

**Photoinduced Electron-Transfer Processes of  
Tetrathiafulvalene-(Spacer)- (Naphthalenediimide)-(Spacer)-Tertrathiafulvalene  
Triads in Solution**

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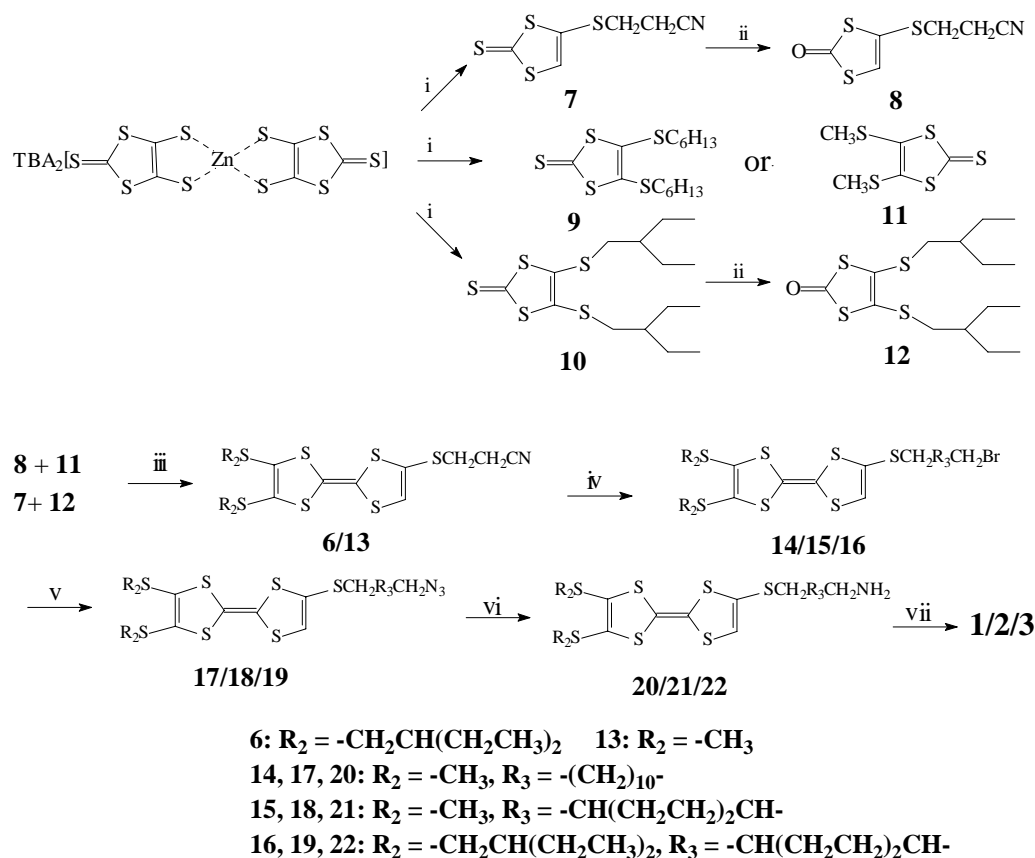
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**Procedure of Synthesis of Tetrathiafulvalene-(Spacer)-  
(Naphthalenediimide)-(Spacer)-Tertrathiafulvalene Triads**

**General descriptions:**

The usual approach to TTF-naphthalenediimide derivatives is based on the condensation reaction between the corresponding primary amines with naphthalene dianhydride. This strategy requires the preparation of primary TTF-amines. *Jan Becher* et al has prepared TTF-amine derivatives using the classic Gabriel transformation.<sup>1</sup> Here we employed another route to synthesize TTF-amines based on the new reaction of TBA<sub>2</sub>[Zn(DMIT)<sub>2</sub>] reported by us recently.<sup>2,3</sup>

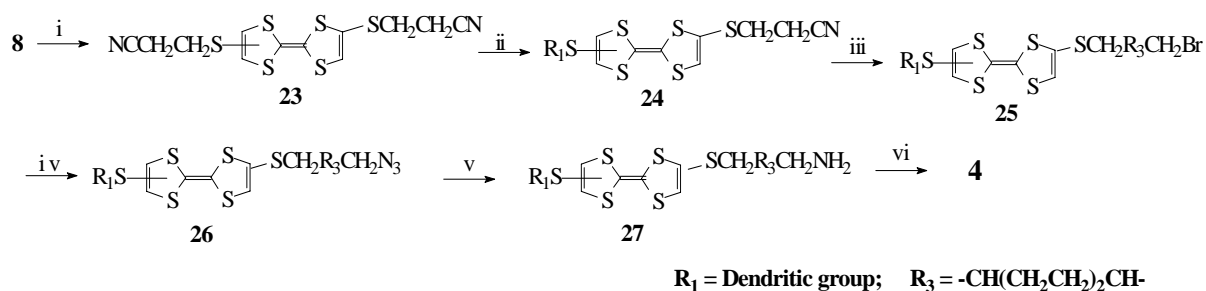
As shown in Chart S1, compound **8** was prepared by oxidation of compound **7** with  $\text{Hg}(\text{OAc})_2$ , which was easily synthesized from  $\text{TBA}_2[\text{Zn}(\text{DMIT})_2]$  and 3-bromopropionitrile in the presence of pyridine hydrogen chloride.<sup>3</sup> Compounds **9-11** was obtained using the reported procedure.<sup>4</sup> Compound **10** was converted to compound **12**. Cross-coupling reaction of compound **12** and **7** in a 1:3 ratio afforded compound **6** in the yield of 62% after column chromatography. Compound **13** was synthesized by the cross-coupling of **8** and **11** in the presence of tri(*i*-propyl)phosphite in the yield of 55% after purification. By using deprotection/alkylation method with cyanoethyl-protected TTF **6** and **13**, compounds **14**, **15** and **16** were obtained, these compounds were directly converted to compounds **17**, **18** and **19** by reaction with large excess of  $\text{NaN}_3$  in dry DMF in high yields, respectively. Reduction of compounds **17**, **18** and **19** in THF solution with  $\text{PPh}_3/\text{H}_2\text{O}$  gave the TTF-amines **20**, **21** and **22**, which were further purified by recrystallization from  $\text{CH}_2\text{Cl}_2$ /petroleum ether after column chromatography. Triads **1**, **2** and **3** (Scheme 1 in text) were produced by the reaction of compounds **20**, **21** and **22** with naphthalene dianhydride, respectively, catalyzed by  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  in the solution of quinoline under an atmosphere of dry  $\text{N}_2$  at  $160^\circ\text{C}$  for 3-4 hours in relatively high yields (about 70% ).



**CHART S1.** *Reagents:* i,  $BrCH_2CH_2CN$  or  $C_6H_{13}Br$  or  $CH_3I$  or  $BrCH_2CH(CH_2CH_3)_2$ ,  $CH_3CN$ ; ii,  $Hg(OAc)_2$ ,  $CH_2Cl_2$ ; iii, tri (*i*-propyl) phosphite,  $120^\circ C$ ; iv,  $CsOH \cdot H_2O$ , THF,  $Br(CH_2)_{12}Br$ /  $BrCH_2CH(CH_2CH_2)_2CHCH_2Br$ ; v, DMF,  $NaN_3$ ; vi,  $PPh_3/H_2O$ , THF; vii, perylene dianhydride,  $Zn(Ac)_2 \cdot 2H_2O$ , quinoline,  $N_2$ ,  $160^\circ C$ .

Scheme S2 shows the synthetic route to triad **4** (Chart 1 in text). Self-coupling reaction of compound **8** in the presence of tri(*i*-propyl)phosphite lead to compound **23** with *cis/trans* isomers. The corresponding thiolate formed *in situ* by removal of one cyanoethyl group reacted with bromo-dendrimer to afford compound **24**. By deprotection of second cyanoethyl group and sequentially reaction with the G2 dendrimer, compound **24** was transformed to compound **25**. Compounds **26** and **27** were prepared similarly as for **17** and **20**, respectively. It should be noted that attempts to obtain triad **4** using the same reaction condition as for triads **1-3** are failed. But,

reaction of compound **27** with naphthalene dianhydride in dry DMF at 120°C overnight followed by column chromatography separation successfully afforded triad **4** in moderate yield.



**CHART S2.** *Reagents:* i, tri (*i*-propyl) phosphite, toluene, 120°C; ii, CsOH·H<sub>2</sub>O, THF, Bromodendrimer (R<sub>1</sub>Br, see Scheme 1); iii, CsOH·H<sub>2</sub>O, THF, BrCH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>Br; iv, DMF, NaN<sub>3</sub>; v, PPh<sub>3</sub>/H<sub>2</sub>O, THF; vi, perylene dianhydride, DMF, N<sub>2</sub>, 120°C

For comparative studies, the reference compound **5** (Chart1 in text) was prepared starting from naphthalene dianhydride and *n*-hexyl amine. Compound **6** (Chart1 in text) was used as another reference compound.

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### General Measurements:

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 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.

THF was distilled from sodium/benzophenone immediately prior to use. DMF was pre-dried by standing over molecular sieves (4Å) 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. 5 and  $\text{TBA}_2[\text{Zn}(\text{DMIT})_2]$  was prepared according to Ref. 6. Compound **7** was prepared according to Ref. 3. Compounds **6**, **8** and **13** were synthesized according to the procedures described in Ref. 4, and compounds **9-12** based on Ref. 5. 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  $\text{N}_2$ .

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### Synthesis procedures and data for the compounds.

**Compound 14:** To a solution of compound **13** (1.00g, 2.62mmol) in anhydrous degassed THF (80mL) was added a solution of  $\text{CsOH}\cdot\text{H}_2\text{O}$  (0.48g, 2.88mmol) in anhydrous degassed MeOH (30mL) over a period of 30min. The mixture was stirred for an additional 30 min, whereupon a solution of 1,12-dibromododecane (1.00g, 3.05mmol) in anhydrous degassed THF (30mL) 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;  $\nu_{\text{max}}/\text{cm}^{-1}$  2924, 2852 (alkyl C-H);  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 6.33 (1 H, s, olefinic), 3.41 (2 H, t, J 6.7,  $\text{CH}_2\text{Br}$ ), 2.75 (2 H, t, J 6.5,  $\text{SCH}_2$ ), 2.43 (6 H, s,  $2\text{SCH}_3$ ), 1.83(2 H, m,  $\text{CH}_2$ ), 1.58 (2 H, m,  $\text{CH}_2$ ), 1.40-1.20 (16 H, m,  $8\text{CH}_2$ );  $m/z$  (EI) 576( $\text{M}^+$ ); Found: C, 41.97; H, 5.36;  $\text{C}_{20}\text{H}_{31}\text{S}_7\text{Br}$  requires C, 41.81; H,

5.44%.

**Compound 15:** Compound **15** was obtained similarly from compound **13** and 1,4-cyclohexanedibromo methane in 75% yield. m.p. 132-133 °C;  $\nu_{\max}/\text{cm}^{-1}$  2920 and 2844(alkyl C-H);  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 6.22 (1 H, s, olefinic), 3.30 (2 H, d, J 6.0,  $\text{BrCH}_2$ ), 2.67 (2 H, d, J 4.0,  $\text{SCH}_2$ ), 2.44 (6 H, s,  $2\text{SCH}_3$ ), 1.95 (4 H, m, alkyl-H), 1.56 (2 H, m, alkyl-H), 1.08 (4 H, m, alkyl-H);  $m/z$  (EI) 518( $\text{M}^+$ ); Found: C, 37.50; H, 4.17;  $\text{C}_{16}\text{H}_{21}\text{S}_7\text{Br}$  requires C, 37.12; H, 4.09%.

**Compound 16:** Compound **16** was prepared in a similar manner from **6** and 1,4-cyclohexanedi bromomethane as an orange oil in 70% yield.  $\nu_{\max}/\text{cm}^{-1}$  2960 and 2921 (alkyl C-H).  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 6.31 (1 H, s, olefinic), 3.30 (2 H, d, J 6.5,  $\text{CH}_2\text{Br}$ ), 2.80 (4 H, d, J 5.8,  $2\text{SCH}_2$ ), 2.65 (2 H, d, J 6.8,  $\text{SCH}_2$ ), 1.94 (4 H, br, alkyl-H), 1.43 (12 H, br, alkyl-H), 0.90 (16 H, br, alkyl-H);  $m/z$  (MALDI-TOF) 657.9; Found: C, 47.20; H, 6.14;  $\text{C}_{26}\text{H}_{41}\text{S}_7\text{Br}$  requires C, 47.46; H, 6.28%.

**Compound 17:** A solution of compound **14** (1.48g, 2.56mmol) in dry DMF (50mL) was treated with  $\text{NaN}_3$  (0.85g, 13.07mmol) at 25 °C under  $\text{N}_2$  for 12h and then 30mL of water was added. The aqueous solution was extracted with (3×50mL)  $\text{CH}_2\text{Cl}_2$ , and the combined extracts were washed with  $\text{H}_2\text{O}$  (2×50mL) and saturated aqueous NaCl (20mL), 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.  $\nu_{\max}/\text{cm}^{-1}$  2096 ( $-\text{N}_3$ );  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 6.33 (1 H, s, olefinic), 3.26 (2 H, t, J 6.7,  $\text{CH}_2\text{N}_3$ ), 2.74 (2 H, t, J 6.9,  $\text{SCH}_2$ ), 2.43 (6 H, s,  $2\text{SCH}_3$ ), 1.59 (4 H, m,  $2\text{CH}_2$ ), 1.40-1.20 (16 H, m,  $8\text{CH}_2$ );  $m/z$  (MALDI-TOF) 537.0 ( $\text{M}^+$ ). Found: C, 44.70; H, 5.87; N, 7.70;  $\text{C}_{20}\text{H}_{31}\text{N}_3\text{S}_7$  requires C, 44.66; H, 5.81; N, 7.81%.

**Compound 18:** Compound **18** was obtained similarly from compound **15** in 92% Yield. M.p. 86-87 °C.  $\nu_{\max}/\text{cm}^{-1}$  2096 (-N<sub>3</sub>).  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.35 (1 H, s, olefinic), 3.16 (2 H, d, J 6.5, CH<sub>2</sub>N<sub>3</sub>), 2.68 (2 H, d, J 6.8, SCH<sub>2</sub>), 2.45 (6 H, s, 2SCH<sub>3</sub>), 1.95 (4 H, m, alkyl-H), 1.56 (2 H, m, alkyl-H), 1.03 (4 H, m, alkyl-H);  $m/z$  (EI) 479 (M<sup>+</sup>); Found: C, 40.40; H, 4.49; N, 8.42; C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>S<sub>7</sub> requires C, 40.05; H, 4.41; N 8.76%.

**Compound 19:** Compound **19** was prepared in a similar manner from **16** as an orange oil in 70% yield.  $\nu_{\max}/\text{cm}^{-1}$  2095 (-N<sub>3</sub>);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.33 (1 H, s, olefinic), 3.18 (2 H, d, J 6.6, CH<sub>2</sub>N<sub>3</sub>), 2.84 (4 H, d, J 5.0, 2SCH<sub>2</sub>), 2.67 (2 H, d, J 6.8, SCH<sub>2</sub>), 1.88 (4 H, m, alkyl-H), 1.47 (12 H, m, alkyl-H), 1.06 (4 H, m, alkyl-H), 0.94 (12 H, m, 4CH<sub>3</sub>);  $m/z$  (MALDI-TOF) 619.1; Found: C, 50.74; H, 6.88; N, 7.02; C<sub>26</sub>H<sub>41</sub>N<sub>3</sub> S<sub>7</sub> requires C, 50.36; H, 6.66; N, 6.78%.

**Compound 20:** A solution of compound **17** (0.50g, 0.93mmol) in THF (10mL) was treated with PPh<sub>3</sub> (0.49g, 1.86mmol) and H<sub>2</sub>O (167uL, 9.29mmol) at 25°C under N<sub>2</sub> and then warmed at 45 °C for 10h. The crude product was first purified by column chromatography and then further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether to give the product as red powders in 87% yield. M.p. 70-71 °C;  $\nu_{\max}/\text{cm}^{-1}$  3376 and 3320 (-NH<sub>2</sub>).  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.33 (1 H, s, olefinic), 2.74 (2 H, t, J 6.9, SCH<sub>2</sub>), 2.62 (2 H, t, J 6.7, NCH<sub>2</sub>), 2.43 (6 H, s, 2CH<sub>3</sub>), 1.60 (6 H, m, 2CH<sub>2</sub>+ NH<sub>2</sub>), 1.40-1.20 (16 H,;m, 8CH<sub>2</sub>).  $m/z$  (EI) 511 (M<sup>+</sup>); Found: C, 47.15; H, 6.44; N, 2.72; C<sub>20</sub>H<sub>33</sub>NS<sub>7</sub> requires C, 46.93; H, 6.50; N, 2.74%.

**Compound 21:** Compound **21** was obtained similarly from **18** as red powders in 71% yield. M.p. 94-95 °C;  $\nu_{\max}/\text{cm}^{-1}$  3320 and 3307 (-NH<sub>2</sub>);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.32 (1 H, s, olefinic), 2.67 (2 H, d, J 6.8, CH<sub>2</sub>N), 2.52 (2 H, d, J 6.4, SCH<sub>2</sub>), 2.43 (6 H, s, 2SCH<sub>3</sub>), 1.90 (4 H, m, alkyl-H), 1.50 (2 H, m, alkyl-H), 1.27 (2 H, br, NH<sub>2</sub>), 0.95 (4

H, m, alkyl-H);  $m/z$  (EI) 453 ( $M^+$ ). Found: C, 42.63; H, 5.27; N, 3.10;  $C_{16}H_{23}NS_7$  requires C, 42.35; H, 5.11; N, 3.09%.

**Compound 22:** Compound **22** was obtained similarly from compound **19** as an orange oil in 80% yield.  $\nu_{\max}/\text{cm}^{-1}$  3445 and 3315 ( $-\text{NH}_2$ );  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 6.28 (1 H, s, olefinic), 2.79 (4 H, d, J 5.3,  $2\text{SCH}_2$ ), 2.63 (2 H, d, J 6.8,  $\text{SCH}_2$ ), 2.51 (2 H, d, J 6.4,  $\text{CH}_2\text{N}$ ), 1.89 (4 H, br, alkyl-H), 1.40 (14 H, br, alkyl-H+ $\text{NH}_2$ ), 0.89 (16 H, br, alkyl-H);  $m/z$  (MALDI-TOF) 593.2; Found: C, 52.01; H, 7.14; N, 2.20;  $C_{26}H_{43}NS_7$  requires C, 52.57; H, 7.30; N, 2.36%.

**Triad 1** (Chart1 in text): Naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.026g, 0.097mmol) was stirred under  $\text{N}_2$  with compound **20** (0.120g, 0.234mmol) and Zinc acetate (0.022g, 0.098mmol) in quinoline (5 mL) at 160 °C for 3h. The reaction mixture was cooled down to room temperature and poured into HCl (1M, 100mL). The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50mL) 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 °C;  $\nu_{\max}/\text{cm}^{-1}$  1703 and 1660 ( $-\text{CON}-$ );  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.76 (4 H, s, Ar-H), 6.32 (2 H, s, olefinic), 4.20 (4 H, t, J 6.7,  $2\text{NCH}_2$ ), 2.72 (4 H, t, J 6.9,  $2\text{SCH}_2$ ), 2.42 (12 H, s,  $4\text{SCH}_3$ ), 1.80-1.60 (8 H, m,  $4\text{CH}_2$ ), 1.40-1.20 (32 H, m,  $16\text{CH}_2$ );  $m/z$  (MALDI-TOF) 1253.9 ( $M^+$ ); Found: C, 51.60; H, 5.25; N, 2.16;  $C_{54}H_{66}N_2O_4S_{14}$  requires C, 51.67; H, 5.30; N, 2.2%.

**Triad 2** (Chart 1 in text): Triad **2** was obtained similarly from **21** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 69% yield. M.p. 164-165 °C;  $\nu_{\max}/\text{cm}^{-1}$  1703, 1664 and 1580 ( $-\text{CON}-$ );  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 8.77 (4 H, s, Ar-H), 6.31 (2 H, s, olefinic), 4.11 (4 H, d, J 6.8,  $2\text{NCH}_2$ ), 2.63 (4 H, d, J 6.8,  $2\text{SCH}_2$ ),



2.43 (12 H, s, 4SCH<sub>3</sub>), 1.90 (8 H, m, alkyl-H), 1.56 (4 H, m, alkyl-H), 1.22-0.88 (8 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 1138.0(M<sup>+</sup>); Found: C, 48.93; H, 4.60; N, 2.59; C<sub>46</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>S<sub>14</sub> requires C, 48.51; H, 4.07; N, 2.46%.

**Triad 3** (Chart 1 in text):: Triad **3** was obtained similarly from **22** and naphthalene-1,4,5,8-tetracarboxylic dianhydride in 70% yield. M.p. 110-111 °C;  $\nu_{\max}/\text{cm}^{-1}$  1703, 1665 and 1581 (-CON-);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.76 (4 H, s, Ar-H), 6.30 (2 H, s, olefinic), 4.10 (4 H, d, J 7.4, 2NCH<sub>2</sub>), 2.81 (8 H, d, J 6.1, 4SCH<sub>2</sub>), 2.63 (4 H, d, J 6.8, 2SCH<sub>2</sub>), 1.87 (8 H, m, alkyl-H), 1.43 (24 H, m, alkyl-H), 1.21 (4 H, m, alkyl-H), 0.89 (32 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 1418.1; Found: C, 55.65; H, 6.08; N, 1.94; C<sub>66</sub>H<sub>86</sub>N<sub>2</sub>O<sub>4</sub>S<sub>14</sub> requires C, 55.82; H, 6.10; N, 1.97%.

**Compound 23:** To a solution of compound **8** (0.20g, 0.98mmol) in toluene (10mL) was added triisopropyl phosphite (2 ml). The resulting suspension was heated to 120 °C under N<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub>/petroleum ether (60-90°C) (1:2, v/v) as eluent afforded compound **23** as a yellow powders in 63% yield. M.p. 114-115 ;  $\nu_{\max}/\text{cm}^{-1}$  2248 (-CN);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 6.29 (2 H, s, olefinic), 3.04 (4 H, t, J 8.4, 2CH<sub>2</sub>CN), 2.72 (4 H, t, J 8.4, 2SCH<sub>2</sub>);  $m/z$  (EI) 374 (M<sup>+</sup>). Found: C, 38.08; H, 2.66; N, 7.46; C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>S<sub>6</sub> requires C, 38.48; H, 2.69; N 7.48%.

**Compound 24:** Compound **24** was prepared in a similar manner as for compound **13** from compound **23** and bromodendrimer (R<sub>1</sub>Br, see Scheme 3) as an orange oil in 72% yield.  $\nu_{\max}/\text{cm}^{-1}$  2250 (-CN);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.57 (20 H, m, Ar-H), 6.66-6.49 (9 H, m, Ar-H), 6.40 (1 H, d, J 7.7, olefinic), 6.08 (1 H, s, olefinic), 5.03 (8 H, s, 4CH<sub>2</sub>), 4.90 (4 H, s, 2CH<sub>2</sub>), 3.83 (2 H, s, CH<sub>2</sub>), 2.83 (2 H, t, J 7.3, CH<sub>2</sub>CN), 2.56 (2 H,

t, J 6.9, SCH<sub>2</sub>);  $m/z$  (MALDI-TOF) 1048.6; Found: C, 66.14; H, 4.64; N, 1.11; C<sub>58</sub>H<sub>49</sub>NO<sub>6</sub>S<sub>6</sub> requires C, 66.45; H, 4.71; N, 1.34%.

**Compound 25:** Compound **25** was prepared in a similar manner as for compound **14** from compounds **24** and 1,4-cyclohexanedibromomethane as an orange oil in 60% yield.  $\nu_{\max}/\text{cm}^{-1}$  1595 and 1449 (Ar);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.46 (20 H, m, Ar-H), 6.73-6.55 (9 H, m, Ar-H), 6.22-6.13 (2 H, m, olefinic), 5.09 (8 H, s, 4CH<sub>2</sub>O), 4.99 (4 H, s, 2OCH<sub>2</sub>), 3.90 (2 H, s, SCH<sub>2</sub>O), 3.31 (2 H, d, J 6.3, BrCH<sub>2</sub>), 2.65 (2 H, d, J 5.6, SCH<sub>2</sub>), 1.96 (4 H, m, alkyl-H), 1.32 (2 H, m, alkyl-H), 0.91 (4 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 1182.0; Found: C, 64.15; H, 5.30; C<sub>63</sub>H<sub>59</sub>O<sub>6</sub>S<sub>6</sub>Br requires C, 63.89; H, 5.02%.

**Compound 26:** Compound **26** was prepared in a similar manner as for compound **17** from compounds **25** as an orange oil in 73% yield.  $\nu_{\max}/\text{cm}^{-1}$  2096 (-CN), 1596 and 1450 (Ar);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.40 (20 H, m, Ar-H), 6.67-6.49 (9 H, m, Ar-H), 6.20-6.00 (2 H, m, olefinic), 5.04 (8 H, s, 4OCH<sub>2</sub>), 4.95 (4 H, s, 2OCH<sub>2</sub>), 3.85 (2 H, s, SCH<sub>2</sub>), 3.10 (2 H, d, J 5.4, CH<sub>2</sub>N<sub>3</sub>), 2.63 (2 H, d, J 5.7, SCH<sub>2</sub>), 1.82 (4 H, m, alkyl-H), 1.26 (2 H, m, alkyl-H), 0.95 (4 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 1144.8; Found: C, 66.30; H, 5.31; N, 3.78; C<sub>63</sub>H<sub>59</sub>N<sub>3</sub>O<sub>6</sub>S<sub>6</sub> requires C, 66.02; H, 5.19; N, 3.66%.

**Compound 27:** Compound **27** was prepared in a similar manner as for compound **20** from compounds **26** as an orange oil in 82% yield.  $\nu_{\max}/\text{cm}^{-1}$  3447 and 3323 (-NH<sub>2</sub>), 1595 and 1450 (Ar);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 7.48 (20 H, m, Ar-H), 6.92-6.57 (9 H, m, Ar-H), 6.22-6.07 (2 H, m, olefinic), 5.04 (8 H, s, 4OCH<sub>2</sub>), 4.95 (4 H, s, 2OCH<sub>2</sub>), 3.85 (2 H, s, SCH<sub>2</sub>O), 2.68 (2 H, d, J 6.5, CH<sub>2</sub>N), 2.62 (2 H, d, J 6.2, SCH<sub>2</sub>), 1.89 (4 H, m, alkyl-H), 1.28 (4 H, m, alkyl-H+NH<sub>2</sub>), 0.97 (4 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 1119.1; Found: C, 67.14; H, 5.19; N, 1.04; C<sub>63</sub>H<sub>61</sub>NO<sub>6</sub>S<sub>6</sub> requires C, 67.50; H, 5.49; N,

1.25%.

**Triad 4** (Chart1 in text): A solution of compound **27** (0.39g, 0.35mmol) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (0.04g, 0.15mmol) in dry DMF (15mL) was heated to 120 °C under N<sub>2</sub> 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 CH<sub>2</sub>Cl<sub>2</sub> / petroleum ether as eluent afforded triad **4** as green powders in 77% yield. M.p. 87-88 °C;  $\nu_{\text{max}}/\text{cm}^{-1}$  1703, 1665 and 1595 (-CON-);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.74 (4 H, s, Ar-H), 7.57 (40 H, m, Ar-H), 6.67-6.50 (18 H, m, Ar-H), 6.50-6.07 (4 H, m, olefinic), 5.04 (16 H, s, 8OCH<sub>2</sub>), 4.96 (8 H, s, 4OCH<sub>2</sub>), 4.09 (4 H, d, J 6.8, 2NCH<sub>2</sub>), 3.85 (4 H, s, 2SCH<sub>2</sub>O), 2.57 (4 H, t, J 6.3, 2SCH<sub>2</sub>), 1.85 (8 H, m, alkyl-H), 1.13 (4 H, m, alkyl-H), 0.89 (8 H, m, alkyl-H);  $m/z$  (MALDI-TOF) 2470.0; Found: C, 67.52; H, 5.30; N, 1.00; C<sub>140</sub>H<sub>122</sub>N<sub>2</sub>O<sub>16</sub> S<sub>12</sub> requires C, 67.99; H, 4.97; N, 1.13%.

Compound **5** (Chart 1 in text): it was prepared similarly from naphthalene-1,4,5,8-tetracarboxylic dianhydride and *n*-hexyl amine in 85% yield. M.p. 223-224°C; Found: C, 71.58; H, 6.95; N, 6.49; C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub> requires C, 71.87; H, 6.96; N, 6.45%.

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