Supplementary Information

SYNTHESIS AND APPLICATION OF STILBENOID PHENOTHIAZINE DENDRIMERS AS ADDITIVE FOR THE DYE SENSITIZED SOLAR CELLS

Mahalingam Ravivarma^a, Chinnadurai Satheeshkumar^a, Shanmugam Ganesan^b, Perumal Rajakumar^{*a}

^aDepartment of Organic Chemistry, University of Madras, Chennai-600 025, Tamil nadu, India

^bDepartment of Chemistry, SRM University, Chennai-603 203, Tamil nadu, India

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General Information: All melting points were determined using a Toshniwal meltingpoint apparatus by open capillary tube method and are uncorrected.¹H NMR and ¹³CNMR spectra were recorded on a Bruker 300 MHz instruments. The IR spectra were recorded on FTIR-8300 spectrophotometer The UV-Vis spectra were recorded on Agilent 8453 spectrophotometer. The emission spectra were recorded on HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. MALDI-TOF mass spectra were recorded on Voyager-DE PRO mass spectrometer using a α -cyano-4-hydroxy cinnamic acid (CHCA) matrix and EI-MS spectra on Jeol DX-303 mass spectrometer. The FAB-MS spectra were recorded on JEOL SX 102/DA-6000 mass spectrometer using p-nitrobenzyl alcohol (NBA) as matrix. DSSC studies using a BAS 100A Electrochemical analyser. Column chromatography was performed on silica gel (ACME, 100e200 mesh). Routine monitoring of the reaction was made using thin layer chromatography developed on glass plates coatedwith silica gel-G (ACME) of 25 mm thickness and visualized with iodine.

General procedure for Heck Coupling (Procedure A): A stirred mixture of bromo compound (1.0 equiv.), Pd(OAc)₂ (0.2/0.3 equiv.) in dry DMF (25 mL) under nitrogen was successively treated with K₂CO₃ (6.0/ 9.0 equiv.) and tetrabutylammonium bromide (0.2/ 0.3 equiv.) and stirred for 30 minutes. Then, the vinyl dendron (2.0/ 3.0 equiv.) was added and the resulting mixture was stirred at 90 °C for 12 h, cooled and filtered. The filtrate was evaporated to dryness in vacuo. The residue was extracted with CHCl₃ (3x100 mL), washed with water (3x100 mL) and dried over anhydrous Na₂SO₄. Evaporation of the organic layer afforded the crude product, which was purified by column chromatography using the eluent as mentioned under each compound to afford the corresponding conjugated dendrimers.

Dendrimer 1: Following the general procedure A for Heck Coupling, the stilbenoid phenothiazine dendrimer **1** was obtained from 2,6dibromopyridine **13** (0.3 g, 1.26 mmol) and 10-n-butyl-3-vinyl-10*H*-phenothiazine **12** (0.74 g, 2.65 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (4:1) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **93** as yellow solid in 68 % yield; M.P. 134-136 °C; IR:(ATR, cm⁻¹) 967; ¹H NMR:(300 MHz, CDCl₃) $\delta_{\rm H} 0.87$ (t, 6H, J = 7.5 Hz); 1.34-1.43 (m, 4H);1.67-1.74 (m, 4H); 3.77 (t, 4H, J = 6.6 Hz); 6.74-6.79 (m, 4H); 6.84 (d, 2H, J = 7.2 Hz); 6.95 (d, 2H, J = 16.2 Hz); 7.04-7.09 (m, 6H); 7.26-7.29 (m, 4H); 7.46 (d, 2H, J = 6 Hz); 7.52 (s, 1H); ¹³C NMR :(75 MHz, CDCl₃) $\delta_{\rm C}$ 12.8, 19.2, 27.9, 46.3, 114.3, 114.4, 119.0,121.5, 123.3, 123.9, 124.6, 125.6, 126.2, 126.4, 126.6, 130.3, 130.6, 135.8, 143.8, 144.2, 154.5; ESI-MS: m/z 638.3 [M⁺]; Anal.calc for C₄₁H₃₉N₃S₂: C, 77.20; H, 6.16; N, 6.59. Found: C, 77.08; H, 6.10; N, 6.51.

Dendrimer 2: Following the general procedure A for Heck Coupling, the stilbenoid phenothiazine dendrimer **2** was obtained from 4-bromo-*N*-(4-bromophenyl)-*N*-ethylaniline **14** (0.4 g, 1.12 mmol) and 10-n-butyl-3-vinyl-10*H*-phenothiazine **12** (0.69 g, 2.47 mmol). The crude product was purified by column chromatography using CHCl₃:MeOH (9:2) as the eluting solvent to give the stilbenoid phenothiazinedendrimer **2** as light yellow solid in 64 % yield; M. P. 80-82 °C; IR:(ATR, cm⁻¹) 957; ¹H NMR:(300MHz, DMSO-d₆): $\delta_{\rm H}$ 0.88 (t, 6H, *J* = 7.2 Hz); 1.15 (t, 3H, *J* =6.6 Hz); 1.34-1.46 (m, 4H); 1.63-1.69 (m, 4H); 3.79 (q, 2H, *J* = 6.9Hz); 3.87 (t, 4H, *J* = 6.6 Hz); 6.91-7.06 (m, 13H); 7.11-7.22 (m, 5H); 7.36 (s, 4H); 7.46 (d, 4H, *J* = 8.1 Hz). ¹³C NMR:(75MHz, DMSO-d₆): $\delta_{\rm C}$ 12.5, 13.6, 19.4, 28.4, 45.8, 46.2, 115.7,115.8, 120.5, 122.4, 123.1, 123.8, 124.3, 124.8, 125.7, 126.6, 127.1, 127.4, 127.6, 130.2, 132.0, 143.6, 144.4, 146.1. Anal.calc for C₅₀H₄₉N₃S₂: C, 79.43; H, 6.53; N, 5.56. Found: C, 79.36; H, 6.41; N, 5.42.

Dendrimer 3: Following the general procedure A for Heck Coupling, the stilbenoid phenothiazine dendrimer **3** was obtained from 3,7-dibromo-10-ethyl-10*H*-phenothiazine **15** (0.6 g, 1.55 mmol)and 10-n-butyl-3-vinyl-10*H*-phenothiazine **12** (0.96 g, 3.42 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (4:1) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **3** as yellowish orange solid in 62 % yield; M. P.95 - 97 °C; IR:(ATR, cm⁻¹) 957; ¹H NMR: 300MHz, CDCl₃): $\delta_{\rm H}$ 0.94 (t, 6H, *J* = 7.2 Hz); 1.39-1.52 (m, 7H);1.74-1.84 (m, 4H); 3.84 (t, 4H, *J* = 7.2 Hz); 3.93 (q, 2H, *J* = 7.2 Hz); 6.79 (s, 2H); 6.81-6.84 (m, 6H); 6.86-6.87 (m, 2H); 6.91(d, 2H, *J* = 6.9 Hz); 7.12 (d, 4H, *J* = 7.5 Hz); 7.16-7.17(m, 1H); 7.19-7.21 (m, 2H); 7.23-7.25 (m, 3H); 7.26 (bs, 2H). ¹³C NMR: (75MHz, CDCl₃): $\delta_{\rm C}$ 12.9, 13.8, 20.2, 29.0, 42.0, 47.2, 114.8,115.3, 122.4, 123.9, 124.4, 124.7, 124.8, 125.1, 125.6, 125.7, 125.9, 127.2, 127.4, 131.9, 143.5, 144.4, 144.9; FAB-MS: *m/z* 786.2 [M+H]⁺; Anal.calc forC₅₀H₄₇N₃S₃; C, 76.39; H, 6.03; N, 5.35. Found: C, 76.31; H, 5.89; N, 5.29.

Dendrimer 4: Following the general procedure A for Heck Coupling, the stilbenoid phenothiazine dendrimer **4** was obtained from 1,3,5-tribromo-2,4,6-trimethylbenzene **16** (0.3 g, 0.84 mmol)and 10-n-butyl-3-vinyl-10*H*-phenothiazine **12** (0.73 g, 2.6 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (4:1) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **4** as yellow solid in 68 % yield; M. P. 60-62 °C; IR:(ATR, cm⁻¹) 966; ¹H NMR: (300MHz, CDCl₃): $\delta_{\rm H}$ 0.94 (t, 9H, *J* = 7.2 Hz); 1.42-1.49 (m, 6H);1.75-1.82 (m, 6H); 2.46 (s, 9H); 3.86 (t, 6H, *J* = 6.9 Hz); 6.32 (d, 3H, *J* = 16.5 Hz); 6.82-6.97 (m, 14H); 7.13 (d, 6H, *J* = 7.8 Hz); 7.23 (d, 4H, *J* = 14.7 Hz). ¹³C NMR: (75MHz, CDCl₃): $\delta_{\rm C}$ 13.8, 18.9, 22.4, 29.0, 47.2, 115.3, 115.4,122.5, 124.8, 125.7, 126.2, 127.1, 127.3, 127.5, 131.7, 133.4, 133.6, 134.7, 136.9, 144.8, 145.0. Anal.calc for C₆₃H₆₃N₃S₃: C, 78.95; H, 6.63; N, 4.38. Found: C, 78.87; H, 6.75; N, 4.29.

Dendrimer 5: Following the general procedure A for Heck Coupling, the stilbenoid phenothiazine dendrimer **5** was obtained from tris(4-bromophenyl)amine **17** (0.4 g, 0.82 mmol)and 10-n-butyl-3-vinyl-10*H*-phenothiazine **12** (0.77 g, 2.7 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (7:3) as the eluting solvent to give thestilbenoid phenothiazine dendrimer **5** as yellow solid in 71 %

yield; M. P.: 113 - 115 °C; IR:(ATR, cm⁻¹) 960; ¹H NMR:(300MHz, CDCl₃): $\delta_{\rm H}$ 0.87 (t, 9H, *J* =7.2 Hz); 1.33-1.45 (m, 6H);1.67-1.77 (m, 6H); 3.77 (t, 6H, *J* = 6.6 Hz); 6.72-6.85 (m, 14H); 6.98-7.09 (m, 12H); 7.15-7.20 (m, 8H); 7.29 (d, 5H, *J* = 8.4 Hz). ¹³C NMR: (75MHz, CDCl₃): $\delta_{\rm C}$ 13.8, 20.2, 29.0, 47.3, 115.4, 122.4, 124.3, 124.4, 124.5, 124.8, 125.1, 125.7, 126.2, 126.5, 127.3, 127.4, 127.5, 132.2, 132.3, 144.4, 144.9, 146.5. MALDI-TOF: *m/z* 1082.3 [M⁺]; Anal.calc for C₇₂H₆₆N₄S₃: C, 79.81; H, 6.14; S, 5.17. Found: C, 79.68; H, 5.98; N, 5.03.

General procedure for Horner-Wadsworth-Emmons coupling reaction (Procedure B): To a stirred suspension of NaH (2.0/3.0 equiv.) in dry THF (100 mL), a solution of the phosphonate ester (2.0/3.0 equiv.) in dry THF (50 mL) was added dropwise under nitrogen atmosphere. The mixture was stirred for 30 minutes and then added dropwise to a solution of aldehyde (1.0 equiv.) in dry THF (20 mL) over a period of one hour and then stirred for 12 h at room temperature. The excess NaH was quenched with ice-cold water and the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography, using the eluent as mentioned under each compound.

Dendrimer 6: Following the general procedure B, the stilbenoid phenothiazine dendrimer **6** was obtained from the phosphonate ester **20** (0.3 g, 0.79 mmol) and pyridine-2,6-dicarbaldehyde **21** (1.1 g, 1.66 mmol). The crude productwas purified by column chromatography using hexane:CHCl₃ (3:2) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **6** as deep fluorescent light yellow solid in 64 %; M. P.104 - 106 °C; IR:(ATR, cm⁻¹) 959; ¹H NMR :(300MHz, CDCl₃): $\delta_{\rm H}$ 0.95 (t, 12H, *J* = 7.5 Hz); 1.40-1.52 (m, 8H);1.75-1.84 (m, 8H); 3.84 (t, 8H, *J* = 6.9 Hz); 6.79-6.96 (m, 12 H); 7.04 (d, 4H, *J* = 13.5 Hz); 7.13 (d, 8H, *J* = 7.5 Hz); 7.28-7.36 (m, 11H); 7.41 (d, 2H, *J* = 7.8 Hz); 7.49 (s, 2H); 7.63 (s, 4H); 7.70 (t, 2H, *J* = 7.5 Hz); 7.79 (d, 2H, *J* = 15.9 Hz); 7.85 (s, 2H).¹³C NMR: (75MHz, CDCl₃): $\delta_{\rm C}$ 13.8, 20.2, 28.9, 47.2, 115.3,

115.4, 121.1,121.5, 122.4, 124.1, 124.3, 124.6, 124.9, 125.0, 126.0, 126.5, 127.2, 127.5, 128.1, 131.6, 131.7, 137.2, 138.2, 144.7, 144.9, 154.4, 155.1. Anal.calc for C₉₃H₈₅N₅S₄: C, 79.73; H, 6.12; N, 5.00. Found: C, 79.68; H, 6.01; N, 4.83.

Dendrimer 7: Following the general procedure B, the stilbenoid phenothiazine dendrimer **7** was obtained from the phosphonate ester **20** (1.06 g, 1.34 mmol) and 4,4'-(ethylazanediyl)dibenzaldehyde **22** (0.15 g, 0.61 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (3:2) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **7** as light yellow solid in 67 % yield; M. P.102 °C; IR:(ATR, cm⁻¹) 960; ¹H NMR: (300MHz, DMSO-d₆+CDCl₃): $\delta_{\rm H}$ 0.84 (t, 3H, *J* = 6.9 Hz); 0.92 (t,12H, *J* = 7.2 Hz); 1.40-1.50 (m, 8H); 1.68-1.77 (m, 8H); 3.89 (t, 10H, *J* = 6.6 Hz); 6.91-7.01 (m, 15H); 7.06-7.10 (m, 7H); 7.14 (d, 8H, *J* = 7.5 Hz); 7.21 (d, 4H, *J* = 8.7 Hz); 7.31 (d, 4H, *J* = 17.1 Hz); 7.40 (bs, 8H); 7.54 (d, 4H, *J* = 8.4 Hz); 7.63 (s, 4H). ¹³C NMR:(75MHz, DMSO-d₆+CDCl₃): $\delta_{\rm C}$ 12.5, 13.6, 19.4, 28.4, 45.9, 46.3,114.3, 115.6, 120.6, 122.3, 122.9, 123.2, 123.9, 124.6, 126.0, 126.5, 126.6, 127.0, 127.3, 127.4, 127.5, 128.4, 128.5, 129.9, 131.5, 137.8, 138.0, 144.1, 144.3, 146.4. MALDI-TOF: *m*/*z* 1518.6 [M⁺] Anal.calc for C₁₀₂H₉₅N₅S₄: C, 80.64; H, 6.30; N, 4.61. Found: C, 80.51; H, 6.26; N, 4.58.

Dendrimer 8: Following the general procedure B, the stilbenoid phenothiazine dendrimer **8** was obtained from the phosphonate ester **20** (0.66 g, 0.083 mmol) and 10-ethyl-10*H*-phenothiazine-3,7-dicarbaldehyde **23** (0.1 g, 0.038 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (3:2) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **8** as yellowish orange solid in 65 % yield; M. P.120 - 123 °C; IR:(ATR, cm⁻¹) 955; ¹H NMR:(300MHz, DMSO-d₆): $\delta_{\rm H}$ 0.89 (t, 12H, *J* = 7.2 Hz); 1.29-1.48 (m,11H); 1.64-1.74 (m, 8H); 3.87-3.99 (m, 10H); 6.95 (t, 4H, *J* = 7.5 Hz); 7.04 (d, 10H, *J* = 6 Hz); 7.15 (d, 4H, *J* = 7.8 Hz); 7.19 (d, 8H, *J* = 7.2 Hz); 7.25 (s, 6H);

7.30 (s, 2H); 7.43 (bs, 12H); 7.65 (bs, 6H). ¹³C NMR: (75MHz, DMSO-d₆): δ_C 13.6, 13.9, 19.4, 28.9, 46.2, 43.9, 115.8, 122.5, 123.0, 123.2, 123.3, 123.4, 123.8 (2C), 123.9, 124.0, 124.5, 124.6 (2C), 124.7, 126.2, 126.5, 126.6, 126.9, 127.1, 127.2, 127.7, 131.6, 137.9, 138.8, 144.2, 144.3. FAB: *m*/*z* 1549.4 (M+H]⁺. Anal.calc for C₁₀₂H₉₃N₅S₅: C, 79.08; H, 6.05; N, 4.52. Found: C, 78.93; H, 5.96; S, 4.39.

Dendrimer 9: Following the general procedure B, the stilbenoid phenothiazine dendrimer **9** was obtained from the phosphonate ester **20** (0.36 g, 0.63 mmol) and 2,4,6-trimethylbenzene-1,3,5-tricarbaldehyde **24** (1.30 g, 1.95 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (3:2) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **9** as light yellow solid in 65 % yield; M. P.77 - 80 °C; IR:(ATR, cm⁻¹) 959; ¹H NMR :(300MHz, CDCl₃): $\delta_{\rm H}$ 0.95 (t, 18H, *J* = 7.5 Hz), 1.40-1.49 (m,12H); 1.75-1.84 (m, 12H); 2.40 (s, 9H); 3.85 (t, 12H, *J* = 6.6 Hz); 6.81-6.93 (m, 22H); 6.99 (d, 10H, *J* = 9.3 Hz); 7.12-7.17 (m, 18H); 7.27-7.31 (m, 10H); 7.35 (s, 6H); 7.46 (s, 3H).¹³C NMR: (75MHz, CDCl₃): $\delta_{\rm C}$ 13.8, 18.9, 20.2, 28.9, 47.2, 115.3, 115.4, 122.4, 122.5, 123.6, 123.7, 123.8, 124.3, 125.0 (2C), 125.9, 126.6, 127.2, 127.3, 127.4, 127.9 (2C), 131.7, 138.1, 141.6, 144.8, 144.9. Anal.calc for C₁₄₁H₁₃₂N₆S₆ : C, 80.53; H, 6.33; N, 4.00. Found: C, 80.47; H, 6.27; N, 3.93.

Dendrimer 10: Following the general procedure B, the stilbenoid phenothiazine dendrimer **10** was obtained from the phosphonate ester **20** (0.60 g, 0.75 mmol) and 4,4',4"-nitrilotribenzaldehyde **25** (0.072 g, 0.22 mmol). The crude product was purified by column chromatography using hexane:CHCl₃ (3:2) as the eluting solvent to give the stilbenoid phenothiazine dendrimer **10** as yellow solid in 62 % yield; M. P.138 °C; IR:(ATR, cm⁻¹) 963; ¹H NMR:(300MHz, CDCl₃): $\delta_{\rm H}$ 0.88 (t, 18H, *J* = 7.2 Hz); 1.36-1.44 (m,12H); 1.69-1.79 (m, 12H); 3.79 (t, 12H, *J* = 6.6 Hz); 6.76-6.89 (m,22H); 6.96 (d, 10H, *J* = 9.6 Hz); 7.02-7.11 (m, 25H); 7.23-7.26 (m,12H); 7.41 (d, 12H, *J* = 6.6 Hz). ¹³C NMR: (75MHz,

CDCl₃): δ_C 13.8, 20.2, 29.0, 47.2, 114.1, 115.3, 115.4,122.4, 123.4, 123.5, 124.0, 124.4, 125.1, 125.9, 126.8, 127.2, 127.4, 127.5, 127.6, 127.9, 128.5, 131.8, 132.2, 138.1, 139.3, 144.7, 144.9, 146.8. MALDI-TOF: *m*/*z* 2227.5 [M⁺]; Anal.calc for C₁₅₀H₁₃₅N₇S₆: C, 80.86; H, 6.11; N, 4.40. Found: C, 80.77; H, 6.06; N, 4.33.

10-n-Butyl-10H-phenothiazine-3-carbaldehyde 11: In DMF (9.1 mL, 5.0 equiv.) at 0 °C, phosphorous oxychloride (15.1 mL, 3.0 equiv) was added drop wise under nitrogen atmosphere. The solution was allowed to warm at room temperature, then 10-n-butyl-10*H*-phenothiazine (5 g, 19.6 mmol) was dissolved in CHCl₃ (75 mL) and slowly added to the reaction mixture. The reaction mixture was heated at 90 °C for 24 h and the reaction mixture was then poured into water (100 mL) and extracted in CHCl₃ (200 mL), washed with water (2x200 mL), brine (100 mL) and dried over anhydrous Na₂SO₄.Crude product obtained after evaporation of CHCl₃, was purified by column chromatography over SiO₂ using hexane:CHCl₃ (2:1) as the eluting solvent to give the 10-n-butyl-10*H*-phenothiazine-3-carbaldehyde **11** as orange solid in 82 % yield; M.P. 55 °C; ¹H NMR:(300MHz, CDCl₃): $\delta_{\rm H}$ 0.85 (t, 3H, *J* = 7.2 Hz); 1.31-1.43 (m, 2H);1.65-1.75 (m, 2H); 3.78 (d, 2H, *J* = 7.2 Hz); 6.78 (d, 2H, *J* = 8.4 Hz); 6.86 (t, 1H, *J* = 7.3 Hz); 6.99-7.09 (m, 2H); 7.46 (d, 1H, *J* = 1.8 Hz); 7.51-7.54 (m, 1H); 9.68 (s, 1H). ¹³C NMR:(75MHz, CDCl₃): $\delta_{\rm C}$ 13.8, 20.1, 28.8, 47.7, 114.8, 115.9, 123.6, 123.8, 125.0, 127.5, 127.6, 128.3, 130.1, 131.0, 143.4, 150.7, 190.0.

10-n-butyl-3-vinyl-10*H*-phenothiazine 12: To a suspension of methyltriphenylphosphonium bromide (2.52 g, 7.07 mmol) in dry THF (100 mL), under nitrogen atmosphere at room temperature was added potassium *tert*-butoxide (7.0 equiv.). The solution was stirred for 1 h and then a solution of 10-n-butyl-10*H*-phenothiazine-3-carbaldehyde 11 (2 g, 7.07 mmol) in dry THF (30 mL) was added slowly. The mixture was stirred at room temperature for 12 h and was evaporated to dryness. The unreacted potassium *tert*-butoxide was quenched with saturated NH₄Cl

solution (10 mL). The reaction mixture was then extracted with CHCl₃ (200 mL), washed with water (2 x 200 mL), brine (100 mL) and then dried over anhydrous Na₂SO₄. Evaporation of the organic layer gave a residue, which was purified by column chromatography using hexane as the eluting solvent to give 10-n-butyl-3-vinyl-10H-phenothiazine **90** as yellow solid in 61 % yield; M.P. 72 °C;¹H NMR : (300 MHz, CDCl₃): $\delta_{\rm H}$ 0.83 (t, 3H, *J* = 7.5 Hz); 1.29-1.37 (m, 2H); 1.61-1.71 (m, 2H); 3.71 (t, 2H, *J* =7.2 Hz); 5.02(d, 1Ha, *J* = 10.8 Hz); 5.49 (d, 1Hb, *J* = 17.7 Hz); 6.47 (dd, 1Hc, *J* = 17.4 Hz, *J* = 10.8 Hz); 6.65-6.99 (m, 3H); 7.02-7.11 (m, 4H). ¹³C NMR: (75 MHz, CDCl₃): $\delta_{\rm C}$ 13.9, 20.2, 29.0, 47.2, 112.2, 115.4, 122.4, 124.5, 124.8, 124.9, 125.5, 127.3, 127.5, 132.2, 135.6, 144.8, 145.1. Anal.calc for C₁₈H₁₉NS: C, 76.82; H, 6.81; N, 4.98. Found: C, 76.68; H, 6.77; N, 4.92.

Phosphonate ester building block 19: The phosphonate ester building block **19** was prepared as brown oil by the reaction of 1,3-dibromo-5-(bromomethyl)benzene **18** (0.60 g, 1.82 mmol) with triethyl phosphite (0.93 ml, 5.47 mmol) at 160 °C for 3 h. The excess triethyl phosphite from the reaction mixture was removed by distillation under reduced pressure. The phosphonate ester **19** was used as such without further purification.

Phosphonate ester Dendron 20: Following the general procedure A, the conjugated dendron **20** was obtained as green-yellow semisolid from the phosphonate ester **19** (1 g, 2.59 mmol) and 10-*n*-butyl-3-vinyl-10*H*-phenothiazine **12** (1.6 g, 5.6 mmol) and after eluting the crude product from column chromatography using hexane:CHCl₃ (9:1) as the eluent in 64 % yield; IR :(ATR, cm⁻¹) 961. ¹H NMR: (300 MHz, CDCl₃): $\delta_{\rm H}$ 0.87 (t, 6H, *J* = 7.5 Hz); 1.18 (t, 6H, *J* = 6.0Hz); 1.34-1.42 (m, 4H); 1.67-1.74 (m, 4H); 3.09 (d, 2H, *J* = 21.3Hz); 3.77 (t, 4H, *J* = 6.9 Hz); 3.92-4.01 (m, 4H); 6.73-6.92 (m,10H); 7.05 (d, 4H, *J* = 7.5 Hz); 7.21-7.22 (m, 6H); 7.37 (s, 1H). ¹³C NMR :(75 MHz, CDCl3): $\delta_{\rm C}$ 13.8, 16.4 (*J* = 5.2

DSSC fabrication: The dye-sensitized solar cell consist of nanocrystalline TiO₂ photoelectrodes covered with a photosensitizing dye cisdithiocyanato-N,N-bis(2,2-bipyridyl-4,4-dicarboxylic acid) ruthenium(II) (N3 dye), an electrolyte solution (I^{-}/I_{3}^{-}) and a Pt coated fluorinated tin oxide (FTO) as counter electrode. The TiO₂ photoelectrode was prepared as described by Srimanne et al¹. The prepared TiO₂ photoelectrodes were immersed in a 10 $\times 10^{-5}$ M solution of (N3 dye) in absolute ethanol for one day. The photoelectrode was washed, dried and immediately used for the characterization of solar cell performance. A sandwich type photoelectrochemical cell was composed of a dye-coated TiO₂ photoanode, and the counter electrode was a platinum coated flourinated tin oxide (FTO) conducting glass. The electrolyte solution was injected into the space between two electrodes. The electrolyte solution composed of KI is 3.6×10^{-5} M; I₂ is 7×10^{-6} M, and dendrimers 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 were used as additives at a concentration of 5.8 x 10^{-6} M in 10 mL DMF as solvent. The photoelectrochemical properties were measured under simulated solar light at 60 mWcm⁻². The photocurrent–photovoltage (I-V curve) characteristics were measured using a BAS 100A Electrochemical analyser. The apparent cell area (active area) of the TiO₂ photoelectrode was $1 \times 1 \text{ cm}^2$. The photovoltaic performance of DSSCs based on the incorporation of stilbenoid phenothiazine dendrimers 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 in the redox electrolyte under above mentioned simulated conditions are listed in Table 2. The present work describes about solar cell applications of conjugated system with electron donating phenothiazine group on the surface.

Reference: 1. P. M. Srimanne, T. Shirata and T. J. Soga, J. Solid State Chem., 2002, 166, 142.



¹H NMR Spectrum (300 MHz, CDCl₃) of dendrimer 1



D:\Data\Division\IV-1_160916175055





Mass (ESI) spectrum of dendrimer 1



¹H NMR Spectrum (300 MHz, DMSO-d₆) of dendrimer 2



¹³C NMR Spectrum (75 MHz, DMSO-d₆) of dendrimer 2







MR-13-57(3NBA)



¹H NMR Spectrum (300 MHz, CDCl₃) of dendrimer 4



¹³C NMR Spectrum (75 MHz, CDCl₃) of dendrimer 4







Mass (MALDI-TOF) spectrum of dendrimer 5



¹H NMR Spectrum (300 MHz, CDCl₃) of dendrimer 6



¹³C NMR Spectrum (75 MHz, CDCl₃) ofdendrimer 6



¹H NMR Spectrum (300 MHz, DMSO-d₆) of dendrimer 7





Mass (MALDI-TOF) spectrum of dendrimer 7



¹H NMR Spectrum (300 MHz, DMSO-d₆) of dendrimer 8









¹H NMR Spectrum (300 MHz, CDCl₃) of dendrimer 9







¹³C NMR Spectrum (75 MHz, CDCl₃) of dendrimer 10



Mass (MALDI-TOF) spectrum of dendrimer 10



¹H NMR Spectrum (300 MHz, CDCl₃) of 10-n-butyl-3-vinyl-10H-phenothiazine 12





¹H NMR Spectrum (300 MHz, CDCl₃) of Dendron 20



¹³C NMR Spectrum (75 MHz, CDCl₃) of Dendron 20