

# Synthesis and Characterization of Donor-Acceptor-Donor Triads Containing Tetrathiafulvalene and Naphthalene Diimide Units: Towards Regulation of the Intermolecular Charge-Transfer Interaction by Varying the Attached Side Groups

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A series of donor-acceptor-donor triads **1**—**6** consisting of tetrathiafulvalene and naphthalene diimide units were synthesized and characterized. UV/Vis spectroscopic and cyclic voltammetric studies indicate that these triads show negligible intramolecular charge transfer interaction in the ground state. In contrast to that of the reference compound **36**, their fluorescence intensities were reduced in the following sequences: **3**≈**4**≈**5**≈**6**<**1**≈**2**, which is probably due to photoinduced electron transfer in triads **1**—**6**. Two solid forms (yellow and green) of triads **1**—**5** were obtained, while only green form for triad **6** was obtained under the same conditions. Studies of the yellow and green forms with UV, XRD and DSC were performed. It was suggested that varying the attached side groups may regulate intermolecular charge transfer interactions in the solid state.

**Keywords**      tetrathiafulvalene, naphthalene diimide, photoinduced electron transfer, charge transfer interaction

## Introduction

Extensive studies have been performed on electron donor-acceptor supramolecular systems, which have been used as models to investigate charge-transfer interactions,<sup>1</sup> photoinduced electron and energy transfer reactions (for understanding the natural photosynthesis mechanisms).<sup>2</sup> In recent years, molecular devices such as molecular shuttles and molecular switches based on electron donor-acceptor supramolecules have been proposed and studied.<sup>3</sup>

Since the synthesis of tetrathiafulvalene (TTF) in 1970's,<sup>4</sup> TTF and its derivatives have been widely studied as components of organic conductors and even superconductors.<sup>5</sup> Meanwhile, by taking the merits of TTF derivatives, *i.e.*, showing two reversible redox reactions at easily accessible potentials, they are being employed as electronic donor moieties in D-A supramolecules to create molecular shuttles as exemplified by the outstanding work of Stoddart and coworkers.<sup>3c-3f</sup> Naphthalene diimide (NI) analogues as well as pyromellitic diimide (PY) and perylene diimide (PI) because of their high electron-withdrawing ability and the characteristic sharp absorption bands of the radical anions, which do not overlap with other transient species,<sup>6</sup> have

received much attention. For example, Wasielewski *et al.*<sup>6a</sup> reported an ultrafast molecular switch based on triads containing perylene diimides by taking full advantage of the characteristic absorptions of radical anion and dianions of PI. Based on these considerations, D-A supramolecules containing TTF and NI (PY and PI) moieties would be interesting targets for studies of intramolecular electron transfer reactions and establishment of possible molecular switches. Indeed, Becher *et al.*<sup>7</sup> reported linear D-A-D triads as well as D-A cyclophane containing TTF and PY units.

In this paper, we report the synthesis and characterization of a series of D-A-D triads with TTF derivatives as donor units and NI as acceptor unit.<sup>8</sup> In these triads, linking groups are —(CH<sub>2</sub>)<sub>12</sub>— for triads **1** and **2**, and 1,4-cyclohexanedimethene for triads **3**, **4**, **5** and **6**. Different side groups are attached to the donor units: —CH<sub>3</sub> for triads **1** and **3**, —C<sub>6</sub>H<sub>13</sub> for triads **2** and **4**, —CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> for triad **5**, and dendritic group for triad **6** (Scheme 1). Preliminary results hint that side groups with large steric hindrance can improve the photostability of these triads in solution, and variation of the attached side groups can regulate the intermolecular charge-transfer interactions.

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## Results and discussion

### Synthesis

The usual approach to naphthalene diimide derivatives is based on the condensation reaction between the corresponding primary amines with naphthalene dianhydride. This strategy requires the preparation of primary TTF-amines. Becher *et al.*<sup>7</sup> has prepared TTF-amine derivatives using the classic Gabriel transformation. Here we like to describe another different simpler route to synthesize TTF-amines based on the unusual reaction of  $\text{TBA}_2[\text{Zn}(\text{DMIT})_2]$  reported by us recently.<sup>9,10</sup>

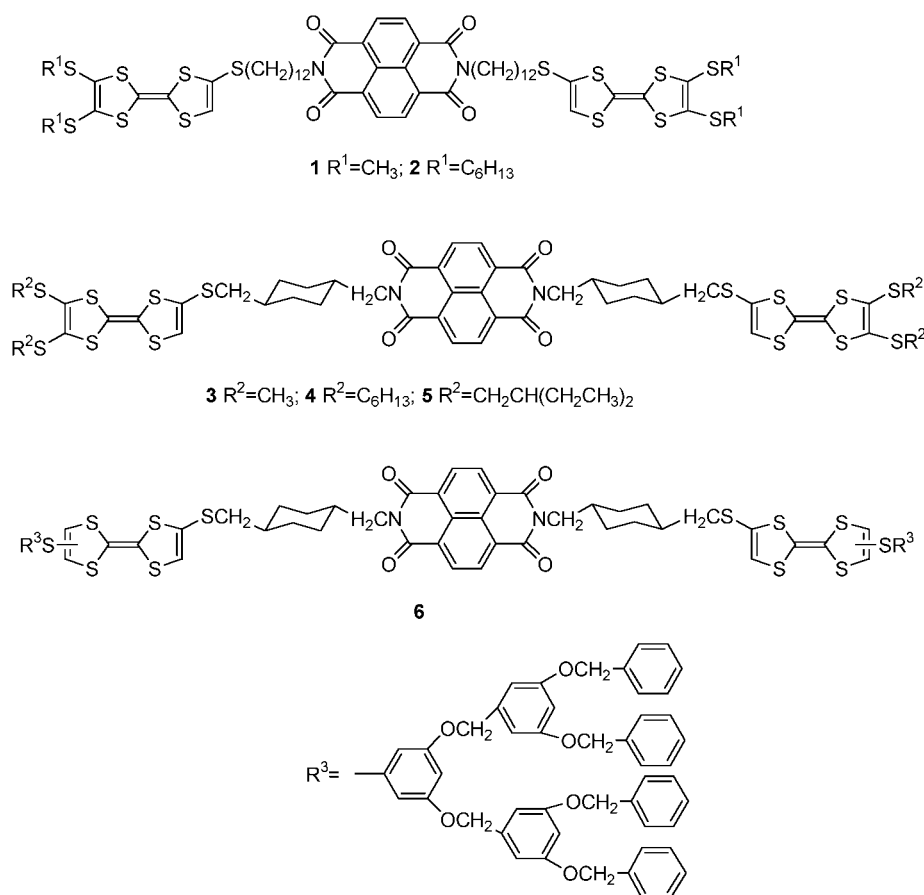
Compound **8** was prepared by oxidation of compound **7** with  $\text{Hg}(\text{OAc})_2$ , which was easily synthesized from  $\text{TBA}_2[\text{Zn}(\text{DMIT})_2]$  and 3-bromo-propionitrile in the presence of pyridine hydrogen chloride.<sup>9</sup> Compounds **9**–**11** were obtained using the reported procedure.<sup>11</sup> Then compound **13** was synthesized by the cross-coupling of **8** and **11** effected by tri(*i*-propyl) phosphite in the yield of 55% after purification (Scheme 2). By using deprotection/alkylation method with cyanoethyl-protected TTF **13**, compounds **14** and **15** were obtained, both of which were directly converted to compounds **16** and **17** by substitution with large excess

of  $\text{NaN}_3$  in dry DMF in high yield respectively. Reduction of compounds **16** and **17** in THF solution with  $\text{PPh}_3/\text{H}_2\text{O}$  gave the TTF-amines **18** and **19**, which were further purified by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{petroleum ether}$  after column chromatography. Triads **1** and **3** were afforded by the reaction of compounds **18** and **19** with naphthalene dianhydride respectively, catalyzed by  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in the solution of quinoline under an atmosphere of dry  $\text{N}_2$  at 160 °C for 3–4 h in relatively high yields (about 70% ).

Triads **2**, **4** and **5** were synthesized similarly as showed in Scheme 3. Due to the limited amount of the starting material 1-bromo-2-ethylbutane, we converted compound **10** to compound **12** (Scheme 2). Further cross-coupling reaction of compound **12** and **7** in a 1 : 3 ratio afforded compounds **27** in the yield of 62% after column chromatography.

Scheme 4 shows the synthetic route to triad **6**. Self-coupling reaction of compound **8** in the presence of tri(*i*-propyl) phosphite led to compound **31** with *cis/trans* isomers. The corresponding thiolate formed *in situ* by removal of one cyanoethyl groups reacted with bromo-dendrimer to afford compound **32**. By deprotection of second cyanoethyl group and sequentially reaction with bisbromo compound **32** was transformed to

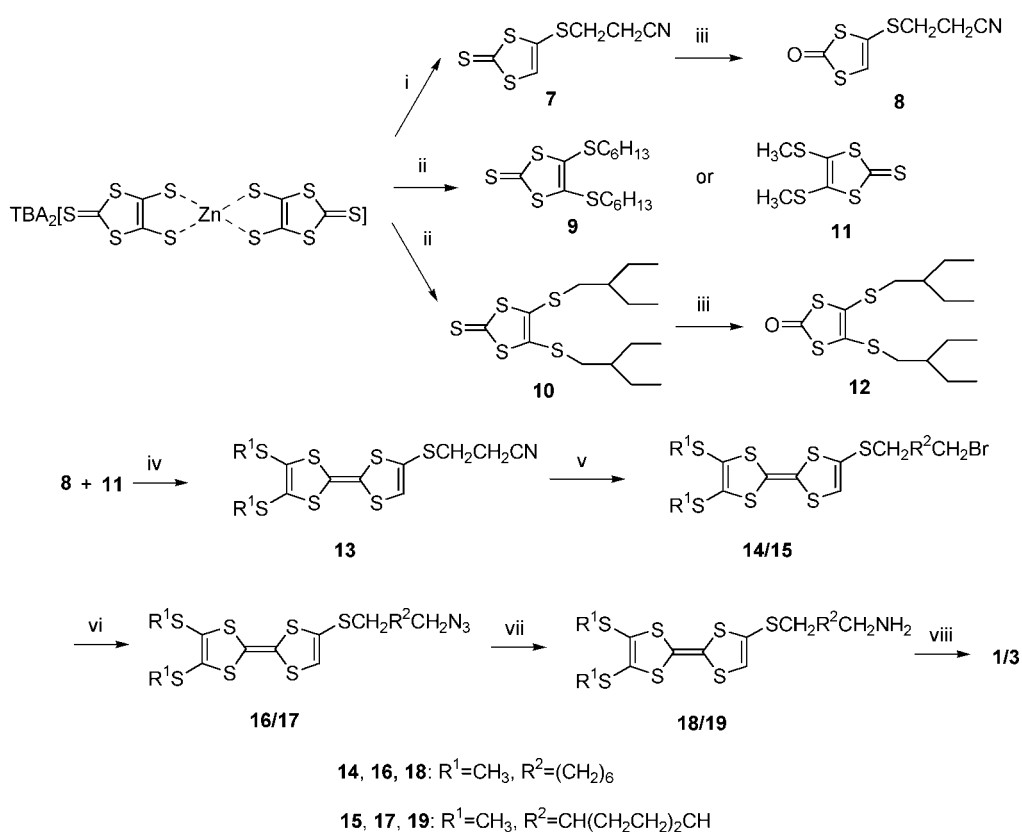
Scheme 1



compound **33**. Compounds **34** and **35** were prepared similarly as for **16** and **18** respectively. It should be noted that attempts to obtain triad **6** using the same reaction condition as for triads **1**–**5** failed. But, reaction

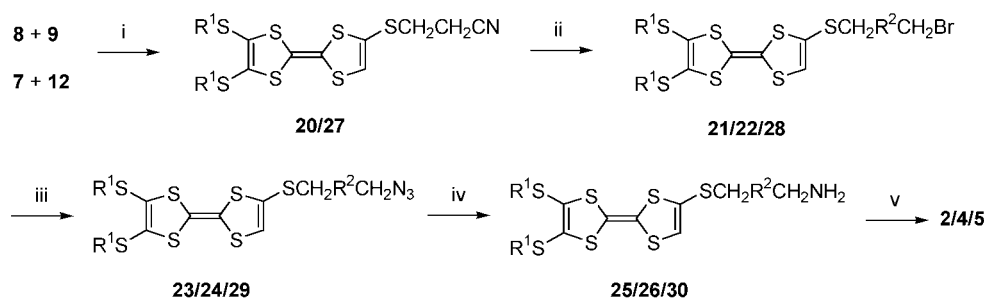
of compound **35** with naphthalene dianhydride in dry DMF at 120 °C overnight followed by column chromatography separation successfully afforded triad **6** in moderate yield.

Scheme 2



Reagents: i, BrCH<sub>2</sub>CH<sub>2</sub>CN/pyridinehydrochloride, CH<sub>3</sub>CN; ii, C<sub>6</sub>H<sub>13</sub>Br or CH<sub>3</sub>I or BrCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>CN; iii, Hg(OAc)<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>; iv, tri(*i*-propyl)phosphite, 120 °C; v, CsOH·H<sub>2</sub>O, THF, Br(CH<sub>2</sub>)<sub>12</sub>Br/BrCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>Br; vi, DMF, NaN<sub>3</sub>; vii, PPh<sub>3</sub>/H<sub>2</sub>O, THF; viii, naphthalene dianhydride, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, quinoline, N<sub>2</sub>, 160 °C

Scheme 3

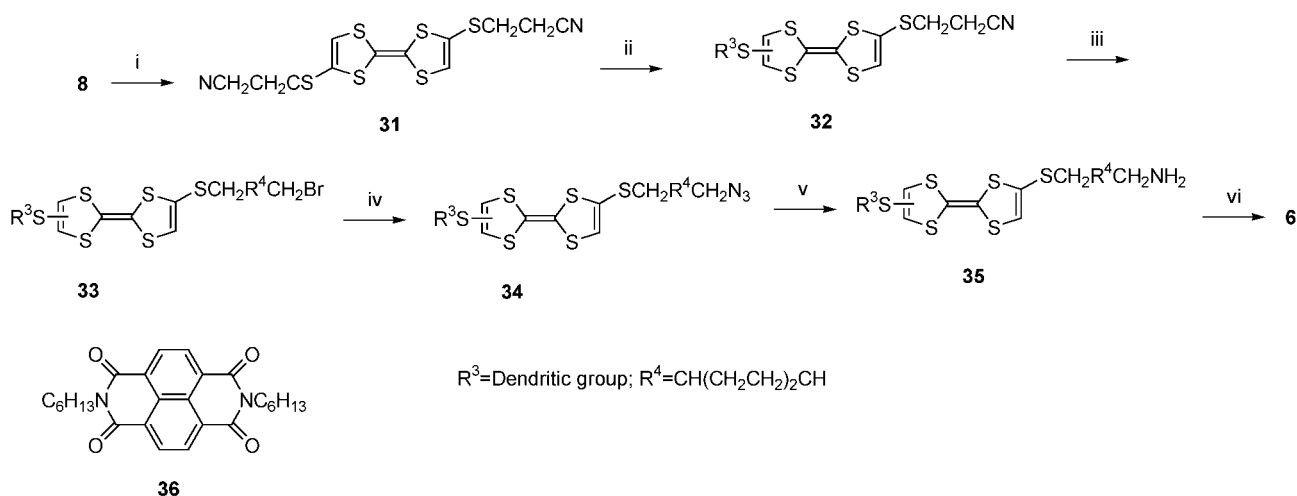


**20:** R<sup>1</sup>=C<sub>6</sub>H<sub>13</sub>; **27:** R<sup>1</sup>=CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>; **21, 23, 25:** R<sup>1</sup>=C<sub>6</sub>H<sub>13</sub>, R<sup>2</sup>=(CH<sub>2</sub>)<sub>6</sub>

**22, 24, 26:** R<sup>1</sup>=C<sub>6</sub>H<sub>13</sub>, R<sup>2</sup>=CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH; **28, 29, 30:** R<sup>1</sup>=CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, R<sup>2</sup>=CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH

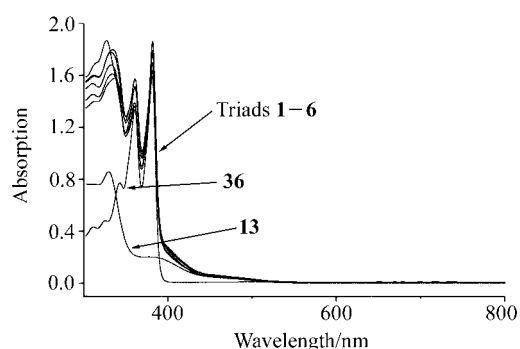
Reagents: i, tri(*i*-propyl)phosphite, 120 °C; ii, CsOH·H<sub>2</sub>O, THF, Br(CH<sub>2</sub>)<sub>12</sub>Br/BrCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>Br; iii, DMF, NaN<sub>3</sub>; iv, PPh<sub>3</sub>/H<sub>2</sub>O, THF; v, perylene dianhydride, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, quinoline, N<sub>2</sub>, 160 °C

## Scheme 4



## Spectral and electrochemical studies

Figure 1 shows the absorption spectra of triads **1–6** together with the reference compounds **13** and **36** for comparison. Their absorption bands correspond well to respective absorptions of compounds **13** and **36**, and no new absorption bands and even shoulders were observed. In fact, the solution of the mixture of **13** and **36** (in 1 : 1 molar ratio) with a concentration of  $2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  showed typical CT absorption band with  $\lambda_{\text{max}} = 620 \text{ nm}$ . These results imply that there is no intramolecular charge-transfer interaction in their ground states of triads **1–6**.



**Figure 1** UV/Vis absorption spectra of **1–6**, **13** and **36** ( $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) in trichloromethane.

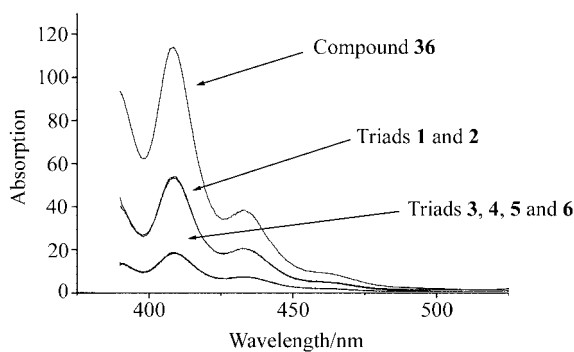
Further insight into the electronic properties of these compounds was gained by electrochemical studies. Redox potentials of triads **1–6** were measured with cyclic voltammetry, and the results are listed in Table 1. The redox potentials of the reference compounds **13** and **36** were also determined under the same conditions. It can be seen clearly from Table 1 that the redox potentials of TTF units and NI unit are virtually unchanged as compared to those of reference compounds **13** and **36**. Thus, it can be concluded that intramolecular charge transfer interactions in solution are negligible for triads

**1–6**, which is in accordance with the results of UV/Vis absorption spectral studies. Theoretical calculation results indicated that for triads **1–6** and the extended conformation is the most stable, even in the case of triads **1** and **3**, in which TTF units were covalently linked with naphthalene diimide units through flexible spacers. Hence, the relatively large separation of D-A units in these triads may be responsible for the negligible intramolecular charge transfer interactions.

**Table 1** Redox potentials of **1–6** (potentials vs. Ag/AgCl)

	$E_{1/2}^1 /$ [V (Re.)]	$E_{1/2}^2 /$ [V (Re.)]	$E_{1/2}^1 /$ [V (Ox.)]	$E_{1/2}^2 /$ [V (Ox.)]
<b>1</b>	−0.83	−1.25	0.47	0.83
<b>2</b>	−0.87	−1.27	0.47	0.84
<b>3</b>	−0.85	−1.26	0.50	0.85
<b>4</b>	−0.86	−1.27	0.48	0.86
<b>5</b>	−0.85	−1.27	0.47	0.85
<b>6</b>	−0.84	−1.26	0.50	0.87
<b>13</b>			0.48	0.86
<b>36</b>	−0.85	−1.26		

Figure 2 shows the fluorescence spectra of triads **1–6** together with the reference compound **36** for comparison. As compared to that of the reference compound **36**, the fluorescence intensities of triads **1–6** are decreased in the following sequences:  $3 \approx 4 \approx 5 \approx 6 < 1 \approx 2$ . This fluorescence quenching is probably owing to the photoinduced electron transfer reactions from TTF to NI units.<sup>12</sup> Since the photoinduced electron transfer reaction rate is dependent on the distance between the donor and acceptor units, the differences of the fluorescence intensity among triads **1–6** may be ascribed to their differences in the donor-acceptor separation.<sup>13</sup>



**Figure 2** Fluorescence spectra of **1–6** ( $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) in trichloromethane. The intensities of triads **1** and **2** are same while those of triads **3**, **4**, **5** and **6** are same.

In addition, it was unexpectedly found that the singlet signal for olefinic hydrogen of TTF units at  $\delta$  6.31 disappeared after irradiating of the  $\text{CDCl}_3$  solution ( $5.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ) of triad **3** in an NMR tube by sun light for about 48 h, and that the signals in high field ( $\delta$  0.8–3.0) were broadened. But, in contrast to the case of triads with two TTF moieties and one PI, no precipitate occurred.<sup>14</sup> Similar changes of  $^1\text{H}$  NMR spectra were observed for triad **5** after irradiating continuously its  $\text{CDCl}_3$  solution by sun light for about 96 h. For the  $\text{CDCl}_3$  solution of triad **6**, however, even after irradiating in the same condition for about 10 d, its NMR spectrum kept unchanged. We tentatively accounted the above phenomena as follows: irradiation by sunlight will probably induce electron transfer from TTF unit to NI unit, and hence lead to formation of radical ions of TTF and NI or radical ion pair; both TTF and NI radical ions have tendency to aggregate in solution due to  $\pi$ - $\pi$  interactions, which will cause the NMR signals to become broad and even to disappear, and also slow down the charge recombination process. By increasing the steric hindrance of the attached side groups, the formation of such aggregates due to  $\pi$ - $\pi$  interactions will probably be prohibited. Thus, in such case like triad **6** the photoinduced electron transfer and charge recombination processes would occur normally and the solution is stable under light irradiation. This result might suggest that the photostability of D-A supramolecular systems containing TTF units could be improved by attaching large steric groups such as dendritic ones. Detailed results of photoinduced electron transfer processes in these triads using time-resolved absorption and fluorescence spectroscopies will be reported elsewhere in due time.

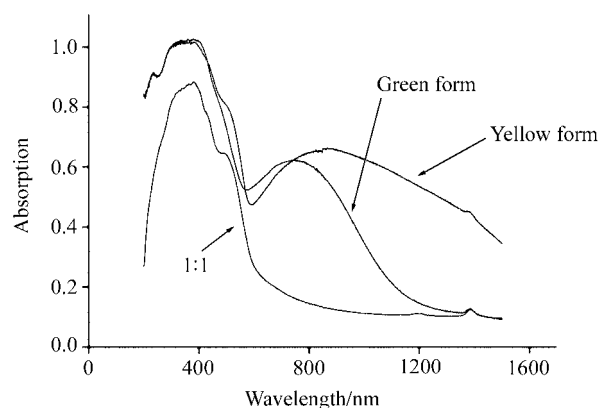
#### Possible influences of the attached groups on the intermolecular charge-transfer interactions

It is interesting that two solid forms of triads **1–5** were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether or toluene: yellow and green forms, which could be separated mechanically and have different physical properties. By heating the yellow form was transformed to the green one, which was

slowly reconverted to the yellow one under extremely cooling condition. On the contrary, under the same conditions, only green form was formed for triad **6**. Becher *et al.*<sup>7</sup> also obtained two different forms of donor-acceptor macrocycles incorporating TTF and pyromellitic diimide: orange and green needles, which were recrystallized from toluene or  $\text{CHCl}_3/\text{MeOH}$ .

The two forms of triads **1–5** are chemically the same as confirmed by NMR, MS and elemental analysis. For example, MALDI-TOF mass spectra of the yellow and green forms of triad **3** obviously show that both of them display the same molecular ion peak ( $m/z = 1138.0$ ) and the isotopic pattern. For triads **1–5**, the corresponding yellow and green forms also show the same decomposition temperature as indicated by TGA analysis.

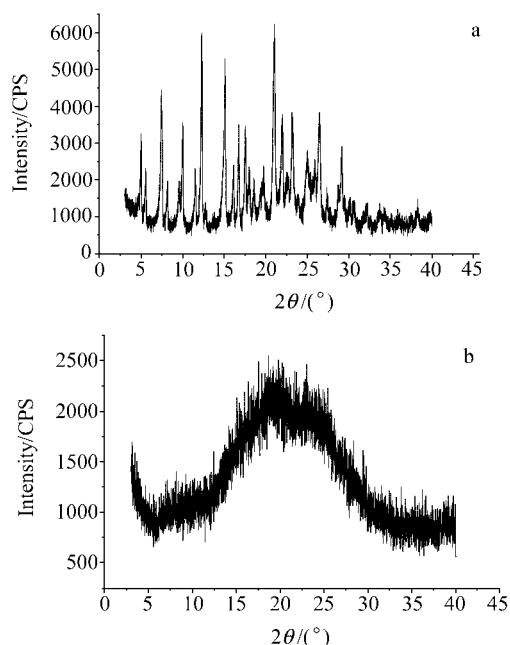
More characterization was performed for the green and yellow forms of triads **1–5**. These two forms of triads **1–5** show different UV spectra measured in solid state. As a representative instance, the yellow and green forms of triad **3** are given in Figure 3. As compared to the mixtures of **13** and **36** (reference compounds in 1 : 1 molar ratio), the yellow form has new absorptions at 870 nm, and absorptions around 725 nm are detected for the green form. The XRD measurements provide information about the molecular arrangements in the solid state. Figure 4 shows the XRD spectra of the green and yellow forms of triad **3**. Several sharp peaks are observed for the yellow form, but only a broad signal was detected for the green form. Clearly, molecules of triad **3** in the yellow form are more orderly arranged, and the green form is more like amorphous solid. DSC studies show that for the yellow form only one transition was detected at 165.0 °C and three transitions were observed for the green form at 80.9, 99.4 and 151.7 °C, respectively.



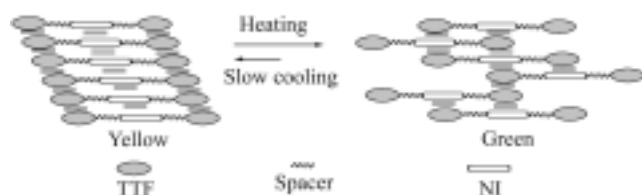
**Figure 3** Solid state absorption of triad **3** and the mixtures of **13** and **36** (in 1 : 1 molar ratio).

It is well known that intermolecular interactions will determine the intermolecular arrangements in the solid state. Since triads **1–6** contain TTF and NI units, the most important intermolecular interactions are  $\pi$ - $\pi$

(among TTF units and NI units themselves), charge-transfer (between TTF and NI units) and S-S (related to TTF units) interactions. For triad **6**, the large steric groups (dendritic group) probably prohibit the direct  $\pi$ - $\pi$  interaction (among TTF units) as well as S-S short contacts<sup>15</sup> and consequently the neighboring molecules will displace each other to make the intermolecular charge-transfer interactions become more favorable. For triads **1**–**5**, on the other hand, the steric hindrance of the attached groups are not significantly large, even in the case of triad **5**, and thus both the direct “overlap” arrangements such as in Figure 5 and the displacement ones are possible. It seems that the intermolecular interaction and hence the intermolecular arrangements may be tuned by varying the steric hindrance of the attached groups. Further investigations in this respect are in progress.



**Figure 4** Powder X-ray diffraction patterns of two forms of triad **3**: yellow (a) and green (b). The difference is manifest in the structure of them. The yellow possesses quite ordered lattice, while the structure of the green is out-of-order.



**Figure 5** Models of the possible arrangements of two extreme states: right is due to only the charge-transfer interactions between TTF and NI units, and left is due to only the  $\pi$ - $\pi$  interaction between themselves.

## Conclusion

In summary, a series of donor-acceptor-donor triads **1**–**6** consisting of tetrathiafulvalene and naphthalene diimide units were synthesized and characterized. From investigations of UV/Vis spectroscopy and cyclic voltammetry, these triads show negligible intramolecular charge transfer interaction. In contrast to that of the reference compound **36**, their fluorescence intensities were reduced in the following sequences:  $3 \approx 4 \approx 5 \approx 6 < 1 \approx 2$ , which is probably due to photoinduced electron transfer in triads **1**–**6**. Two solid forms (yellow and green) of triads **1**–**5** were obtained, while only green form for triad **6** was obtained under the same conditions. Studies of the yellow and green forms with XRD, DSC and UV were performed. Based on these results, it is suggested that by variation of the attached side groups it might be possible to regulate intermolecular charge transfer interactions in the solid state.

## Experimental

### Chemical reagents and methods

Melting points were measured with an XT<sub>4</sub>-100X apparatus and uncorrected. <sup>1</sup>H NMR spectra were recorded with Bruker 300 MHz or Varian 200 MHz spectrometers. All chemical shifts were quoted relative to TMS. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with an AEI-MS50-MS or a MALDI-TOF-MS spectrometer. Elemental analysis was performed on a Carlo-Erba-1106 instrument. Absorption spectra were measured with a 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/s in CHCl<sub>3</sub> using Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte, platinum as counter and work electrodes and Ag/AgCl as reference electrode.

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 d before use. Pyridine hydrogen chloride, 1,12-dibromododecane, and 1,4-cyclohexanedimethanol were purchased from Acros Chemicals. 1,4-Cyclohexanedibromomethane was prepared from 1,4-cyclohexanedimethanol according to Ref. 16 and TBA<sub>2</sub>[Zn(DMIT)<sub>2</sub>] was prepared according to Ref. 17. Compound **7** was prepared according to Ref. 9. 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<sub>2</sub>.

**Compound 8:** To a solution of 4-(2'-cyanoethiothio)-1,3-dithiole-2-thione (0.27 g, 1.23 mmol) in dichloromethane (45 mL) was added to mercuric acetate (1.18 g, 3.69 mmol), and the resulting white suspension was stirred under N<sub>2</sub> for 2 h at room temperature. The resulting voluminous white precipitate was removed by

filtration using celite and wash thoroughly with dichloromethane. The combined organic phases were concentrated *in vacuo*, and then the remaining solid was obtained as colourless needles by recrystallization from dichloromethane and petroleum ether in 80% yield. m.p. 56—57 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 2.75 (t,  $J=6.8$  Hz, 2H), 3.06 (t,  $J=6.8$  Hz, 2H), 7.12 (s, 1H); IR (KBr)  $\nu$ : 2247, 1632  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 203 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_6\text{H}_5\text{NOS}_3$ : C 35.45, H 2.48, N 6.89; found C 35.29, H 2.37, N 6.77.

**Compound 13:** A solution of compound **8** (1.00 g, 4.29 mmol) and compound **11** (3.33 g, 14.8 mmol) $^{11}$  in triisopropyl phosphite (30 mL) was heated to 120 °C under  $\text{N}_2$  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  $\text{CH}_2\text{Cl}_2$ /petroleum (60—90 °C) (1/3, V/V) as eluent afforded compound **13** as an orange oil in 65% yield. m.p. 102—104 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.59 (s, 1H), 3.95 (t,  $J=7.3$  Hz, 2H), 2.70 (t,  $J=7.3$  Hz, 2H), 2.42 (s, 6H); IR (KBr)  $\nu$ : 2251  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 381 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{11}\text{H}_{11}\text{S}_7\text{N}$ : C 34.62, H 2.91, N 3.67; found C 34.80, H 2.82, N 3.58.

**Compound 20:** Compound **20** was prepared in a similar manner from **8** and **9** $^{11}$  as an orange oil in 67% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.55 (s, 1H), 2.96 (t,  $J=6.4$  Hz, 2H), 2.82 (t,  $J=5.2$  Hz, 4H), 2.70 (t,  $J=6.4$  Hz, 2H), 1.60—1.20 (br, 16H), 0.89 (t,  $J=4.6$  Hz, 6H); IR (KBr)  $\nu$ : 2249  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 521 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{21}\text{H}_{31}\text{S}_7\text{N}$ : C 48.33, H 5.99, N 2.68; found C 48.41, H 6.03, N 2.73.

**Compound 27:** Compound **27** was prepared in a similar manner from **8** and **12** $^{11}$  as an orange oil in 62% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.58 (s, 1H), 2.96 (t,  $J=6.8$  Hz, 2H), 2.83 (d,  $J=4.8$  Hz, 4H), 2.70 (t,  $J=6.8$  Hz, 2H), 1.46 (m, 10H), 0.89 (t,  $J=7.2$  Hz, 12H); IR (KBr)  $\nu$ : 2252  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 521 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{21}\text{H}_{31}\text{S}_7\text{N}$ : C 48.33, H 5.99, N 2.68; found C 48.32, H 6.03, N 2.59.

**Compound 14:** To a solution of compound **13** (1.00 g, 2.62 mmol) in anhydrous degassed THF (80 mL) was added a solution of  $\text{CsOH} \cdot \text{H}_2\text{O}$  (0.48 g, 2.88 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 (1.00 g, 3.05 mmol) in anhydrous degassed THF (30 mL) was added. The solution was stirred overnight and then column chromatographed to afford the crude products which can be further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether as red powders in 72% yield. m.p. 33—34 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.33 (s, 1H), 3.41 (t,  $J=6.7$  Hz, 2H), 2.75 (t,  $J=6.5$  Hz, 2H), 2.43 (s, 6H), 1.80—1.87 (m, 2H), 1.55—1.59 (m, 2H), 1.40—1.20 (m, 16H); IR (KBr)  $\nu$ : 2924, 2852  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 576 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{20}\text{H}_{31}\text{S}_7\text{Br}$ : C 41.81, H 5.44; found C 41.97, H 5.36.

**Compound 15:** Compound **15** was obtained similarly from compound **13** and 1,4-cyclohexane-dibromo-

methane in 75% yield. m.p. 132—133 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.22 (s, 1H), 3.30 (d,  $J=6.0$  Hz, 2H), 2.67 (d,  $J=4.0$  Hz, 2H), 2.44 (s, 6H), 1.95 (m, 4H), 1.56 (m, 2H), 1.08 (m, 4H); IR (KBr)  $\nu$ : 2920, 2844  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 518 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{16}\text{H}_{21}\text{S}_7\text{Br}$ : C 37.12, H 4.09; found C 37.60, H, 4.17.

**Compound 21:** Compound **21** was obtained similarly from compound **20** and 1,12-dibromododecane as an orange oil in 90% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.32 (s, 1H), 3.40 (t,  $J=6.2$  Hz, 2H), 2.80 (m, 6H), 1.82 (m, 2H), 1.59 (m, 8H), 1.39 (br, 26H), 0.89 (t,  $J=6.4$  Hz, 6H); IR (KBr)  $\nu$ : 2954, 2926, 2854  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 716 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{30}\text{H}_{51}\text{S}_7\text{Br}$ : C 50.32, H 7.18; found C 50.70, H 7.30.

**Compound 22:** Compound **22** was obtained similarly from compound **20** and 1,4-cyclohexane-dibromomethane as an orange oil in 80% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.32 (s, 1H), 3.30 (d,  $J=6.2$  Hz, 2H), 2.81 (t,  $J=6.9$  Hz, 4H), 2.66 (d,  $J=6.8$  Hz, 2H), 1.96 (br, 4H), 1.62 (m, 4H), 1.43 (m, 6H), 1.30 (m, 8H), 1.01 (m, 4H), 0.89 (m, 6H); IR (KBr)  $\nu$ : 2953, 2925, 2853  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 656.3 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{26}\text{H}_{41}\text{S}_7\text{Br}$ : C 47.46, H 6.28; found C 47.69, H 6.43.

**Compound 28:** compound **28** was prepared in a similar manner from **27** and 1,4-cyclohexanedibromomethane as an orange oil in 70% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.31 (s, 1H), 3.30 (d,  $J=6.5$  Hz, 2H), 2.80 (d,  $J=5.8$  Hz, 4H), 2.65 (d,  $J=6.8$  Hz, 2H), 1.94 (br, 4H), 1.43 (br, 12H), 0.90 (br, 16H); IR (KBr)  $\nu$ : 2960, 2921  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 657.9 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{26}\text{H}_{41}\text{S}_7\text{Br}$ : C 47.46, H 6.28; found C 47.20, H 6.14.

**Compound 16:** A solution of compound **14** (1.48 g, 2.56 mmol) in dry DMF (50 mL) was treated with  $\text{NaN}_3$  (0.85 g, 13.07 mmol) at 25 °C under  $\text{N}_2$  for 12 h and then 30 mL of water was added. The aqueous solution was extracted with (3  $\times$  50 mL)  $\text{CH}_2\text{Cl}_2$ , and the combined extracts were washed with  $\text{H}_2\text{O}$  (2  $\times$  50 mL) and saturated aqueous NaCl (20 mL), dried ( $\text{MgSO}_4$ ) and concentrated *in vacuo*. Column chromatography afforded the crude product which can be further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether as red powders in 90% yield. m.p. 43—44 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.33 (s, 1H), 3.26 (t,  $J=6.7$  Hz, 2H), 2.74 (t,  $J=6.9$  Hz, 2H), 2.43 (s, 6H), 1.59 (m, 4H), 1.40—1.20 (m, 16H); IR (KBr)  $\nu$ : 2096  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 537.0 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{20}\text{H}_{31}\text{S}_7\text{N}_3$ : C 44.66, H 5.81, N 7.81; found C 44.70, H 5.87, N 7.70.

**Compound 17:** Compound **17** was obtained similarly from compound **15** in 92% Yield. m.p. 86—87 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.35 (s, 1H), 3.16 (d,  $J=6.5$  Hz, 2H), 2.68 (d,  $J=6.8$  Hz, 2H), 2.45 (s, 6H), 1.95 (m, 4H), 1.56 (m, 2H), 1.03 (m, 4H); IR (KBr)  $\nu$ : 2096  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 479 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{16}\text{H}_{21}\text{S}_7\text{N}_3$ : C 40.05, H 4.41, N 8.76; found C 40.50, H 4.49, N 8.42.

**Compound 23:** Compound **23** was prepared simi-

larly from compound **21** as an orange oil in 91% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.25 (s, 1H), 3.19 (t,  $J=6.3$  Hz, 2H), 2.74 (m, 6H), 1.55 (br, 10H), 1.29 (br, 26H), 0.83 (t,  $J=6.4$  Hz, 6H); IR (KBr)  $\nu$ : 2094  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 677.5 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{30}\text{H}_{51}\text{S}_7\text{N}_3$ : C 53.13, H 7.58, N 6.20; found C 53.45, H 7.86, N 6.36.

**Compound 24:** Compound **24** was prepared similarly from compound **22** as an orange oil in 85% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.32 (s, 1H), 3.16 (d,  $J=6.6$  Hz, 2H), 2.84 (t,  $J=6.4$  Hz, 4H), 2.66 (d,  $J=6.9$  Hz, 2H), 1.88 (m, 4H), 1.63 (m, 4H), 1.42 (m, 6H), 1.29 (m, 8H), 1.01 (m, 4H), 0.89 (m, 6H); IR (KBr)  $\nu$ : 2096  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 619.2 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{26}\text{H}_{41}\text{S}_7\text{N}_3$ : C 50.36, H 6.66, N 6.78; found C 50.76, H 6.95, N 6.27.

**Compound 29:** Compound **29** was prepared in a similar manner from **28** as an orange oil in 70% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.33 (s, 1H), 3.18 (d,  $J=6.6$  Hz, 2H), 2.84 (d,  $J=5.0$  Hz, 4H), 2.67 (d,  $J=6.8$  Hz, 2H), 1.88 (m, 4H), 1.47 (m, 12H), 1.06 (m, 4H), 0.94 (m, 12H); IR (KBr)  $\nu$ : 2095  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 619.1 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{26}\text{H}_{41}\text{S}_7\text{N}_3$ : C 50.36, H 6.66, N 6.78; found C 50.74, H 6.88, N 7.02.

**Compound 18:** A solution of compound **16** (0.50 g, 0.93 mmol) in THF (10 mL) was treated with  $\text{PPh}_3$  (0.49 g, 1.86 mmol) and  $\text{H}_2\text{O}$  (167  $\mu\text{L}$ , 9.29 mmol) at 25  $^\circ\text{C}$  under  $\text{N}_2$  and then warmed at 45  $^\circ\text{C}$  for 10 h. The volatiles were purified by column chromatography to afford the crude product which can be further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether to give the product as red powders in 87% yield. m.p. 70–71  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.33 (s, 1H), 2.74 (t,  $J=6.9$  Hz, 2H), 2.62 (t,  $J=6.7$  Hz, 2H), 2.43 (s, 6H), 1.60 (m, 6H), 1.40–1.20 (m, 16H); IR (KBr)  $\nu$ : 3376, 3320  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 511 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{20}\text{H}_{33}\text{S}_7\text{N}$ : C 46.93, H 6.50, N 2.74; found C 47.15, H 6.44, N 2.72.

**Compound 19:** Compound **19** was obtained similarly from **17** as red powders in 71% yield. m.p. 94–95  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 6.32 (s, 1H), 2.67 (d,  $J=6.8$  Hz, 2H), 2.52 (d,  $J=6.4$  Hz, 2H), 2.43 (s, 6H), 1.90 (m, 4H), 1.50 (m, 2H), 1.27 (br, 2H), 0.95 (m, 4H); IR (KBr)  $\nu$ : 3320, 3307  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 453 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{16}\text{H}_{23}\text{S}_7\text{N}$ : C 42.35, H 5.11, N 3.09; found C 42.63, H 5.27, N 3.10.

**Compound 25:** Compound **25** was obtained similarly from compound **23** as an orange oil in 78% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 6.32 (s, 1H), 2.81 (m, 6H), 2.68 (t,  $J=6.8$  Hz, 2H), 1.63 (m, 10H), 1.27 (br, 28H), 0.89 (t,  $J=6.3$  Hz, 6H); IR (KBr)  $\nu$ : 3321, 3301  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 651.4 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{30}\text{H}_{53}\text{S}_7\text{N}$ : C 55.25, H 8.19, N 2.15; found C 55.35, H 8.17, N 2.02.

**Compound 26:** Compound **26** was obtained similarly from compound **24** as an orange oil in 81% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 6.28 (s, 1H), 2.79 (d,  $J=5.3$  Hz, 4H), 2.63 (d,  $J=6.8$  Hz, 2H), 2.51 (d,  $J=6.4$  Hz, 2H), 1.89 (br, 4H), 1.40 (br, 14H), 0.89 (br, 16H); IR

(KBr)  $\nu$ : 3445, 3367  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 593.2. Anal. calcd for  $\text{C}_{26}\text{H}_{43}\text{S}_7\text{N}$ : C 52.57, H 7.30, N 2.36; found C 52.01, H 7.14, N 2.20.

**Compound 30:** Compound **30** was obtained similarly from compound **29** as an orange oil in 80% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 6.28 (s, 1H), 2.79 (d,  $J=5.3$  Hz, 4H), 2.63 (d,  $J=6.8$  Hz, 2H), 2.51 (d,  $J=6.4$  Hz, 2H), 1.89 (br, 4H), 1.40 (br, 14H), 0.89 (br, 16H); IR (KBr)  $\nu$ : 3445, 3315  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 593.2. Anal. calcd for  $\text{C}_{26}\text{H}_{43}\text{S}_7\text{N}$ : C 52.57, H 7.30, N 2.36; found C 52.11, H 7.14, N 2.20.

**Triad 1:** Naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.026 g, 0.097 mmol) was stirred under  $\text{N}_2$  with compound **18** (0.120 g, 0.234 mmol) and zinc acetate (0.022 g, 0.098 mmol) in quinoline (5 mL) at 160  $^\circ\text{C}$  for 3 h. The reaction mixture was cooled down to room temperature and poured into HCl (1 mol  $\cdot\text{L}^{-1}$ , 100 mL). The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL) and then purified by column chromatography. After removing the solvent *in vacuo*, the remaining solid was recrystallized from  $\text{CH}_2\text{Cl}_2$ /petroleum ether to afford the product as yellow-green powders in 71% yield. m.p. 108–109  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.76 (s, 4H), 6.32 (s, 2H), 4.20 (t,  $J=6.7$  Hz, 4H), 2.72 (t,  $J=6.9$  Hz, 4H), 2.42 (s, 12H), 1.80–1.60 (m, 8H), 1.40–1.20 (m, 32H); IR (KBr)  $\nu$ : 1703, 1660  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1253.9 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{54}\text{H}_{66}\text{S}_{14}\text{O}_4\text{N}_2$ : C 51.67, H 5.30, N 2.20; found C 51.60, H 5.25, N 2.16.

**Triad 2:** Triad **2** was obtained similarly from **25** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 73% yield. m.p. 169–170  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.75 (s, 4H), 6.32 (s, 2H), 4.20 (t,  $J=6.7$  Hz, 4H), 2.81 (m, 12H), 1.62 (m, 20H), 1.36 (m, 52H), 0.87 (t,  $J=6.3$  Hz, 12H); IR (KBr)  $\nu$ : 1704, 1669, 1579  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1534.2 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{74}\text{H}_{106}\text{S}_{14}\text{N}_2\text{O}_4$ : C 57.92, H 6.83, N 1.83; found C 57.66, H 6.97, N 1.69.

**Triad 3:** Triad **3** was obtained similarly from **19** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 69% yield. m.p. 164–165  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.77 (s, 4H), 6.31 (s, 2H), 4.11 (d,  $J=6.8$  Hz, 4H), 2.63 (d,  $J=6.8$  Hz, 4H), 2.43 (s, 12H), 1.90 (m, 8H), 1.56 (m, 4H), 1.22–0.88 (m, 8H); IR (KBr)  $\nu$ : 1703, 1664, 1580  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1138.0 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{46}\text{H}_{46}\text{S}_{14}\text{N}_2\text{O}_4$ : C 48.51, H 4.07, N 2.46; found C 48.93, H 4.60, N 2.59.

**Triad 4:** Triad **4** was obtained similarly from **26** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 75% yield. m.p. 122–123  $^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.75 (s, 4H), 6.29 (s, 2H), 4.09 (d,  $J=6.9$  Hz, 4H), 2.80 (t,  $J=7.2$  Hz, 8H), 2.62 (d,  $J=6.7$  Hz, 4H), 1.90 (m, 8H), 1.61 (m, 8H), 1.41–1.28 (m, 28H), 0.90 (m, 20H); IR (KBr)  $\nu$ : 1703, 1661, 1580  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1418.3 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{66}\text{H}_{86}\text{S}_{14}\text{N}_2\text{O}_4$ : C 55.82, H 6.10, N 1.97; found C 55.43, H 6.05, N 1.85.

**Triad 5:** Triad **5** was obtained similarly from **30** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 70%



yield. m.p. 110—111 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.76 (s, 4H), 6.30 (s, 2H), 4.10 (d,  $J = 7.4$  Hz, 4H), 2.81 (d,  $J = 6.1$  Hz, 8H), 2.63 (d,  $J = 6.8$  Hz, 4H), 1.87 (m, 8H), 1.43 (m, 24H), 1.21 (m, 4H), 0.89 (m, 28H); IR (KBr)  $\nu$ : 1703, 1665, 1581  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1418.1 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{66}\text{H}_{86}\text{S}_{14}\text{N}_2\text{O}_4$ : C 55.82, H 6.10, N 1.97; found C 55.65, H 6.08, N 1.94.

**Compound 31:** To a solution of compound **8** (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  $\text{N}_2$  and stirred at this temperature for 3 h. Column chromatography of the crude reaction mixture, after removing the excess triisopropylphosphite under reduced pressure, on silica gel with  $\text{CH}_2\text{Cl}_2$ /petroleum (60—90 °C) (1 : 2, V/V) as eluent afforded compound **31** as a yellow powder in 63% yield. m.p. 114—115 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 6.29 (s, 2H), 3.04 (t,  $J = 8.4$  Hz, 4H), 2.72 (t,  $J = 8.4$  Hz, 4H); IR (KBr)  $\nu$ : 2248  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 374 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{12}\text{H}_{10}\text{S}_6\text{N}_2$ : C 38.48, H 2.69, N 7.48; found C 38.08, H 2.66, N 7.46.

**Compound 32:** Compound **32** was prepared in a similar manner as for compound **14** from compound **31** and bromodendrimer as an orange oil in 72% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.57 (m, 20H), 6.66—6.49 (m, 9H), 6.40 (d,  $J = 7.7$  Hz, 1H), 6.08 (s, 1H), 5.03 (s, 8H), 4.90 (s, 4H), 3.83 (s, 2H), 2.83 (t,  $J = 7.3$  Hz, 2H), 2.56 (t,  $J = 6.9$  Hz, 2H); IR (KBr)  $\nu$ : 2250  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1048.6 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{58}\text{H}_{49}\text{S}_6\text{O}_6\text{N}$ : C 66.45, H 4.71, N 1.34; found C 66.14, H 4.64, N 1.11.

**Compound 33:** Compound **33** was prepared in a similar manner as for compound **14** from compounds **32** and 1,4-cyclohexanedibromomethane as an orange oil in 60% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.46 (m, 20H), 6.73—6.55 (m, 9H), 6.22—6.13 (m, 2H), 5.09 (s, 8H), 4.99 (s, 4H), 3.90 (s, 2H), 3.31 (d,  $J = 6.3$  Hz, 2H), 2.65 (d,  $J = 5.6$  Hz, 2H), 1.96 (m, 4H), 1.32 (m, 2H), 0.91 (m, 4H); IR (KBr)  $\nu$ : 1595, 1449  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1182.0 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{63}\text{H}_{59}\text{S}_6\text{O}_6\text{Br}$ : C 63.89, H 5.02; found C 64.20, H 5.30.

**Compound 34:** Compound **34** was prepared in a similar manner as for compound **16** from compounds **33** as an orange oil in 73% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.40 (m, 20H), 6.67—6.49 (m, 9H), 6.20—6.00 (m, 2H), 5.04 (s, 8H), 4.95 (s, 4H), 3.85 (s, 2H), 3.10 (d,  $J = 5.4$  Hz, 2H), 2.63 (d,  $J = 5.7$  Hz, 2H), 1.82 (m, 4H), 1.26 (m, 2H), 0.95 (m, 4H); IR (KBr)  $\nu$ : 2096, 1596, 1450  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 1144.8 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{63}\text{H}_{59}\text{S}_6\text{O}_6\text{N}_3$ : C 66.00, H 5.19, N 3.66; found C 66.40, H 5.31, N 3.78.

**Compound 35:** Compound **35** was prepared in a similar manner as for compound **18** from compounds **34** as an orange oil in 82% yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 7.48 (m, 20H), 6.92—6.57 (m, 9H), 6.22—6.07 (m, 2H), 5.04 (s, 8H), 4.95 (s, 4H), 3.85 (s, 2H), 2.68 (d,  $J = 6.5$  Hz, 2H), 2.62 (d,  $J = 6.2$  Hz, 2H), 1.89 (m, 4H), 1.28 (m, 4H), 0.97 (m, 4H); IR (KBr)  $\nu$ : 3447, 3323, 1595, 1450  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ :

1119.1 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{63}\text{H}_{61}\text{S}_6\text{O}_6\text{N}$ : C 67.53, H 5.49, N 1.25; found C 67.14, H 5.09, N 1.04.

**Triad 6:** A solution of compound **35** (0.39 g, 0.35 mmol) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.04 g, 0.15 mmol) in dry DMF (15 mL) was heated to 120 °C under  $\text{N}_2$  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  $\text{CH}_2\text{Cl}_2$ /petroleum ether as eluent afforded triad **6** as green powders in 77% yield. m.p. 87—88 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 8.74 (s, 4H), 7.57 (m, 40H), 6.67—6.50 (m, 18H), 6.50—6.07 (m, 4H), 5.04 (s, 16H), 4.96 (s, 8H), 4.09 (d,  $J = 6.8$  Hz, 4H), 3.85 (s, 4H), 2.57 (t,  $J = 6.3$  Hz, 4H), 1.85 (m, 8H), 1.13 (m, 4H), 0.89 (m, 8H); IR (KBr)  $\nu$ : 1703, 1665, 1595  $\text{cm}^{-1}$ ; MS (MALDI-TOF)  $m/z$ : 2470.0 ( $\text{M}^+$ ). Anal. calcd for  $\text{C}_{140}\text{H}_{122}\text{S}_{12}\text{O}_{16}\text{N}_2$ : C 67.99, H 4.97, N 1.13; found C 67.52, H 5.36, N 1.00.

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