Supplementary information

Enhanced Photovoltaic Performance and Long-term Stability of Quasi-Solid State Dye-Sensitized Solar Cells

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Contents of Supplementary Data

Experimental section

1. General method

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Solvent were distilled from appropriate reagent.. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.00 and 75.44 MHz, respectively. Mass spectra were recorded on a JEOL JMS-SX102A instrument. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

2. Cyclovoltagram

Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical System, Inc.). A three-electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. Redox potential of the dyes on TiO_2 was measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ with a scan rate of 50mV s^{-1} (vs. Fe/Fe^+)

3. Fabrication and characterization of DSSC

For the preparation of DSSC, a washed FTO (Pilkington, 8 Ω sq-1) glass plate was immerged in 40mM $TiCl_4$ (aqueous) at 70 ℃ for 30 min and washed with water and ethanol. The first TiO_2 layer of 13 μm thickness was prepared by screen printing TiO_2 paste (Solaronic, 20 nm anatase), and the second scattering layer containing 400 nm sized anatase particles (Catalysis ＆ Chemicals Ind. Co. Ltd.) was deposited by twice screen printing. The TiO_2 electrodes were immersed into the JK-70 and JK-71 solution (0.3 mM in ethanol containing 1 mM 3a, 7a-dihydroxy-5b-cholic acid (cheno)) and kept at room temperature for 18 h. Amount of JK-2, JK-70 and JK-71 absorbed on TiO_2 are obtained (1.9 ± 0.2) × 10-7 mol/mg of TiO_2, (1.5 ± 0.2) × 10-7 mol/mg of TiO_2 and (1.3 ± 0.2) × 10-7 mol/mg of TiO_2 respectively. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate. The dye-absorbed TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell. A drop of electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidium thiocyanate, and 0.28 M 4-*tert*-butylpyridine in acetonitrile. The quasi-solid gel electrolyte was composed of 5 wt% poly(vinylidenefluoride-*co*-hexafluoropropylene),[1] 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M iodine, 0.5 M *N*-methylbenzimidazole in 3-methoxypropionitrile and were assembled using a modified procedure of previous reference.[2] The cells were measured using 1000 W xenon light source, whose power of an AM 1.5 Oirel solar simulator was calibrated by using KG5 filtered Si reference solar solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements).

9,9-Dimethylfluorene (1)

To fluorene (5 g, 17.1 mmol) in tetrahydrofuran (THF) was added potassium *tert*-butoxide (4.61 g, 41.1 mmol) at 0℃, followed by methylation with methyliodide (4.26 ml, 68.46 mmol). The solution was warmed to room temperature and stirred for additional 2 hrs. After removal of THF in vacuo, the reaction mixture was extracted with dichloromethane and water. The crude product was purified by column chromarography using a *n*-hexane. (yield 80%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81 (d, *J*=6.6 Hz, 2H), 7.52 (d, *J*=6.6 Hz, 2H), 7.41 (m, 4H), 1.57 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 153.7, 139.3, 127.3, 127.0, 122.7, 120.1, 46.9, 27.2. FAB MS(m/z): 194.07 (M^+). Anal calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.66; H, 7.21.

1-(9,9-Dimethylfluoren-2-yl)hexan-1-one (2).

To a stirred solution of 9,9-dimethylfluorene (5 g, 25.7 mmol) in anhydrous dichloromethane was added $AlCl_3$ (3.78 g, 28.3 mmol). The solution was cooled to 0 ℃ under ice bath. Hexanoyl chloride (3.96 ml, 28.3 mmol) dissolved in dichloromethane was added dropwise via dropping funnel. The ice bath removed and solution was warm to room temperature with stirring for 2h. The mixture was poured into a mixture ice and concentrated HCl, extracted with dichloromethane, washed Na_2CO_3 solutions, and dried over $MgSO_4$. The organic layer was removed in vacuo. The pure product 2 was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:10) as an eluent (yield 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08 (s, 1H), 7.98 (d, *J*=7.5 Hz, 1H), 7.78 (s, 1H) 7.77 (d, *J*=7.8 Hz, 1H), 7.48 (d, *J*=8.1 Hz, 1H), 7.39 (m, 2H), 3.02 (t, *J*=7.2 Hz, 2H), 1.79 (m, 2H), 1.52 (s, 6H), 1.41 (m, 4H), 0.94 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 200.5, 154.9, 153.9, 143.9, 130.8, 136.1, 128.6, 127.9, 127.3, 122.9, 122.3, 121.0, 119.8, 47.1, 38.8, 31.7, 27.0, 24.4, 22.7, 14.1. FAB MS(m/z):292.09 (M^+). Anal calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.19; H, 8.21.

1-(9,9-Dimethylfluoren-2-yl)nonan-1-one (3).

To a stirred solution of 9,9-dimethylfluorene (5 g, 25.7 mmol) in anhydrous dichloromethane was added $AlCl_3$ (3.78 g, 28.3 mmol). The solution was cooled to 0 ℃ under ice bath. Hexanoyl chloride (5.11 ml, 28.3 mmol) dissolved in dichloromethane was added dropwise via dropping funnel. The ice bath removed and solution was warm to room temperature with stirring for 2h. The mixture was poured into a mixture ice and concentrated HCl, extracted with dichloromethane, washed Na_2CO_3 solutions, and dried over $MgSO_4$. The organic layer was removed in vacuo. The pure product **3** was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:10) as an eluent (yield 88%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08 (s, 1H), 7.98 (d, *J*=8.1 Hz, 1H), 7.79 (s, 1H) 7.77 (d, *J*=7.5 Hz, 1H), 7.48 (d, *J*=8.1 Hz, 1H), 7.38 (m, 2H), 3.03 (t, *J*=7.2 Hz, 2H), 1.79 (m, 2H), 1.53 (s, 6H), 1.30 (m, 10H), 0.91 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 200.4, 154.9, 153.9, 143.9, 130.8, 136.1, 128.6, 127.9, 127.3, 122.9, 122.3, 120.9, 119.8, 47.1, 38.8, 31.9, 29.6, 29.5, 29.3, 27.0, 24.7, 22.8, 14.2. FAB MS(m/z):334.18 (M^+). Anal calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 86.12; H, 8.99..

2-Hexyl-9,9-dimethylfluorene (4).

A mixture of 1-(9,9-dimethylfluoren-2-yl)hexan-1-one (4 g, 13.7 mmol), potassium hydroxide (2.53 g, 45.1 mmol), hydrazine hydrate (2.1 ml) and triethylene glycol (20 ml) was refluxed for 12h. The cooled solution was diluted with water and poured slowly into 6 *N* hydrochloric acid. The crude product was purified by column chromarography using a n-hexane (yield 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J*=7.5 Hz, 1H), 7.71 (d, *J*=7.8 Hz, 1H), 7.49 (d, *J*=7.5 Hz, 1H), 7.04 (t, *J*=7.2 Hz, 1H), 7.38 (t, *J*=7.5 Hz, 1H), 7.33 (s, 1H), 7.24 (d, *J*=7.8 Hz, 1H) 2.78 (t, *J*=7.8 Hz, 2H), 1.76 (m, 2H), 1.57 (s, 6H), 1.43 (m, 6H), 0.99 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 153.9, 153.7, 142.4, 139.4, 136.9, 127.3, 126.9, 126.8, 122.7, 122.6, 119.8, 119.7, 46.8, 36.5, 32.0, 31.9, 29.3, 27.4, 22.8, 14.3. FAB MS(m/z): 278.11 (M^+). Anal calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.47; H, 9.33.

9,9-Dimethyl-2-nonylfluorene (5).

A mixture of 1-(9,9-dimethylfluoren-2-yl)nonan-1-one (5 g, 14.9 mmol), potassium hydroxide (2.77 g, 49.3 mmol), hydrazine hydrate (3.0 ml) and triethylene glycol (25 ml) was refluxed for 12h. The cooled solution was diluted with water and poured slowly into 6 *N* hydrochloric acid. The crude product was purified by column chromarography using a n-hexane. (yield 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (d, *J*=7.5 Hz, 1H), 7.70 (d, *J*=7.8 Hz, 1H), 7.49 (d, *J*=7.5 Hz, 1H), 7.39 (t, *J*=7.2 Hz, 1H), 7.37 (t, *J*=7.5 Hz, 1H), 7.33 (s, 1H), 7.23 (d, *J*=7.8 Hz, 1H) 2.76 (t, *J*=7.8 Hz, 2H), 1.75 (m, 2H), 1.56 (s, 6H), 1.37 (m, 12H), 0.989 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 153.9, 153.7, 142.5, 139.5, 136.9, 127.3, 126.9, 126.8, 122.7, 122.6, 119.8, 119.7, 46.8, 36.5, 32.1, 31.9, 29.8, 29.7, 29.6, 29.5, 27.4, 22.9, 14.3. FAB MS(m/z): 320.14 (M^+). Anal calcd for $C_{24}H_{32}$: C, 89.94; H, 10.06. Found: C, 89.88; H, 9.98.

2-Hexyl-7-iodo-9,9-dimethylfluorene (6).

A stirred mixture of **2-hexyl-9,9-dimethylfluorene** (1.5 g, 5.38 mmol), iodine (0.59 g, 2.31 mmol), periodic acid (0.26 g, 1.15 mmol), sulfuric acid (0.4 ml), H_2O (4 ml), and acetic acid anhydride (25 ml) was stirred at 90 ℃ for approximately 1 hour until the color of iodine disappears. The reaction mixture is diluted with water and solid that separates is collected on a Büchner funnel and washed three times with water. The crude product was purified by column chromarography using a n-hexane. (yield 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (s, 1H), 7.67 (d, *J*=8.1 Hz, 1H), 7.61 (d, *J*=7.5 Hz, 1H), 7.45 (d, *J*=8.4 Hz, 1H), 7.26 (s, 1H), 7.19 (d, *J*=8.1 Hz, 1H), 2.71 (t, *J*=7.2 Hz, 2H), 1.69 (m, 2H), 1.49 (s, 6H), 1.38 (m, 6H), 0.94 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.9, 153.3, 143.2, 139.1, 135.9, 135.8, 132.1, 127.5, 122.5, 121.5, 119.9, 91.9, 46.9, 36.5, 31.9, 31.8, 29.2, 27.2, 22.8, 14.3. FAB MS(m/z): 404.01 (M^+). Anal calcd for $C_{21}H_{25}I$: C, 62.38; H, 6.23. Found: C, 62.27; H, 6.16.

2-Iodo-9,9-dimethyl-7-nonylfluorene (7).

A stirred mixture of 9,9-dimethyl-2-nonylfluorene (1.5 g, 4.68 mmol), iodine (0.51 g, 2.01 mmol), periodic acid (0.23 g, 1.00 mmol), sulfuric acid (0.4 ml), H_2O (4 ml), and acetic acid anhydride (25 ml) was stirred at 90 ℃ for approximately 1 hour until the color of iodine disappears. The reaction mixture is diluted with water and solid that separates is collected on a Büchner funnel and washed three times with water. The crude product was purified by column chromarography using a n-hexane. (yield 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (s, 1H), 7.67 (d, *J*=8.1 Hz, 1H), 7.62 (d, *J*=7.5 Hz, 1H), 7.45 (d, *J*=8.1 Hz, 1H), 7.26 (s, 1H), 7.19 (d, *J*=7.8 Hz, 1H), 2.71 (t, *J*=8.1 Hz, 2H), 1.69 (m, 2H), 1.49 (s, 6H), 1.32 (m, 12H), 0.93 (t, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.9, 153.3, 143.2, 139.1, 135.9, 135.8, 132.1, 127.5, 122.7, 121.5, 119.9, 91.9, 46.9, 36.5, 32.0, 31.9, 29.7, 29.6, 29.4, 27.2, 22.8, 14.3. FAB MS(m/z): 446.11 (M^+). Anal calcd for $C_{21}H_{25}I$: C, 64.57; H, 7.00. Found: C, 64.49; H, 6.96.

_N,N_-Bis(7-hexyl-9,9-dimethylfluoren-2-yl)-4-bromoaniline (8).

A mixture of 2-hexyl-7-iodo-9,9-dimethylfluorene (1.52 g, 3.76 mmol), 4-bromoaniline (0.29 g, 1.68 mmol), powdered anhydrous potassium carbonate (0.69g, 5.06 mmol), copper bronze (0.32g, 5.06 mmol), 18-crown-6 (0.13g, 0.51 mmol), and 1,2-dichlorobenzene (20 ml) was refluxed for 24h. After removal of 1,2-dichlorobenzene in vacuo, the crude product was extracted with methylene chloride and water. The organic layer was separated and dried in $MgSO_4$. The organic layer was removed in vacuo. The pure product **8** was obtained by silica gel chromatography using a mixture of methylene chloride and n-hexane (1:7) as an eluent (yield 68%). Mp: 154 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, 4H), 7.38 (d, 2H), 7.23 (s, 2H), 7.22 (s, 2H), 7.17 (d, 2H), 7.10 (d, 2H), 7.09 (d, 2H), 2.71 (t, 4H), 1.69 (m, 4H), 1.43 (s, 12H), 1.38 (m, 12H), 0.94 (t, 6H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.2, 153.8, 147.4, 146.6, 141.8, 136.5, 134.7, 132.2, 127.3, 125.2, 123.2, 122.7, 120.4, 119.3, 118.8, 114.5, 46.8, 36.4, 31.9, 31.8, 29.2, 27.2, 22.8, 14.3. FAB MS(m/z): 723.22 (M^+). Anal calcd for $C_{48}H_{54}BrN$: C, 79.54; H, 7.51. Found: C, 79.39; H, 7.33.

***N*,*N*-Bis(9,9-dimethyl-7-nonylfluoren-2-yl)-4-bromoaniline (9).**

A mixture of 2-iodo-9,9-dimethyl-7-nonylfluorene (1.71 g, 3.84 mmol), 4-bromoaniline (0.30 g, 1.74 mmol), powdered anhydrous potassium carbonate (0.72g, 5.23 mmol), copper bronze (0.33g, 5.23 mmol), 18-crown-6 (0.14g, 0.52 mmol), and 1,2-dichlorobenzene (20 ml) was refluxed for 24h. After removal of 1,2-dichlorobenzene in vacuo, the crude product was extracted with methylene chloride and water. The organic layer was separated and dried in $MgSO_4$. The organic layer was removed in vacuo. The pure product **9** was obtained by silica gel chromatography using a mixture of methylene chloride and n-hexane (1:7) as an eluent (yield 68%). Mp: 151 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, 4H), 7.39 (d, 2H), 7.26 (s, 2H), 7.25 (s, 2H), 7.16 (d, 2H), 7.13 (d, 2H), 7.10 (d, 2H), 2.73 (t, 4H), 1.72 (m, 4H), 1.46 (s, 12H), 1.38 (m, 24H), 0.95 (t, 6H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.2, 153.8, 147.4, 146.7, 141.8, 136.6, 134.8, 132.2, 127.4, 125.2, 123.3, 122.7, 120.4, 119.3, 118.8, 114.6, 46.8, 36.4, 32.1, 31.9, 29.7, 29.6, 29.5, 29.4, 27.3, 22.8, 14.3. FAB MS(m/z): 809.35 (M^+). Anal calcd for $C_{54}H_{66}BrN$: C, 80.17; H, 8.22. Found: C, 79.96; H, 8.17.

4-[5'-(5,5-Dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl]-N,N-Bis(7-hexyl-9,9-dimethylfluoren-2-yl)benzeneamine (10).

A mixture **8** (0.4 g, 0.55 mmol), 2-[5'-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (0.27 g, 0.66 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.03mmol), and 2M K_2CO_3 aqueous solution (2.8 ml, 5.5 mmol) in THF (30ml) was refluxed for 12h. After cooling the solution, H_20 (15 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The organic layer was removed in vacuo. The pure product **10** was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:10) as an eluent (yield 71%). Mp: 191 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, 2H), 7.57 (d, 2H), 7.49 (d, 2H), 7.24 (d, 2H), 7.21 (d, 2H), 7.20 (d, 2H), 7.15 (d, 2H), 7.14 (m, 3H), 7.09 (d, 2H), 7.06 (d, 2H), 5.63 (s, 1H), 3.79 (d, 2H), 3.66 (d, 2H), 2.69 (t, 4H), 1.68 (m, 4H), 1.42 (s, 12H), 1.35 (m, 12H), 1.31 (s, 3H), 0.91 (t, 6H), 0.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.2, 153.8, 147.8, 146.7, 143.5, 141.7, 140.1, 138.2, 136.6, 135.8, 134.7, 127.9, 127.3, 126.5, 125.9, 124.9, 123.9, 123.5, 123.2, 122.8, 122.7, 120.4, 119.3, 119.1, 98.3, 77.6, 77.5, 46.8, 36.4, 31.9, 31.0, 30.3, 29.2, 27.2, 23.1, 22.8, 21.9, 14.3. FAB MS(m/z): 923.39 (M^+). Anal calcd for $C_{62}H_{69}NO_2S_2$: C, 80.56; H, 7.52. Found: C, 80.42; H, 7.39.

4-[5'-(5,5-Dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl]-N,N-Bis(9,9-dimethyl-7-nonylfluoren-2-yl)benzeneamine (11).

A mixture **9** (0.4 g, 0.49 mmol), 2-[5'-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (0.24 g, 0.59 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.02mmol), and 2M K_2CO_3 aqueous solution (2.5 ml, 4.9 mmol) in THF (30ml) was refluxed for 12h. After cooling the solution, H_20 (15 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The organic layer was removed in vacuo. The pure product **11** was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:10) as an eluent (yield 73%). Mp: 188 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, 2H), 7.58 (d, 2H), 7.49 (d, 2H), 7.24 (d, 2H), 7.22 (d, 2H), 7.20 (d, 2H), 7.15 (d, 2H), 7.13 (m, 3H), 7.10 (d, 2H), 7.06 (d, 2H), 5.63 (s, 1H), 3.79 (d, 2H), 3.65 (d, 2H), 2.69 (t, 4H), 1.68 (m, 4H), 1.43 (s, 12H), 1.36 (s, 3H), 1.31 (m, 24H), 0.91 (t, 6H), 0.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 155.2, 153.9, 147.8, 146.7, 143.5, 141.8, 140.1, 138.1, 136.6, 135.8, 134.7, 127.9, 127.3, 126.5, 125.9, 124.9, 123.9, 123.6, 123.2, 122.8, 122.7, 120.4, 119.3, 119.0, 98.3, 77.6, 77.5, 48.8, 36.4, 32.0, 31.9, 30.3, 29.7, 29.6, 29.5, 29.4, 27.3, 23.1, 22.8, 21.9, 14.3. FAB MS(m/z): 1007.43 (M^+). Anal calcd for $C_{68}H_{81}NO_2S_2$: C, 80.98; H, 8.10. Found: C, 80.88; H, 8.04.

5'-[*N*,*N*-Bis(7-hexyl-9,9-dimethylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-carbaldehyde (12).

THF (30 ml) and water (10 ml) were added to a flask containing **10** (0.43g, 0.47 mmol). Then TFA (3ml) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **12** was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:8) as an eluent (yield 95%). Mp: 181 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.86 (s, 1H), 7.67 (d, 1H), 7.58 (d, 2H), 7.56 (d, 2H), 7.49 (d, 2H), 7.34 (d, 2H), 7.25-7.20 (m, 6H), 7.14 (m, 4H), 7.11 (d, 1H), 2.68 (t, 4H), 1.66 (m, 4H), 1.42 (s, 12H), 1.34 (m, 12H), 0.90 (t, 6H) ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 182.5, 155.3, 153.9, 148.5, 147.7, 146.5, 141.9, 141.4, 139.5, 137.6, 136.6, 135.0, 134.1, 127.4, 126.9, 126.7, 123.8, 123.7, 123.5, 123.2, 122.9, 122.7, 120.5, 119.4, 119.3, 46.9, 36.4, 31.9, 31.8, 29.2, 27.3, 22.8, 14.2. FAB MS(m/z): 837.19 (M^+). Anal calcd for $C_{57}H_{59}NOS_2$: C, 81.67; H, 7.09. Found: C, 81.55; H, 7.01.

5'-[*N*,*N*-Bis(9,9-dimethyl-7-nonylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-carbaldehyde (13).

THF (30 ml) and water (10 ml) were added to a flask containing **10** (0.50g, 0.49

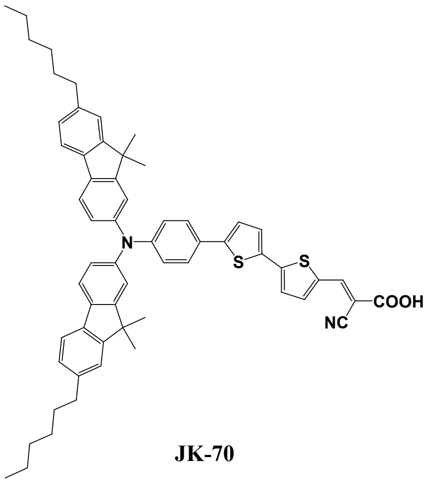
mmol). Then TFA (3ml) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature. The solution was quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with $MgSO_4$. The organic layer was removed in vacuo. The pure product **13** was obtained by silica gel chromatography using a mixture of ethyl acetate and n-hexane (1:7) as an eluent (yield 94%). Mp: 175 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.86 (s, 1H), 7.66 (d, 1H), 7.58 (d, 2H), 7.57 (d, 2H), 7.49 (d, 2H), 7.33 (d, 2H), 7.23-7.18 (m, 6H), 7.15 (m, 4H), 7.12 (d, 1H), 2.68 (t, 4H), 1.66 (m, 4H), 1.42 (s, 12H), 1.28 (m, 24H), 0.89 (t, 6H) ^{13}C NMR ($CDCl_3$, 75.44 MHz): δ 182.6, 155.2, 153.8, 148.4, 147.6, 146.8, 146.4, 141.9, 141.3, 137.7, 136.5, 134.9, 134.0, 127.4, 126.9, 126.7, 123.8, 123.6, 123.5, 123.2, 122.7, 120.4, 120.3, 119.3, 119.2, 46.8, 36.4, 32.0, 31.9, 29.7, 29.6, 29.5, 29.4, 27.2, 22.8, 14.3. FAB MS(m/z): 921.44 (M^+). Anal calcd for $C_{63}H_{71}NOS_2$: C, 82.04; H, 7.76. Found: C, 81.98; H, 7.68.

3-{5'-[*N*,*N*-Bis(7-hexyl-9,9-dimethylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid.

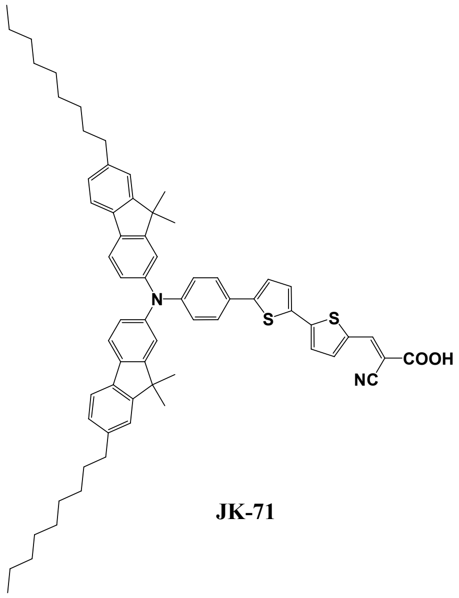
The resulting carbaldehyde bithophene (0.30 g, 0.35 mmol) and cyanoacetic acid (0.04 g, 0.43 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.02 ml, 0.18 mmol). The solution was refluxed for 6 hrs. After removal of acetonitrile in vacuo, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromarography using methanol as an eluent to give red solid product 3-{5'-[*N*,*N*-Bis(7-hexyl-9,9-dimethylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid (0.24 g, 0.27 mmol, yield 75%). Mp: 221 ℃. ^{1}H NMR (DMSO-*d*$_6$, 300 MHz): δ 8.01 (s, 1H), 7.69 (d, 2H), 7.62 (d, 4H), 7.60 (d, 1H), 7.45 (s, 2H), 7.41 (d, 1H), 7.29 (d, 4H), 7.13 (d, 2H), 7.06 (d, 2H), 7.03 (d, 2H), 2.62 (t, 4H), 1.59 (m, 4H), 1.34 (s, 12H), 1.28 (m, 12H), 0.85 (t, 6H). ^{13}C NMR (DMSO-d_6, 75.44 MHz): δ 162.4, 154.9, 153.4, 147.5, 145.9, 143.8, 141.2, 140.8, 139.5, 135.9, 134.4, 133.9, 127.2, 127.1, 126.8, 126.6, 126.5, 126.4, 124.1, 123.4, 123.1, 122.7, 122.6, 121.5, 120.9, 119.6, 119.5, 118.8, 46.4, 35.5, 31.1, 30.8, 28.5, 26.8, 22.1, 13.9. FAB MS(m/z): 904.32 (M$^+$). Anal calcd for $C_{60}H_{60}N_2O_2S_2$: C, 79.61; H, 6.68. Found: C, 79.41; H, 6.61.

3-{5'-[*N*,*N*-Bis(9,9-dimethyl-7-nonylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid.

The resulting carbaldehyde bithophene (0.37 g, 0.40 mmol) and cyanoacetic acid (0.05 g, 0.60 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.02 ml, 0.20 mmol). The solution was refluxed for 6 hrs. After removal of acetonitrile in vacuo, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromarography using methanol as an eluent to give red solid product 3-{5'-[*N*,*N*-Bis(9,9-dimethyl-7-nonylfluoren-2-yl)phenyl]-2,2'-bithiophen-5-yl}-2-cyanoacrylic acid (0.29 g, 0.29 mmol, yield 73%). Mp: 218 ℃. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 8.01 (s, 1H), 7.67 (d, 2H), 7.60 (d, 4H), 7.59 (d, 1H), 7.42 (s, 2H), 7.36 (d, 1H), 7.26 (d, 4H), 7.11 (d, 2H), 7.07 (d, 2H), 7.04 (d, 2H), 2.63 (t, 4H), 1.48 (m, 4H), 1.35 (s, 12H), 1.26 (m, 24H), 0.86 (t, 6H). ^{13}C NMR (DMSO-d_6, 75.44 MHz): δ 162.4, 154.8, 153.4, 147.3, 145.8, 143.6, 141.2, 140.6, 139.2, 135.8, 134.3, 133.8, 128.6, 127.1, 126.8, 126.6, 126.4, 126.3, 123.9, 123.3, 122.6, 122.5, 121.5, 120.7, 119.7, 119.6, 119.5, 118.7, 46.4, 35.5, 31.5, 31.2, 29.5, 29.4, 28.8, 28.7, 26.8, 22.0, 13.9. FAB MS(m/z): 988.46 (M$^+$). Anal calcd for $C_{66}H_{72}N_2O_2S_2$: C, 80.12; H, 7.33. Found: C, 80.03; H, 7.27.

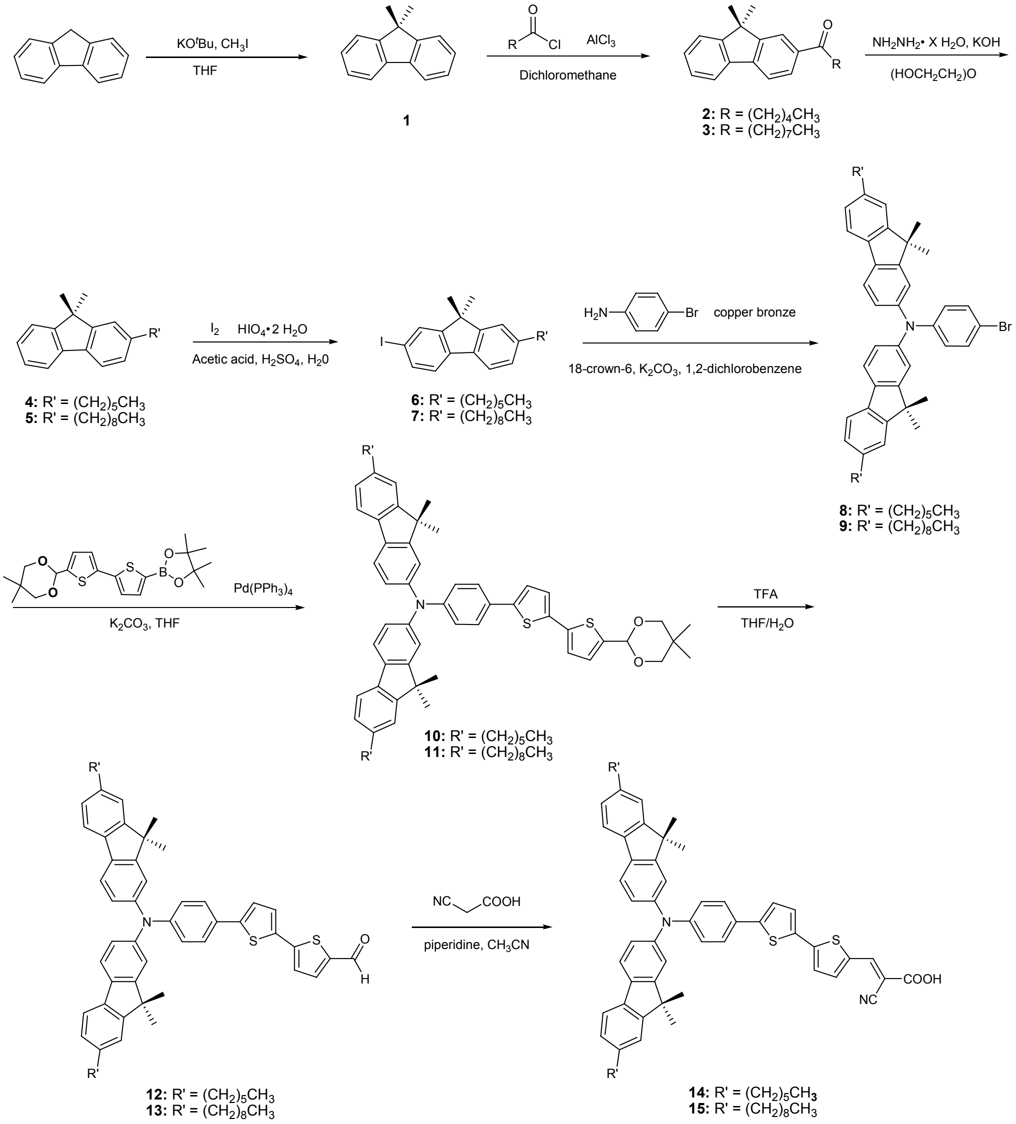


JK-70



JK-71

Figure S1. Structure of the dyes of **JK-70** and **JK-71**.



Scheme S1. Schematic diagram for the synthesis of organic dyes **JK-70** and **JK-71**

(a)

HOMO-1 **HOMO**

LUMO **LUMO+1**

(b)

HOMO-1 **HOMO**

LUMO **LUMO+1**

Figure S2. The molecular structures and the frontier molecular orbitals of the HOMO-1, HOMO, LUMO and LUMO-1 calculated with B3LYP/3-21G* of **JK-70** (a) and **JK-71**(b)

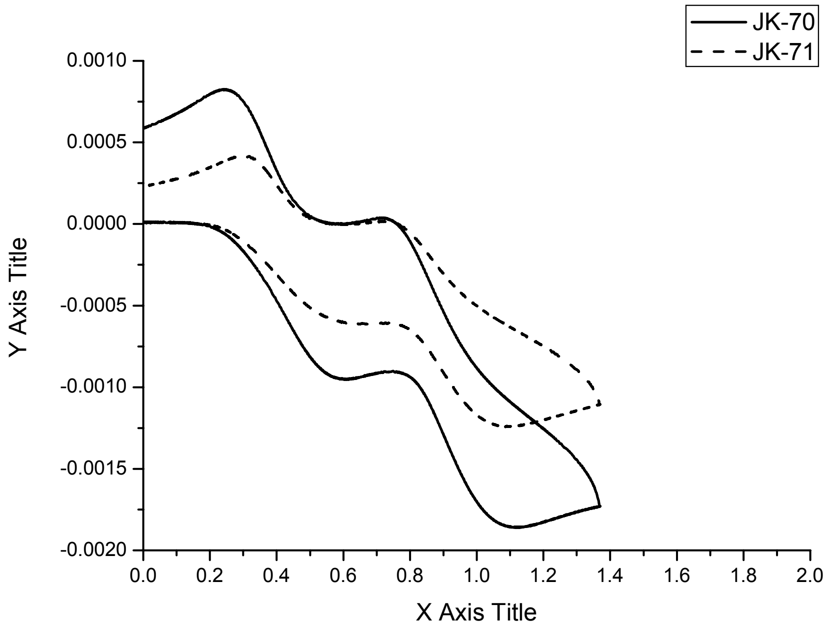


Figure S3. Cyclic voltammetry of **JK-70** (solid line) and **JK-71** sensitizers (dashed line) attached to a nanocrystalline TiO_2 film deposited on conducting FTO glass.

Reference

1. J. Fuller, A. C. Breda, R. T. Carlin, *J. Electrochem. Soc.* 1997, **144**, L67.
2. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nature Mater.*, 2003, **2**, 402.