Solar Cells

K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation
Organic Dyes Containing Thienylfluorene Conjugation For

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Experimental

General. All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-400 mesh, Macherey-Nagel GmbH & Co.) as the stationary phase in a column of 30 cm long and 2.0 cm diameter.

The ¹H NMR spectra were measured by using Bruker AC300 or AMX400 spectrometer. Mass spectra were recorded on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan). Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature (26 °C) with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and E_p^c are the

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 Organic Dyes Containing Thienylfluorene Conjugation anodic and cathodic peak potentials, respectively. The potentials are quoted against the ferrocene internal standard. The solvent in all experiments was dichloromethane and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate.

Electronic absorption spectra were obtained on a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer for tetrahydrofuran solutions. Emission spectra were recorded in tetrahydrofuran solution at 298 K with an Jobin Yvon SPEX Fluorolog-3 spectrofluorometer. The emission spectra were collected on samples with o.d. <0.1 at the excitation wavelength. The spectra were corrected for instrumental response. UV-Visible spectra were checked before and after irradiation to monitor possible sample degradation. Emission maxima were reproducible to within 2 nm. Luminescence quantum yields (Φ_{em}) were calculated using Coumarin 1 as primary standard ($\Phi_{em} = 0.99$ in ethylacetate). Luminescence quantum yields were reproducible to within 10%.

The precursor 2-(7-bromo-9,9-diethyl-9*H*-fluoren-2-yl)thiophene (**2**) was obtained as reported in the literature from 2,7-dibromo-9,9-diethyl-9*H*-fluorene and 2-thienylmagnesium bromide utilizing $Pd(PPh_3)_2Cl_2$ as catalyst.¹ *N*-Phenylpyren-1-amine² and *N*-phenyl anthracen-9-amine³ were prepared by following the reported procedures.

9,9-Diethyl-*N*-(naphthalen-1-yl)-*N*-phenyl-7-(thiophen-2-yl)-9*H*-fluoren-2-amine (3).

A schlenk flask was charged with 2-(7-bromo-9,9-diethyl-9*H*-fluoren-2-yl)thiophene (**2**, 3.83 g, 10 mmol), N-phenylnaphthalen-1-amine (2.63 g, 12 mmol), sodium *tert*-butoxide (1.44 g, 15 mmol), Pd(dba)2 (57 mg, 0.1 mmol), tri-*tert*-butylphosphine (30.3 mg, 0.15 mmol), and toluene (40 mL). The mixture was heated to 80 °C for 8 h with constant stirring. At the end of the reaction it was cooled and poured into water. The organic

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K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation product was extracted with diethyl ether (3 × 40 mL). The combined organic extract was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to dryness to leave the crude product as a pale yellow viscous solid. It was adsorbed on silica gel and purified by column chromatography using hexane/dichloromethane (4:1) mixture as eluant. Colourless solid. Yield: 3.75 g (72%). MS (FAB) *m/z*: 521.2 (M⁺). ¹H NMR (δ, CDCl₃): 0.35 (t, *J* = 7.3 Hz, 6 H), 1.82-1.98 (m, 4 H), 6.93-6.96 (m, 2 H), 7.06-7.09 (m, 4 H), 7.20-7.26 (m, 3 H), 7.32-7.36 (m, 3 H), 7.42-7.50 (m, 5 H), 7.56 (s, 2 H), 7.76 (d, *J* = 8.2 Hz, 1 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 1 H). ¹³C NMR (δ, CDCl₃): 151.4, 150.5, 148.8, 148.1, 145.3, 143.9, 141.0, 135.3, 135.2, 132.2, 130.9, 129.3, 129.1, 128.5, 128.4, 128.0, 126.7, 126.3, 126.2, 126.1, 126.0, 125.7, 124.9, 124.4, 124.2, 122.5, 121.9, 121.6, 121.4, 120.3, 120.1, 119.2, 117.4, 116.9, 56.1, 32.7, 8.5.

N-(9,9-diethyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)-*N*-phenylanthracen-9-amine (4). It was prepared in 82% yield from 2-(7-bromo-9,9-diethyl-9*H*-fluoren-2-yl)thiophene (2) and *N*-phenyl anthracen-9-amine as described above for **3**. Yellow solid. MS (FAB) *m/z*: 571.1 (M⁺). ¹H NMR (δ, CDCl₃): 0.35 (t, J = 7.3 Hz, 6 H), 1.81-2.00 (m, 4 H), 6.74 (dd, J = 4.0, 1.0 Hz, 1 H), 6.88 (t, J = 7.9 Hz, 1 H), 7.05-7.17 (m, 5 H), 7.23 (d, J = 4.0 Hz, 1 H), 7.31-7.53 (m, 11 H), 8.05 (d, J = 8.3 Hz, 1 H), 8.12 (d, J = 8.5 Hz, 1 H), 8.50 (s, 1 H). ¹³C NMR (δ, CDCl₃): 151.4, 150.4, 148.1, 147.6, 145.3, 141.1, 137.4, 134.7, 132.8, 132.2, 130.5, 129.2, 128.9, 127.9, 126.8, 126.5, 125.4, 124.9, 124.4, 124.1, 122.5, 121.0, 120.5, 120.1, 120.0, 119.1, 115.2, 56.1, 32.7, 8.5.

N-(9,9-diethyl-7-(thiophen-2-yl)-9*H*-fluoren-2-yl)-*N*-phenylpyren-1-amine (5). It was prepared in 91% yield from 2-(7-bromo-9,9-diethyl-9*H*-fluoren-2-yl)thiophene (2) and *N*-

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K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation phenylpyren-1-amine as described above for **3**. Yellow solid. MS (FAB) *m/z*: 595.1 (M⁺).
¹H NMR (δ, CDCl₃): 0.35 (t, J = 7.3 Hz, 6 H), 1.76-1.85 (m, 2 H), 1.88-1.97 (m, 2 H), 6.94-6.98 (m, 2 H), 7.05-7.12 (m, 4 H), 7.19-7.23 (m, 2 H), 7.32 (dd, J = 4.0, 1.0 Hz, 1 H), 7.47-7.49 (m, 2 H), 7.54 (d, J = 2.0 Hz, 2 H), 7.83 (d, J = 8.2 Hz, 1 H), 7.88 (d, J = 8.2 Hz, 1 H), 7.96 (t, J = 7.6 Hz, 1 H), 8.05 (s, 2 H), 8.08 (d, J = 7.4 Hz, 1 H), 8.12-8.17 (m, 3 H). ¹³C NMR (δ, CDCl₃): 151.6, 150.5, 148.4, 145.3, 141.2, 135.4, 132.3, 131.3, 131.1, 129.4, 129.2, 128.0, 127.6, 127.3, 127.2, 127.0, 126.2, 126.0, 125.1, 125.0, 124.9, 124.2, 123.5, 122.6, 122.1, 121.7, 120.4, 120.1, 119.3, 117.1, 56.1, 32.7, 8.5.

5-(9,9-Diethyl-7-(naphthalen-1-yl(phenyl)amino)-9H-fluoren-2-yl)thiophene-2-

carbaldehyde (6). A mixture of 9,9-Diethyl-*N*-(naphthalen-1-yl)-*N*-phenyl-7-(thiophen-2-yl)-9*H*-fluoren-2-amine (**3**, 1.04 g, 2 mmol) and tetrahydrofuran (20 mL) was cooled to -78 °C using acetone-liquid N₂ bath. n-Butyl lithium (1.4 mL, 1.6 M solution in hexanes, 2.2 mmol) was added drop wise over 10 min with vigorous stirring. It was brought to 0 °C during 1h and kept at this temperature for additional 1h. Again the mixture was cooled to -78 °C and dry dimethylformamide (1 mL) was added at once. The solution was brought to room temperature and stirred overnight. The reaction was quenched by the addition of dil HCl (1 mL) in 20 mL water and extracted with diethyl ether (3 × 20 mL). The combined organic extract was dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated to yield the crude product as dark yellow solid. It was purified by column chromatography on silica gel using hexane/dichloromethane mixture (1:1) as eluant. Yellow solid. Yield: 0.75 g (68%). MS (FAB) *m/z*: 549.2 (M⁺). ¹H NMR (δ , CDCl₃): 0.33 (t, *J* = 7.3 Hz, 6 H), 1.80-1.96 (m, 4 H), 6.92-6.98 (m, 2 H), 7.03(d, *J* = 2.0 Hz, 1 H),

K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation 7.06-7.08 (m, 2 H), 7.19-7.23 (m, 2 H), 7.28-7.34 (m, 2 H), 7.41-7.50 (m, 4 H), 7.53 (d, J = 2 Hz, 1 H), 7.57-7.62 (m, 2 H), 7.72 (d, J = 4.0 Hz, 1 H), 7.76 (d, J = 8.2 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.91 (d, J - 8.2 Hz, 1 H), 9.87 (s, 1 H). ¹³C NMR (ô, CDCl₃): 182.6, 155.5, 151.7, 150.8, 148.8, 148.5, 143.7, 143.2, 141.7, 137.5, 135.3, 134.4, 130.9, 130.6, 129.2, 128.4, 126.8, 126.4, 126.3, 126.2, 126.1, 125.6, 124.3, 123.5, 122.2, 122.0, 121.2, 120.7, 120.5, 119.4, 116.5, 56.2, 32.6, 8.5.

5-(7-(anthracen-9-yl(phenyl)amino)-9,9-diethyl-9H-fluoren-2-yl)thiophene-2-

carbaldehyde (7). It was prepared from **4** as described above for **6**. Yield: 54%. Orange solid. MS (FAB) *m/z*: 599.1 (M⁺). ¹H NMR (δ, CDCl₃): 0.34 (t, J = 7.3 Hz, 6 H), 1.83-1.99 (m, 4 H), 6.74 (dd, J = 4.0, 1.0 Hz, 1H), 6.90 (t, J = 7.9 Hz, 1 H), 7.07-7.10 (m, 2 H), 7.14-7.20 (m, 2 H), 7.32-7.45 (m, 7 H), 7.50-7.60 (m, 3 H), 7.71 (d, J = 4.0 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 1 H), 8.11 (d, J = 8.5 Hz, 1 H), 8.51 (s, 1 H). ¹³C NMR (δ, CDCl₃): 182.5, 151.7, 150.7, 148.3, 147.8, 143.2, 141.6, 137.4, 137.3, 133.9, 132.8, 130.5, 130.4, 129.2, 128.9, 126.9, 126.6, 125.5, 125.45, 124.2, 123.4, 121.4, 121.0, 120.4, 119.8, 119.3, 56.2, 32.6, 8.4.

5-(9,9-diethyl-7-(phenyl(pyren-1-yl)amino)-9H-fluoren-2-yl)thiophene-2-

carbaldehyde (8). It was obtained in 79% yield from **5** as described earlier for **6**. Dark yellow solid. MS (FAB) *m/z*: 623.1 (M⁺). ¹H NMR (δ, CDCl₃): 0.34 (t, J = 7.3 Hz, 6 H), 1.78-1.85 (m, 2 H), 1.88-1.96 (m, 2 H), 6.95-6.99 (m, 2 H), 7.08-7.12 (m, 3 H), 7.19-7.23 (m, 3 H), 7.41 (d, J = 4.0 Hz, 1 H), 7.49-7.52 (m, 2 H), 7.57-7.63 (m, 2 H), 7.72 (d, J = 4.0 Hz, 1 H), 7.83 (d, J = 8.2 Hz, 1 H), 7.88 (d, J = 8.2 Hz, 1 H), 7.97 (t, J = 7.6 Hz, 1 H), 8.06 (s, 2 H), 8.08-8.12 (m, 2 H), 8.15-8.18 (m, 2 H). ¹³C NMR (δ, CDCl₃): 182.6, 155.4,

K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation 151.9, 150.8, 149.1, 148.8, 143.2, 141.7, 141.0, 137.4, 134.5, 131.3, 131.1, 130.7, 129.5, 129.3, 127.7, 127.3, 127.2, 127.1, 126.4, 126.2, 126.0, 125.6, 125.2, 125.1, 124.9, 123.5, 123.4, 122.5, 122.1, 121.5, 120.8, 120.5, 119.5, 116.7, 56.2, 32.6, 8.5.

(E)-2-cyano-3-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9H-fluoren-2-

yl)thiophen-2-yl)acrylic acid (9). A mixture of 5-(9,9-Diethyl-7-(naphthalen-1yl(phenyl)amino)-9*H*-fluoren-2-yl)thiophene-2-carbaldehyde (6, 0.550 g, 1 mmol), 2cyanoacetic acid (0.17 g, 2 mmol), ammonium acetate (16 mg, 0.2 mmol) and acetic acid (10 mL) were heated to reflux for 4 h. After cooling the precipitate formed was filtered and thoroughly washed with water, cold methanol and hexane/diethylether (1:1) mixture. It was reprecipitated from tetrahydrofuran by pouring into hexane/diethylether (1:1) mixture. Red solid. Yield: (0.49 g, 79%). MS (FAB) *m/z*: 616.1 (M⁺). Anal. Calcd. for $C_{41}H_{32}N_2O_2S$: C, C, 79.84; H, 5.23; N, 4.54. Found: C, 79.72; H, 5.07; N, 4.51%. ¹H NMR (δ , dmso-d₆): 0.23 (t, J = 7.3 Hz, 6 H), 1.76-1.82 (m, 2 H), 1.95-2.02 (m, 2 H), 6.84 (dd, J = 4.0, 1.0 Hz, 1 H), 6.96-6.99 (m, 4 H), 7.26 (t, J = 7.9 Hz, 2 H), 7.35-7.40 (m, 2 H), 7.49 (t, J = 7.4 Hz, 1 H), 7.57 (t, J = 7.9 Hz, 1 H), 7.68-7.84 (m, 6 H), 7.89 (d, J = 8.2 Hz, 1 H), 7.99-8.02 (m, 2 H), 8.48 (s, 1 H).

(E)-3-(5-(7-(anthracen-9-yl(phenyl)amino)-9,9-diethyl-9H-fluoren-2-yl)thiophen-2-

yl)-2-cyanoacrylic acid (10). It was synthesized in 81% yield from 7 as described above. Dark red solid. MS (FAB) m/z: 666.1 (M⁺). Anal. Calcd. for C₄₅H₃₄N₂O₂S: C, 81.05; H, 5.14; N, 4.20. Found: C, 80.92; H, 5.09; N, 3.98%. ¹H NMR (δ , dmso-d₆): 0.24 (t, J = 7.3 Hz, 6 H), 1.80-1.85 (m, 2 H), 1.96-2.01 (m, 2 H), 6.68 (dd, J = 4.0, 1.0 Hz, 1 H), 6.91 (t, J = 7.9 Hz, 1 H), 6.98 (d, J = 8.0 Hz, 2 H), 7.20-7.24 (m, 3 H), 7.43-7.53 (m, 4 H), 7.59 (d,

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J = 8.3 Hz, 1 H), 7.69 (s, 1 H), 7.78-7.81 (m, 2 H), 8.00-8.07 (m, 3 H), 8.20 (d, J = 8.5 Hz, 1 H), 8.48 (s, 1 H), 8.74 (s, 1 H).

(E)-2-cyano-3-(5-(9,9-diethyl-7-(phenyl(pyren-1-yl)amino)-9H-fluoren-2-

yl)thiophen-2-yl)acrylic acid (11). It was synthesized in 81% yield from 8 as described previously for 9. Dark red solid. MS (FAB) m/z: 690.2 (M⁺). Anal. Calcd. for C₄₇H₃₄N₂O₂S: C, 81.71; H, 4.96; N, 4.05. Found: C, 81.54; H, 5.02; N, 3.86%. ¹H NMR (δ , dmso-d₆): 0.25 (t, J = 7.3 Hz, 6 H), 1.76-1.81 (m, 2 H), 1.95-2.00 (m, 2 H), 6.90 (dd, J = 4.0, 1.0 Hz, 1 H), 6.98-7.05 (m, 3 H), 7.08 (d, J = 2.0 Hz, 1 H), 7.28 (t, J = 7.9 Hz, 2 H), 7.64-7.80 (m, 5 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.94-8.08 (m, 5 H), 8.20 (s, 2 H), 8.22 (d, J = 8.2 Hz, 1 H), 8.31 (d, J = 8.2 Hz, 1 H), 8.35 (d, J = 8.2 Hz, 1 H), 8.44 (s, 1 H).

7-(5-(9,9-diethyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-N-

(naphthalen-1-yl)-N-phenyl-9H-fluoren-2-amine (B). A tetrahydrofuran solution of A 3 (2.08 g, 4 mmol) and tetrahydrofuran (20 mL) was cooled to -78 °C. n-Butyl lithium (1.4 mL, 1.6 M solution in hexanes, 2.2 mmol) was added drop wise over 10 min with vigorous stirring. It was brought to 0 °C during 1h and kept at this temperature for additional 1h. Again the mixture was cooled to -78 °C and tri(*n*-butyl)tinchloride (1.56 g, 4.8 mmol, 1.2 eq.) was added and allowed to attain room temperature. After stirring for 8 h, it was poured into ice water and extracted with diethylether. The combined organic extract was dried over MgSO₄ and filtered through a short column of Al₂O₃. The viscous liquid, obtained after the evaporation of the volatiles, was taken in a Schlenk's flask and mixed with 2 (1.38 g, 3.6 mmol) and Pd(PPh₃)₂Cl₂ (28 mg, 0.04 mmol). It was dissolved in dimethylformamide (10 mL) and heated at 75 °C for 17 h. After that time, it was

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K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation cooled and poured into methanol (50 mL) and the precipitate formed was filtered and washed with methanol liberally. This crude product was purified by column chromatography on silica gel using dichloromethane/hexane mixture (4:1). Yield: 2.40 g (81%). Yellow solid. MS (FAB) *m/z*: 823.4 (M⁺). ¹H NMR (δ, CDCl₃):0.38-0.46 (m, 12 H), 1.86-1.91 (m, 2 H), 1.98-2.03 (m, 2 H), 2.11-2.17 (m, 4 H), 6.97-6.99 (m, 2 H), 7.10-7.13 (m, 4 H), 7.23-7.29 (m, 2 H), 7.30 (dd, J = 4.0, 1.0 Hz, 1 H), 7.36-7.41 (m, 5 H), 7.46-7.53 (m, 3 H), 7.57-7.65 (m, 6 H), 7.67-7.71 (m, 3 H), 7.78 (d, J = 8.2 Hz, 1 H), 7.90 (d, J = 8.2 Hz, 1 H), 7.98 (d, J = 8.2 Hz, 1 H). ¹³C NMR (δ, CDCl₃): 151.4, 150.9, 150.5, 148.7, 148.2, 145.1, 144.2, 143.8, 143.6, 141.1, 140.6, 140.5, 135.3, 135.2, 133.3, 132.2, 130.9, 129.1, 128.4, 128.0, 16.7, 126.3, 126.2, 126.1, 126.0, 125.0, 124.5, 124.4, 123.8, 123.5, 122.9, 121.9, 121.6, 121.4, 120.3, 120.2, 120.1, 120.0, 119.8, 119.7, 119.3, 116.9, 56.3, 56.1, 32.8, 32.7, 8.6, 8.5.

5-(7-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9*H***-fluoren-2-yl)thiophen-2yl)-9,9-diethyl-9***H***-fluoren-2-yl)thiophene-2-carbaldehyde (C). It was prepared from above compound as described earlier for 6**. Yield: 76%. Orange solid. MS (FAB) *m/z*: 851.4 (M⁺).¹H NMR (δ, CDCl₃): 0.48-0.45 (m, 12 H), 1.85-1.90 (m, 2 H), 1.94-2.00 (m, 2 H), 2.04-2.14 (m, 4 H), 6.96-6.99 (m, 2 H), 7.09-7.11 (m, 3 H), 7.21-7.25 (m, 2 H), 7.33-7.40 (m, 4 H), 7.43-7.52 (m, 4 H), 7.56-7.74 (m, 10 H), 7.78 (d, J = 8.2 Hz, 1 H), 7.89 (d, J = 8.2 Hz, 1 H), 7.97 (d, J = 8.2 Hz, 1 H), 9.90 (s, 1 H). ¹³C NMR (δ, CDCl₃): 182.6, 155.0, 151.4, 151.1, 150.5, 144.5, 143.8, 143.2, 142.6, 142.0, 141.2, 139.9, 137.4, 135.3, 135.1, 134.0, 132.0, 131.7, 130.9, 129.1, 128.3, 126.7, 126.3, 126.2, 126.1, 126.0,

K. R. J. Thomas et. al. Organic Dyes Containing Thienylfluorene Conjugation 124.7, 124.5, 124.4, 124.1, 123.8, 123.5, 121.9, 121.6, 121.4, 120.6, 120.5, 120.3, 120.2, 119.8, 1197, 119.3, 116.8, 56.4, 56.1, 32.7, 32.6, 8.6, 8.5.

(E)-2-cyano-3-(5-(7-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9*H*-fluoren-2yl)thiophen-2-yl)-9,9-diethyl-9*H*-fluoren-2-yl)thiophen-2-yl)acrylic acid (12). It was obtained in 86% from above aldehyde and 2-cyanoacetic acid as described earlier for 9. Red solid. MS (FAB) *m/z*: 918.3 (M⁺). Anal Calcd. for $C_{62}H_{50}N_2O_2S_2$: C, 81.01; H, 5.48; N, 3.05. Found: C, 80.75; H, 5.31; N, 2.92%. ¹H NMR (δ , CDCl₃): 0.23-0.29 (m, 12 H), 1.77-1.82 (m, 2 H), 1.95-2.0 (m, 2 H), 2.07-2.16 (m, 4 H), 6.85 (dd, J = 4.0, 1.0 Hz, 1 H), 6.94-6.97 (m, 3 H), 7.02 (d, J = 2.0 Hz, 1 H), 7.24 (t, J = 7.9 Hz, 2 H), 7.34-7.39 (m, 2 H), 7.49 (t, J = 7.9 Hz, 1 H), 7.56 (t, J = 7.9 Hz, 1 H), 7.61-7.73 (m, 8 H), 7.69-7.94 (m, 8 H), 7.99 (d, J = 8.2 Hz, 1 H), 8.05 (d, J = 4.0 Hz, 1 H), 8.51 (s, 1 H).

7-(5-(7-(5-(9,9-diethyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-

9H-fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-N-(naphthalen-1-yl)-N-phenyl-9H-

fluoren-2-amine (D). It was synthesized by following the procedure described before for 7-(5-(9,9-diethyl-7-(thiophen-2-yl)-9*H*-fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-*N*-

(naphthalen-1-yl)-N-phenyl-9H-fluoren-2-amine (**B**) using '**B**' in place of **3**. Yield: 69%. Dark yellow solid. MS (FAB) *m/z*: 1125.5 (M⁺). ¹H NMR (δ , CDCl₃): 0.36-0.46 (m, 18 H), 1.84-1.89 (m, 2 H), 1.96-2.01 (m, 2 H), 2.10-2.16 (m, 8 H), 6.94-6.98 (m, 2 H), 7.07-7.12 (m, 4 H), 7.21-7.23 (m, 2 H), 7.28-7.40 (m, 9 H), 7.44-7.50 (m, 4 H), 7.54-7.71 (m, 16 H), 7.77 (d, J = 8.2 Hz, 1 H), 7.89 (d, J = 8.2 Hz, 1 H), 7.95 (d, J = 8.2 Hz, 1 H).¹³C NMR (δ , CDCl₃): 151.4, 150.9, 150.6, 148.3, 145.1, 144.3, 144.0, 141.1, 140.6, 135.3,

Organic Dyes Containing Thienylfluorene Conjugation K. R. J. Thomas et. al. 133.3, 133.2, 129.1, 128.4, 128.1, 126.3, 126.2, 126.1, 124.6, 124.5, 124.4, 123.9, 123.5, 122.9, 121.9, 120.2, 120.1, 119.9, 119.3, 116.9, 56.3, 56.1, 32.9, 32.7, 8.6, 8.5. 5-(7-(5-(7-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9H-fluoren-2vl)thiophen-2-vl)-9,9-diethyl-9H-fluoren-2-vl)thiophen-2-vl)-9,9-diethyl-9H-fluoren-2-yl)thiophene-2-carbaldehyde (E). It was obtained in 77% from the above compound (D) by following the procedure described for 6. Orange solid. MS (FAB) m/z: 1153.5 (M^+) . ¹H NMR (δ , CDCl₃): 0.35-0.45 (m, 18 H), 1.83-1.88 (m, 2 H), 1.95-2.0 (m, 2 H), 2.12-21.6 (m, 8 H), 6.93-6.97 (m, 2 H), 7.06-7.09 (m, 3 H), 7.16-7.22 (m, 2 H), 7.32-7.40 (m, 7 H), 7.45-7.50 (m, 4 H), 7.54-7.75 (m, 19 H), 7.88 (d, J = 8.2 Hz, 1 H), 7.95 (d, J = 8.2 Hz, 1 H), 9.90 (s, 1 H). ¹³C NMR (δ, CDCl₃): 182.6, 155.0, 151.4, 151.2, 150.9, 150.6, 148.2, 144.3, 143.7, 142.6, 142.0, 141.1, 140.8, 140.5, 140.0, 127.4, 135.3, 133.9, 133.4, 133.1, 131.8, 129.1, 128.4, 126.8, 126.3, 126.2, 126.1, 125.7, 124.8, 124.7, 124.4, 124.1, 123.8, 123.6, 121.9, 120.7, 120.5, 120.3, 120.1, 119.9, 119.3, 116.9, 56.4, 56.3, 56.1, 32.9, 32.8, 32.7, 8.63, 8.59, 8.5.

(E)-2-cyano-3-(5-(7-(5-(7-(5-(9,9-diethyl-7-(naphthalen-1-yl(phenyl)amino)-9H-

fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-9H-fluoren-2-yl)thiophen-2-yl)-9,9-diethyl-

9H-fluoren-2-yl)thiophen-2-yl)acrylic acid (13). It was prepared from the above compound and 2-cyanoacetic acid by refluxing in a benzene/chloroform (1:1) mixture and using a drop of piperidine as a catalyst. Yield: 80%. Red solid. MS (FAB) *m/z*: 1220.4 (M^+). Anal Calcd. for C₈₃H₆₈N₂O₂S₃: C, 81.60; H, 5.61; N, 2.29. Found: C, 81.39; H, 5.52; N, 2.03%. ¹H NMR (δ, CDCl₃): 0.33-0.43 (m, 18 H), 1.82-1.87 (m, 2H), 1.93-1.96 (m, 2 H), 2.09-2.15 (m, 8 H), 6.92-7.05 (m, 5 H), 7.19-7.23 (m, 2 H), 7.29-7.32 (m,

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2 H), 7.37-7.52 (m, 9 H), 7.59-7.69 (m, 11 H), 7.72-7.79 (m, 4 H), 7.80 (d, J = 4.0 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.92 (d, J = 8.2 Hz, 1 H) 8.35 (s, 1 H).

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Fig. S1. I-V curve observed for the dye-sensitized solar cells constructed from the dyes 9,

10, 11, 12 and 13.



Fig. S2. Action spectra for the dyes 10, 11, 12 and 13.

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Fig. S3. Energy minimized ground state structure of 9.



Fig. S4. Energy minimized excited state structure of 9.

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Fig. S5. Energy minimized ground state structure of 12.

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Fig. S6. Energy minimized excited state structure of 12.

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Scheme S1. Synthesis of the 2^{nd} and 3^{rd} generation dyes.



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Table S1. Calculated (semi-empirical PM3, SPARTAN) orbital energies and related parameters

dye	ground state				excited state			
	energy, kcal/mol	HOMO, eV	LUMO, eV	dipole, Debye	energy, kcal/mol	HOMO, eV	LUMO, eV	dipole, Debye
9	126.854	-7.980	-1.533	5.903	165.670	-6.285	-1.098	10.937
10	134.560	-8.182	-1.655	6.023	169.817	-7.272	-1.360	5.231
11	134.780	-8.141	-1.531	5.454	173.250	-7.086	-1.298	5.453
12	201.375	-7.894	-1.576	6.160	234.067	-7.478	-1.288	5.850