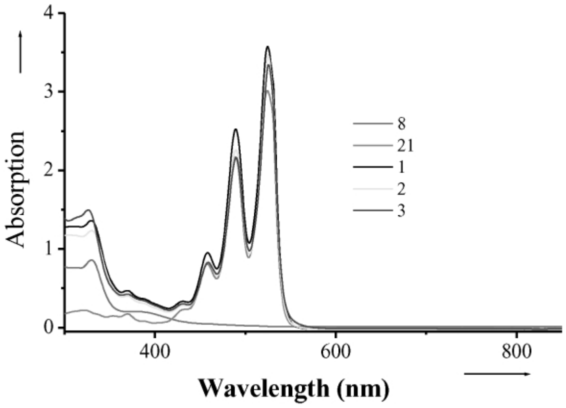


Figure 1. UV/vis absorption spectra of **1**–**3**, **8** and **21** (5.0×10^{-5} M) in trichloromethane.

Further insight into the electronic properties of these compounds was gained by cyclic voltammetry. Table 1 lists the redox potentials of triads **1**–**3** together with those of the reference compounds **8** and **21** for comparison. Triads **1**–**3** show almost the same reduction potentials at ca. −0.67 and −0.85 V, and oxidation potentials at ca. 0.47 and 0.85 V. Obviously, their reduction potentials are very close to those of the reference compound **21** (−0.67 and −0.85 V), and their oxidation potentials are almost the same as those of the reference compound **8** (0.47 and 0.85 V). Thus, the TTF and PI units in triads **1**–**3** can be treated independently. This result is consistent with the UV/vis spectral studies as mentioned above.

In addition, TTF units absorb strongly around 320 nm, while PI unit shows strong absorption bands from 420 to 550 nm. Hence, it is possible to selectively excite TTF and PI units. Therefore, triads **1**–**3**, in which no distinctive charge-transfer interactions are found, are good examples for studies of photoinduced electron transfer processes.

Table 1. Redox potentials of **1**–**3** (potentials vs. Ag/AgCl, scan rate 0.1 V s^{-1}, work electrode Pt, supporting eletrolyte NBu_4PF_4 in trichloromethane)

	$E^{1}_{1/2}$/V (Re.)	$E^{2}_{1/2}$/V (Re.)	$E^{1}_{1/2}$/V (Ox.)	$E^{2}_{1/2}$/V (Ox.)
1	−0.67	−0.85	0.48	0.86
2	−0.67	−0.85	0.47	0.83
3	−0.68	−0.86	0.47	0.85
8			0.47	0.85
21	−0.67	−0.85		

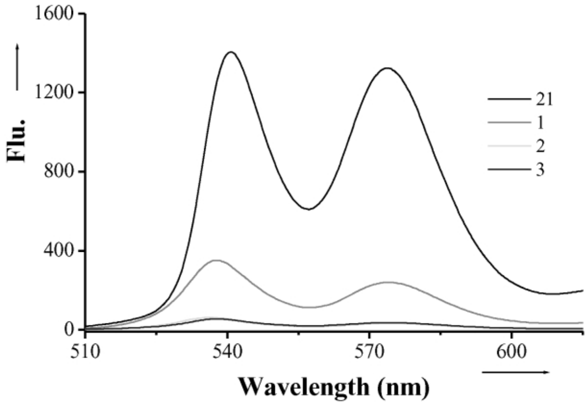


Figure 2. Fluorescence spectra of **1–3** and **21** (5.0×10^{-5} M) in trichloromethane excited at 480 nm.

2.3. Fluorescence spectral studies

The fluorescent spectra of triads **1–3** are shown in Figure 2. For comparison, the fluorescent spectrum of compound **21** is also included in Figure 2. Clearly, except for the intensity difference the fluorescent spectra of triads **1–3** are very similar to that of compound **21** (for triads **2** and **3** the fluorescent spectra are almost coincident). Their fluorescence spectra with two bands at λ_{max}=540 and 574 nm are indeed the mirror images of UV/vis absorption spectrum of compound **21** (see Figures 1 and 2). These results imply that the fluorescence of triads **1–3** is due to the PI units. As compared to that of compound **21**, the fluorescent intensities of triads are reduced. Moreover, on comparison with triad **1**, triads **2** and **3** show much lower fluorescence intensities, but the fluorescence intensities of triads **2** and **3** are almost the same.

The fluorescence lifetimes of triads **1–3** were measured by time-resolved fluorescence spectroscopy. Their fluorescence decay curves (Fig. 3) can be well fitted by single-exponential forms, and their fluorescence lifetimes were deduced: 1.01 ns for **1**, 195 ps for **2** and 178 ps for **3**. For comparative studies, the fluorescence lifetime of compound **21** was also measured (3.66 ns). Similar to the fluorescence intensity reduction from compound **21** to triads **1–3**, their fluorescence lifetimes show the same tendency.

We prefer to ascribe the photophysical properties of triads **1–3** (fluorescence intensity reduction and shorter fluorescence lifetimes) to photoinduced electron transfer reaction between the PI units and TTF units in triads **1–3** because of the following facts: (1) ΔG values[23] for the photoinduced electron transfer reactions are negative, and thus these reactions are thermodynamically favorable; (2) there is no spectral overlap between the absorption spectrum of TTF units and fluorescence spectrum of PI unit. Hence, the energy transfer process due to the Förster mechanism will be prohibited.[24] Time-resolved absorption spectral studies (detection of absorption of radical anions of the PI unit and absorption of radical cations of the TTF unit) will be needed to provide further evidence for the above assumption. The different photophysical behavior between **1** and **2** (and **3**) may be due to the difference in spatial separation between TTF and PI units: 25 Å for **1**; 12 Å for **2**; 12 Å for **3**.[22]

If the TTF units of **1–3** are oxidized chemically or electrochemically, the photoinduced electron-transfer from TTF to PI units would be hindered. As a result, the fluorescence of **1–3** would be enhanced. Indeed, this approach has been pursued in recent years for the construction of new molecular switches.[25] Unfortunately, treatment of the solutions of **1–3**, respectively with 2 equiv. of $Fe(ClO_4)_3$ did not result in fluorescence enhancement. As an example, Figure 4 shows the fluorescence spectra of **2** before and after oxidation by 2 equiv. of $Fe(ClO_4)_3$. This result should be ascribed to the following facts: (1) the TTF radical cation shows broad absorption in the wavelength range of 580–800 nm as indicated in the inset of Figure 4, which is in accordance with the previous report;[26] (2)

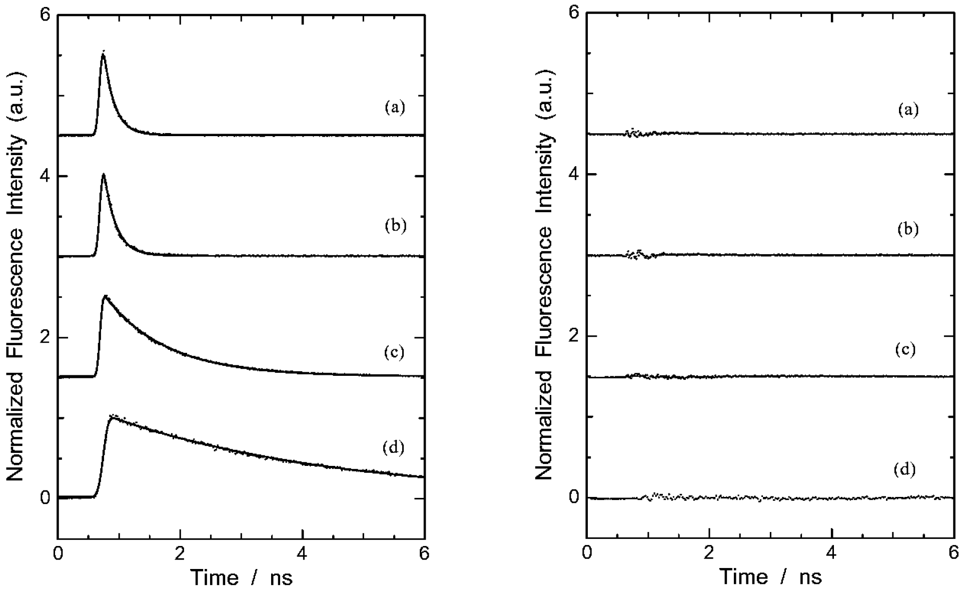


Figure 3. Time-resolved fluorescence decay curves of triads **3** (a), **2** (b), **1** (c) and the reference compound **21** (d): the experimental and fitting curves are left; the residual curves are right. The excitation wavelength is 480 nm.

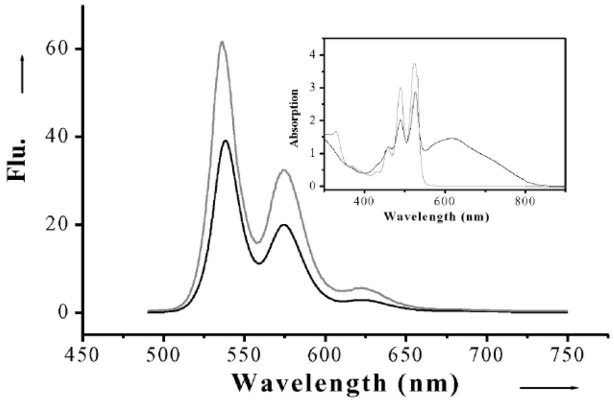


Figure 4. Fluorescence spectra of triad **2** (5.0×10^{-5} M) before (red) and after addition of 2 equiv. of $Fe(ClO_4)_3$ (black) in trichloromethane excited at 480 nm. Inset: UV/vis absorption spectra of triad **2** (5.0×10^{-5} M) before (red) and after addition of 2 equiv. of $Fe(ClO_4)_3$ (black) in trichloromethane.

obviously, there is large spectral overlap between the absorption spectrum of the TTF radical cation and the fluorescence spectrum of the PI unit, and hence intramolecular energy transfer can take place effectively between the PI unit and TTF cation. Consequently, the fluorescence of the PI unit of **1**–**3**, which would be increased by oxidation of TTF units, was quenched due to the energy transfer between the PI unit and TTF cation.

In addition, it was found that dark-colored precipitates[27] occurred after the trichloromethane solution of **1** (5.2×10^{-3} M) was irradiated by normal sunlight for 4 h. It was also observed that the ^{1}H NMR signal at 6.31 ppm (the olefinic hydrogen of TTF units) disappeared and other signals became broad after the d-trichloromethane solution of **1** in a normal NMR tube was left under sunlight for 4 h. In contrast, after leaving the solution of **1** in darkness for 10 days, the ^{1}H NMR spectrum of **1** remained unchanged and no colored precipitates were detected. In comparison, under the same conditions, the solution of **2** was unchanged after sunlight irradiation for about 5 h. Interestingly, no change was observed for the solution of **3** even after exposure to sunlight for 20 h. The formation of colored precipitates and the change of its ^{1}H NMR spectrum for **1** after sunlight irradiation are probably owing to the generation of radical ions (e.g. $TTF^{\cdot+}$–$PI^{\cdot-}$–TTF) by photoinduced electron transfer reaction. These radical ions tend to aggregate in solution, probably due to π–π interactions which may lead to formation of dark-colored precipitates. The incorporation of steric groups such as the 2-ethylbutyl group in **2** and the G2 dendritic group in **3** will reduce the tendency of such aggregation, and hence improve their photostability. Detailed investigations in this respect are underway.

2.4. Summary

Three donor–acceptor–donor triads **1**–**3** each containing two TTF units and one PI unit were synthesized and characterized. They all show negligible intramolecular charge transfer interactions in their ground states. Probably due to photoinduced electron transfer interactions, their fluorescences were partially quenched. The different photophysical behaviors between **1** and **2** (and **3**) might be due to their difference in the spatial separation of TTF and PI units. Preliminary results imply that incorporation of groups with steric hindrance into TTF units may improve the photostability of such triads. Therefore, triads with structures similar to **1**–**3** are worthwhile for further investigations, which may lead to the design and construction of new fast molecular switches.

3. Experimental

3.1. General

Melting points were measured with an XT_4-100X apparatus and uncorrected. ^{1}H NMR spectra were recorded with Bruker 300 MHz or Varian 200 MHz spectrometers. All chemical shifts were quoted in ppm relative to TMS. Infrared spectra were obtained on a Perkin–Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with AEI-MS50-MS or MALDI-TOF-MS. Elemental analysis was performed on Carlo-Erba-1106 instrument. Absorption spectra were measured with Hitachi (model U-3010) UV–Vis spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) Spectrophotometer in a 1-cm quartz cell. Cyclic voltammetric experiments were performed on an EGDG PAR 370 system at a scan rate of 100 mV in $CHCl_3$ using Bu_4NPF_6 as electrolyte, platinum as counter and work electrodes and Ag/AgCl as reference electrode. Time-resolved fluorescence decay spectra were measured with a picosecond time-correlated single-photo counting system. A regeneratively amplified Ti: Sapphire laser (Tsunami, Spectra Physics) pumped by a mode-locked argon ion laser (Beamlock, Spectra Physics) was used as a light source to produce a laser pulse at 800 nm (Fwhm=120 fs, 1 kHz, 0.5 mJ). It was tuned to 480 nm through optical parametric amplifier (OPA-800C, Spectra Physics) and was focused onto the sample with pump energy 1.5 μJ. The resulting fluorescence was collected into a multichromator (Hamamatsu C5094) and detected with a streak camera (Hamamatsu C2909). The instrumental response time was about 30 ps. The software used to fit the fluorescence decay curves was compiled based on Matlab 5.2 (Mathworks).

THF was distilled from sodium/benzophenone immediately prior to use. DMF was pre-dried by standing over molecular sieves (4 Å) for at least 3 days before use. Pyridine hydrogen chloride, 1,12-dibromodecane, and 1,4-cyclohexanedimethanol were purchased from Acros Chemicals. 1,4-cyclohexanedibromomethane was prepared from 1,4-cyclohexanedimethanol according to Ref. 28, and $TBA_2[Zn(DMIT)_2]$ was prepared according to Ref. 29. All other reagents and solvents (standard grade) were used as received unless otherwise stated. All reactions involving compounds containing TTF units were carried out under an atmosphere of dry N_2.

3.1.1. Compound 5. To a solution of 4-(2-cyanoethythio)-1,3-dithole-2-thione[18] (0.27 g. 1.23 mmol) in dichloromethane (45 mL) was added mercuric acetate (1.18 g, 3.69 mmol), and the resulting white suspension was stirred under N_2 for 2 h at room temperature. The resulting voluminous white precipitate was removed by filtration using celite and washed thoroughly with dichloromethane.

The combined organic phases were concentrated in vacuum, and then the remaining solid was subjected to crystallization from dichloromethane and petroleum ether to give the compound **5** (0.20 g, 80%) as colorless needles, mp 56–57°C. [Found: C, 35.29; H, 2.37; N, 6.77. $C_6H_5NOS_3$ requires C, 35.45; H, 2.48; N, 6.89%]; ν_{max} (KBr, cm^{-1}) 2247 (–CN); 1632 (–C=O). δ_H (200 MHz, $CDCl_3$) 2.75 (2H, t, *J*=6.8 Hz, CH_2S), 3.06 (2H, t, *J*=6.8 Hz, CH_2CN), 7.12 (1H, s, olefinic); MS (EI): M^+, found 203. $C_6H_5NOS_3$ requires 203.

3.1.2. Compound 8. A solution of compound **5** (0.50 g, 2.46 mmol) and compound **6** (2.7 g, 7.39 mmol)[19] in triisopropyl phosphite (20 mL) was heated to 120°C under N_2 and stirred at this temperature for 3 h. Column chromatography of the crude reaction mixture, after removing the excess triisopropyl phosphite under reduced pressure, on silica gel with CH_2Cl_2/petroleum (60–90°C) (1:3, v/v) as eluant afforded compound **8** as an orange oil (0.86 g) in 67% yield. [Found: C, 48.41; H, 6.03; N, 2.73. $C_{21}H_{31}S_7N$ requires C, 48.33; H, 5.99; N, 2.68%]; ν_{max} (KBr, cm^{-1}) 2249 (–CN); δ_H (200 MHz, $CDCl_3$) 6.55 (1H, s, olefinic), 2.96 (2H, t, *J*=6.4 Hz, CH_2CN), 2.82 (4H, t, *J*=5.2 Hz, $2SCH_2$), 2.70 (2H, t, *J*=6.4 Hz, SCH_2), 1.60–1.20 (16H, br, $8CH_2$); 0.89 (6H, t, *J*=4.6 Hz, $2CH_3$); MS (EI): M^+, found 521. $C_{21}H_{31}S_7N$ requires 521.

3.1.3. Compound 9. This was prepared in a similar manner from **5** and **7**[19] as an orange oil in 62% yield. [Found: C, 48.32; H, 6.03; N 2.59. $C_{21}H_{31}S_7N$ requires C, 48.33; H, 5.99; N, 2.68%]; ν_{max} (KBr, cm^{-1}) 2252 (–CN); δ_H (300 MHz, $CDCl_3$) 6.58 (1H, s, olefinic), 2.96 (2H, t, *J*=6.8 Hz, CH_2CN), 2.83 (4H, d, *J*=4.8 Hz, $2SCH_2$), 2.70 (2H, t, *J*=6.8 Hz, SCH_2), 1.46 (10H, m, $4CH_2$+$2CH$), 0.89 (12H, t, *J*=7.2 Hz, $4CH_3$); MS (EI): M^+, found 521. $C_{21}H_{31}S_7N$ requires 521.

3.1.4. Compound 10. To a solution of **8** (1.00 g, 1.92 mmol) in anhydrous degassed THF (80 mL) was added a solution of $CsOH\cdot H_2O$ (0.48 g, 2.85 mmol) in anhydrous degassed MeOH (30 mL) over a period of 30 min. The mixture was stirred for an additional 30 min whereupon a solution of 1,12-dibromododecane (1.25 g, 3.81 mmol) in anhydrous degassed THF (30 mL) was added. The solution was stirred overnight. After separation by column chromatography compound **10** was obtained (1.23 g) in 90% yield. [Found: C, 50.70; H, 7.30. $C_{30}H_{51}S_7Br$ requires C, 50.32; H, 7.18%]; ν_{max} (KBr, cm^{-1}): 2954, 2926, 2854 (alkyl C–H); δ_H (300 MHz, $CDCl_3$) 6.32 (1H, s, olefinic), 3.40 (2H, t, *J*=6.2 Hz, CH_2Br), 2.80 (6H, m, $3SCH_2$), 1.82 (2H, m, CH_2); 1.59 (8H, m, $4CH_2$), 1.39 (26H, br, $13CH_2$), 0.89 (6H, t, *J*=6.4 Hz, $2CH_3$). MS (MALDI-TOF): M^+, found 714.3 (716.3). $C_{30}H_{51}S_7Br$ requires 714.1 (716.1).

3.1.5. Compound 11. This was obtained similarly from **9** and 1,4-cyclohexanedibromomethane as an orange oil in 70% yield. [Found: C, 47.20; H, 6.14. $C_{26}H_{41}S_7Br$ requires C, 47.46; H, 6.28%]; ν_{max} (KBr, cm^{-1}): 2960, 2921 (alkyl C–H). δ_H (300 MHz, $CDCl_3$) 6.31 (1H, s, olefinic), 3.30 (2H, d, *J*=6.5 Hz, CH_2Br), 2.80 (4H, d, *J*=5.8 Hz, $2SCH_2$), 2.65 (2H, d, *J*=6.8 Hz, SCH_2), 1.94 (4H, br, alkyl-H), 1.43 (12H, br, alkyl-H), 0.90 (16H, br, alkyl-H); MS (MALDI-TOF): M^+, found 655.9 (657.9). $C_{26}H_{41}S_7Br$ requires 656.0 (658.0).

3.1.6. Compound 12. A solution of **10** (1.30 g, 1.80 mmol) in dry DMF (50 mL) was treated with NaN_3 (2.13 g, 3.28 mmol) at 25°C under N_2. The resulting reaction mixture was warmed at 80°C for 12 h before 30 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3×50 mL), and the combined extracts were washed with H_2O (2×50 mL) and saturated aqueous NaCl (20 mL), dried ($MgSO_4$) and concentrated in vacuo. After column chromatography on silica gel with CH_2Cl_2/petroleum (60–90°C) (1:4, v/v) as eluant, **12** was obtained as an orange oil (1.11 g) in 91% yield. [Found: C, 53.45; H, 7.86; N, 6.36. $C_{30}H_{51}S_7N_3$ requires C, 53.13; H, 7.58; N, 6.20%]; ν_{max} (KBr, cm^{-1}) 2094 ($-N_3$); δ_H (300 MHz, $CDCl_3$) 6.25 (1H, s, olefinic), 3.19 (2H, t, *J*=6.3 Hz, CH_2N_3); 2.74 (6H, m, $3SCH_2$), 1.55 (10H, br, $5CH_2$), 1.29 (26H, br, $13CH_2$), 0.83 (6H, t, *J*=6.4 Hz, $2CH_3$); MS (MALDI-TOF): M^+, found 677.5. $C_{30}H_{51}S_7N_3$ requires 677.2.

3.1.7. Compound 13. This was obtained similarly from **11** as an orange oil in 70% yield. [Found: C, 50.74; H, 6.88; N, 7.02. $C_{26}H_{41}S_7N_3$ requires C, 50.36; H, 6.66; N, 6.78%]; ν_{max} (KBr, cm^{-1}) 2095 ($-N_3$). δ_H (300 MHz, $CDCl_3$) 6.33 (1H, s, olefinic), 3.18 (2H, d, *J*=6.6 Hz, CH_2N_3), 2.84 (4H, d, *J*=5.0 Hz, $2SCH_2$), 2.67 (2H, d, *J*=6.8 Hz, SCH_2), 1.88 (4H, m, alkyl-H), 1.47 (12H, m, alkyl-H), 1.06 (4H, m, alkyl-H), 0.94 (12H, m, $4CH_3$); MS (MALDI-TOF): M^+, found 619.1. $C_{26}H_{41}S_7N_3$ requires 619.1.

3.1.8. Compound 14. A solution of **12** (1.20 g, 1.77 mmol) in THF (60 mL) was treated with PPh_3 (0.93 g, 3.54 mmol) and H_2O (318 μL, 17.7 mmol) at 25°C under N_2. The resulting reaction mixture was warmed at 45°C for 10 h. The solvents were removed in vacuo and the residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluant to afford compound **14** as an orange oil (0.90 g) in 78% yield. [Found: C, 55.35; H, 8.17; N, 2.02. $C_{30}H_{53}S_7N$ requires C, 55.25; H, 8.19; N, 2.15%]; ν_{max} (KBr, cm^{-1}) 3320, 3307 ($-NH_2$); δ_H (300 MHz, $CDCl_3$) 6.32 (1H, s, olefinic), 2.81 (6H, m, $3SCH_2$), 2.68 (2H, t, *J*=6.8 Hz, NCH_2), 1.63 (10H, m, $5CH_2$), 1.27 (28H, br, $13CH_2$+NH_2), 0.89 (6H, t, *J*=6.3 Hz, $2CH_3$). MS (MALDI-TOF): M^+, found 651.4. $C_{30}H_{53}S_7N$ requires 651.2.

3.1.9. Compound 15. This was synthesized in a similar manner from **13** as an orange oil in 81% yield. [Found: C, 52.01; H, 7.14; N, 2.20. $C_{26}H_{43}S_7N$ requires C, 52.57; H, 7.30; N, 2.36%]; ν_{max} (KBr, cm^{-1}) 3445, 3315 ($-NH_2$); δ_H (300 MHz, $CDCl_3$) 6.28 (1H, s, olefinic), 2.79 (4H, d, *J*=5.3 Hz, $2SCH_2$), 2.63 (2H, d, *J*=6.8 Hz, SCH_2), 2.51 (2H, d, *J*=6.4 Hz, CH_2N), 1.89 (4H, br, alkyl-H), 1.40 (14H, br, alkyl-H+NH_2), 0.89 (16H, br, alkyl-H); MS (MALDI-TOF): M^+, found 593.2. $C_{26}H_{43}S_7N$ requires 593.1.

3.1.10. Triad 1. Perylene-1,4,5,8-tetracarboxylic acid dianhydride (0.08 g, 0.20 mmol) was mixed with **14** (0.31 g, 0.47 mmol) and zinc acetate (0.043 g, 0.20 mmol) in quinoline (10 mL), and the mixture was stirred at 160°C for 3–4 h under N_2. The reaction mixture was cooled down to room temperature and poured into HCl (1 M, 100 mL).

The resulting precipitate was collected on a glass filter funnel, washed with water (50 mL) and methanol (20 mL), then purified by column chromatography on silica gel with $CHCl_3/CH_3OH$ (100:1, v/v) as eluant. After removing the solvents in vacuo, the remaining solid was crystallized from CH_2Cl_2/petroleum ether to afford the product as a red powder (0.23 g) in 69% yield: mp 169–170°C. [Found: C, 60.76; H, 6.73; N, 1.86. $C_{84}H_{110}S_{14}O_4N_2$ requires C, 60.75; H, 6.68; N, 1.69%]; ν_{max} (KBr, cm^{-1}) 1695, 1657, 1594, 1346 (–CON–); δ_H (300 MHz, $CDCl_3$) 8.66 (4H, d, *J*=7.9 Hz, Ar-H), 8.56 (4H, d, *J*=8.0 Hz, Ar-H), 6.30 (2H, s, olefinic), 4.20 (4H, t, *J*=7.6 Hz, 2C*H*$_2$N), 2.77 (12H, m, 6SC*H*$_2$), 1.81 (4H, m, 2C*H*$_2$), 1.64 (16H, m, 8C*H*$_2$), 1.37 (52H, m, 26C*H*$_2$), 0.89 (12H, t, *J*=6.4 Hz, 4C*H*$_3$); MS (MALDI-TOF): M^+, found 1658.5. $C_{84}H_{110}S_{14}O_4N_2$ requires 1658.5.

3.1.11. Triad 2. This was obtained in a similar manner from **15** and Perylene-1,4,5,8-tetracarboxylic acid dianhydride as a red powder in 62% yield: mp >280°C. [Found: C, 58.90; H, 5.92; N, 1.96. $C_{76}H_{90}S_{14}O_4N_2$ requires C, 59.11; H, 5.87; N, 1.81%]; ν_{max} (KBr, cm^{-1}) 1695, 1657, 1594, 1343 (–CON–); δ_H (300 MHz, $CDCl_3$) 8.70 (4H, d, *J*=8.0 Hz, Ar-H), 8.63 (4H, d, *J*=8.1 Hz, Ar-H), 6.31 (2H, s, olefinic), 4.14 (4H, d, *J*=7.0 Hz, 2C*H*$_2$N), 2.83 (8H, d, *J*=4.3 Hz, 4SC*H*$_2$), 2.63 (4H, d, *J*=6.7 Hz, 2SC*H*$_2$), 1.94 (8H, m, alkyl-H), 1.45–1.21 (24H, m, alkyl-H), 0.89 (32H, m, alkyl-H); MS (MALDI-TOF): M^+, found 1542.6. $C_{76}H_{90}S_{14}O_4N_2$ requires 1542.3.

3.1.12. Compound 16. To a solution of compound **5** (0.20 g, 0.98 mmol) in toluene (10 mL) was added triisopropyl phosphite (2 mL). The resulting suspension was heated to 120°C under N_2 and stirred at this temperature for 3 h. Column chromatography of the crude reaction mixture, after removing the excess triisopropyl phosphite under reduced pressure, on silica gel with CH_2Cl_2/petroleum (60–90°C) (1:2, v/v) as eluant afforded compound **16** as a yellow powder (0.12 g) in 63% yield: mp 114–115°C. [Found: C, 38.08; H, 2.66; N, 7.46. $C_{12}H_{10}S_6N_2$ requires C, 38.48; H, 2.69; N, 7.48%]; ν_{max} (KBr, cm^{-1}) 2248 (–CN); δ_H (300 MHz, $CDCl_3$) 6.29 (2H, s, olefinic), 3.04 (4H, t, *J*=8.4 Hz, 2C*H*$_2$CN), 2.72 (4H, t, *J*=8.4 Hz, 2SCH$_2$); MS (EI): M^+, found 374. $C_{12}H_{10}S_6N_2$ requires 374.

3.1.13. Compound 17. This was prepared in a similar manner as compound **10** using compound **16** and the G2 dendrimer with benzyl bromide units as an orange oil in 72% yield. [Found: C, 66.14; H, 4.64; N, 1.11. $C_{58}H_{49}S_6O_6N$ requires C, 66.45; H, 4.71; N, 1.34%]; ν_{max} (KBr, cm^{-1}) 2250 (–CN). δ_H (300 MHz, $CDCl_3$) 7.57 (20H, m, Ar-H), 6.66–6.49 (9H, m, Ar-H), 6.40 (1H, d, *J*=7.7 Hz, olefinic), 6.08 (1H, s, olefinic), 5.03 (8H, s, 4C*H*$_2$), 4.90 (s, 4H, 2C*H*$_2$), 3.83 (2H, s, C*H*$_2$), 2.83 (2H, t, *J*=7.3 Hz, C*H*$_2$CN), 2.56 (2H, t, *J*=6.9 Hz, SCH$_2$); MS (MALDI-TOF): MH^+, found 1048.6. $C_{58}H_{49}S_6O_6N$ requires 1048.2.

3.1.14. Compound 18. This was synthesized similarly as for compound **10** using compounds **17** and 1,4-cyclohexanedibromomethane as an orange oil in 60% yield. [Found: C, 64.20; H, 5.30. $C_{63}H_{59}S_6O_6Br$ requires C, 63.89; H, 5.02%]; ν_{max} (KBr, cm^{-1}) 1595, 1449 (Ar); δ_H (300 MHz, $CDCl_3$) 7.46 (20H, m, Ar-H), 6.73–6.55 (9H, m, Ar-H), 6.22–6.13 (2H, m, olefinic), 5.09 (8H, s, 4C*H*$_2$O), 4.99 (4H, s, 2 OC*H*$_2$), 3.90 (2H, s, SC*H*$_2$O), 3.31 (2H, d, *J*=6.3 Hz, BrC*H*$_2$), 2.65 (2H, d, *J*=5.6 Hz, SC*H*$_2$), 1.96 (4H, m, alkyl-H), 1.32 (2H, m, alkyl-H), 0.91 (4H, m, alkyl-H); MS (MALDI-TOF): M^+, found 1182.0. $C_{63}H_{59}S_6O_6Br$ requires 1182.2.

3.1.15. Compound 19. This was obtained in a similar manner as for compound **12** from compound **18** as an orange oil in 73% yield. [Found: C, 66.40; H, 5.31; N, 3.78. $C_{63}H_{59}S_6O_6N_3$ requires C, 66.00; H, 5.19; N, 3.66%]; ν_{max} (KBr, cm^{-1}) 2096 (–CN), 1596, 1450 (Ar); δ_H (300 MHz, $CDCl_3$) 7.40 (20H, m, Ar-H), 6.67–6.49 (9H, m, Ar-H), 6.20–6.00 (2H, m, olefinic), 5.04 (8H, s, 4 OC*H*$_2$), 4.95 (4H, s, 2 OC*H*$_2$), 3.85 (2H, s, SC*H*$_2$), 3.10 (2H, d, *J*=5.4 Hz, C*H*$_2$N$_3$), 2.63 (2H, d, *J*=5.7 Hz, SC*H*$_2$), 1.82 (4H, m, alkyl-H), 1.26 (2H, m, alkyl-H), 0.95 (4H, m, alkyl-H); MS (MALDI-TOF): M^+, found 1144.8. $C_{63}H_{59}S_6O_6N_3$ requires 1145.3.

3.1.16. Compound 20. This was prepared in a similar manner as for compound **14** from compound **19** as an orange oil in 82% yield. [Found: C, 67.14; H, 5.09; N, 1.04. $C_{63}H_{59}S_6O_6N_3$ requires C, 67.53; H, 5.49; N, 1.25%]; ν_{max} (KBr, cm^{-1}) 3447, 3323 (–NH$_2$), 1595, 1450 (Ar); δ_H (300 MHz, $CDCl_3$) 7.48 (20H, m, Ar-H), 6.92–6.57 (9H, m, Ar-H), 6.22–6.07 (2H, m, olefinic), 5.04 (8H, s, 4 OC*H*$_2$), 4.95 (4H, s, 2 OCH$_2$), 3.85 (2H, s, SC*H*$_2$O), 2.68 (2H, d, *J*=6.5 Hz, C*H*$_2$N), 2.62 (2H, d, *J*=6.2 Hz, SC*H*$_2$), 1.89 (4H, m, alkyl-H), 1.28 (2H, m, alkyl-H), 0.97 (4H, m, alkyl-H), MS (MALDI-TOF): M^+, found 1119.1. $C_{63}H_{61}S_6O_6N$ requires 1119.3.

3.1.17. Triad 3. A solution of compound **20** (0.20 g, 0.18 mmol) and perylene-1,4,5,8-tetracarboxylic acid dianhydride (0.03 g, 0.08 mmol) in dry DMF (15 mL) was heated to 120°C under N_2 and stirred at this temperature for 3 h. Column chromatography of the crude reaction mixture, after removing the solvent under reduced pressure, on silica gel with $CHCl_3/CH_3OH$ (100:3, v/v) as eluant afforded *cis*/*trans* mixture **3** as a red powder (0.13 g) in 61% yield: mp168–169°C. [Found: C, 68.99; H, 4.74; N, 1.26. $C_{150}H_{126}S_{12}O_{16}N_2$ requires C, 69.39; H, 4.89; N, 1.08%]; ν_{max} (KBr, cm^{-1}) 1694, 1657 (–CON–), 1595, 1448 (Ar); δ_H (300 MHz, $CDCl_3$) 8.71 (4H, d, *J*=7.6 Hz, Ar-H), 8.66 (4H, d, *J*=7.9 Hz, Ar-H), 7.45–7.32 (40H, m, Ar-H), 6.68–6.51 (18H, m, Ar-H), 6.21–6.07 (4H, m, olefinic), 5.05 (16H, s, 8CH$_2$O), 4.97 (8H, s, 4 OC*H*$_2$), 4.12 (4H, d, *J*=6.9 Hz, 2 NC*H*$_2$), 3.87 (4H, s, 2SC*H*$_2$O), 2.59 (4H, t, *J*=6.2 Hz, 2SC*H*$_2$), 1.85 (8H, m, alkyl-H), 1.17 (4H, m, alkyl-H), 0.94 (8H, m, alkyl-H); MS (MALDI-TOF): M^+, found 2594.3. $C_{150}H_{126}S_{12}O_{16}N_2$ requires 2594.6.

Acknowledgements

We thank Professor J.- P. Zhang of our institute for his kind help. The present research was financially supported by NSFC (90101025), Chinese Academy of Sciences and State Key Basic Research Program (G2000077500). D.- Q. Zhang thanks National Science Fund for Distinguished Young Scholars. We also thank the anonymous reviewers for their critical comments and suggestion, which help us to improve the manuscript.

References

1. Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carson, K. D.; Geiser, U.; Wang, H. H. A.; Kini, M.; Whangbo, M. H. *Organic Superconductors (Including Fullerenes) Synthesis, Structure, Properties, and Theory*; 1992; pp11–64.
2. Collier, P. C.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172–1175.
3. Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2001**, *40*, 1216–1221.
4. Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 333–337.
5. Segura, J. L.; Martín, N. *Angew. Chem. Int. Ed.* **2001**, *40*, 1372–1409.
6. Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11–23, and references therein.
7. Martín, N.; Sánchez, L.; IIlescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547.
8. Martín, N.; Sánchez, L.; Herranz, M. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648–4657.
9. Nielsen, M. B.; Hansen, J. G.; Becher, J. *Eur. J. Org. Chem.* **1999**, 2807–2815.
10. Hansen, J. G.; Bang, K. S.; Thorup, N.; Becher, J. *Eur. J. Org. Chem.* **2000**, 2135–2144.
11. Tsiperman, E.; Regev, L.; Becker, J. Y.; Bernstein, J.; Ellern, A.; Khodorkovsky, V.; Shames, A.; Shapiro, L. *Chem. Commun.* **1999**, 1125–1126.
12. Sheih, S.; Cava, M. P.; Baldwin, J. W.; Metzger, R. M. *J. Org. Chem.* **1998**, *63*, 1198–1204.
13. Aqad, E.; Eller, A.; Shapiro, L.; Khodorkovsky, V. *Tetrahedron Lett.* **2000**, *41*, 2983–2986.
14. Ashton, P. A.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951–3957.
15. (a) Perepichka, D. F.; Bryce, M. R.; Mclnnes, E. J. L.; Zhao, J. P. *Org. Lett.* **2001**, *3*, 1431–1434. (b) Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; McInnes, E. J. L.; Zhao, J. P.; Farley, R. D. *Chem. Eur. J.* **2002**, *8*, 4656–4669.
16. O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63–65.
17. On one hand, these groups will improve their solubility in organic solvents. On the other hand, the steric hindrance of these groups will affect their tendency to aggregate, possibly due to $\pi-\pi$ interactions. This is due to fact that both neutral TTF and PI units as well as their radical ions after oxidation or after reduction tend to aggregate in solution.
18. Jia, C-Y.; Zhang, D-Q.; Xu, W.; Zhu, D-B. *Org. Lett.* **2001**, *3*, 1941–1944.
19. Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mork, P.; Kristernsen, G. J.; Becher, J. *Synthesis* **1996**, 407–418.
20. Efforts were made to separate the *cis*/*trans* isomers, but failed. However, theoretical calculation indicates that these *cis*/*trans* isomers show similar electronic structures. Thus, these *cis*/*trans* isomers should have no significant difference in their electronic spectra as well as redox potentials. The calculation was performed using the semiempirical AM1 method (Ampec6.7 program).
21. The spectra were measured at low concentrations in order to study the intrinsic intramolecular charge-transfer interaction for triads **1**-**3**.
22. The fact that intramolecular charge-transfer interactions in triads **1**-**3** are negligible is unexpected, in particular for triad **1**, for which a rather long and flexible spacer is employed. Structural optimization, using the standard procedure for energy minimization with Ampec6.7 program, indicates that the most stable conformations for triads **1**-**3** are extended ones, even in the case of triad **1**. Consequently, we preliminarily ascribe this experimental finding to the difference in spatial separation of electron donor and acceptor units for these triads. The spatial distances between TTF and PI units were estimated by semiempirical AM1 method with Ampec6.7 program as follows: 25 Å for **1**; 12 Å for **2**; 12 Å for **3**. For this estimation, we assume the 'cyclohexane' spacers in triads **2** and **3** are in the chair conformation.
23. Photoexcitation of the PI unit increases its acceptor strength, and hence electron transfer from TTF units to the PI* proceeds readily and results in fluorescence quenching. ΔG values (kJ/mol) were obtained for triad **1** (-113.8), triad **2** (-114.8) and triad **3** (-113.8) respectively estimated by the Rehm–Weller equation according to the reference Rehm, D.; Weller, D. *Isr. J. Chem.* **1970**, *8*, 259–271.
24. Here, we mean the energy 'donor' is PI unit, while the energy 'acceptor' is TTF unit.
25. Farren, C.; Christensen, C. A.; FitzGerald, S.; Bryce, M. R.; Beeby, A. *J. Org. Chem.* **2002**, *67*, 9130–9139.
26. Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486–9494.
27. The dark-colored precipitate showed the molecular ion peak at m/z=1658.5 in MS spectrum (measured by MALDI-TOF) which was the same as that of triad **1**.
28. Machinek, R.; Lüttke, W. *Synthesis* **1975**, 255–256.
29. Steimecke, G.; Sieler, H. J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49–55.