Electronic Supplementary Information (ESI)

Circle Chain Embracing Donor-Acceptor Organic Dye: Simultaneous Improvement of Photocurrent and Photovoltage for Dye-Sensitized Solar Cells

Jian Liu, Youhei Numata, Chuanjiang Qin, Ashraful Islam, Xudong Yang, and Liyuan Han*

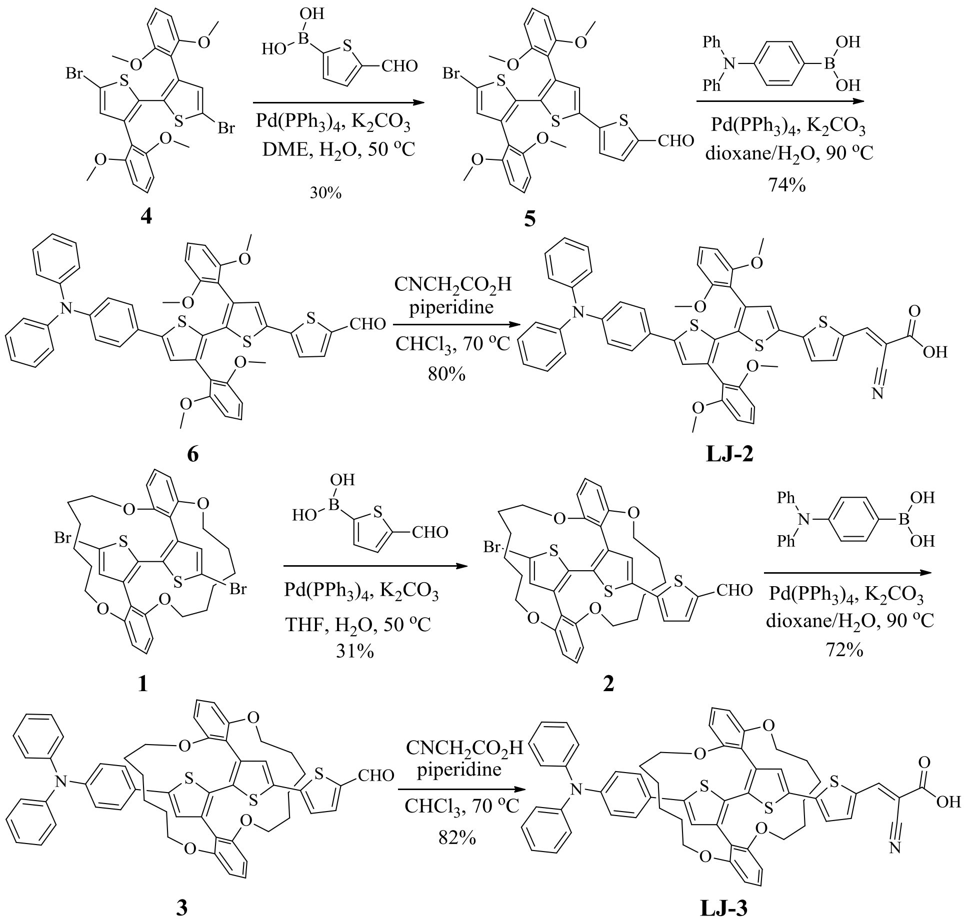
Photovoltaic Materials Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan, Fax: (+)81-29-859-2301, E-mail: HAN.Liyuan@nims.go.jp

Contents:

General

All chemicals and reagents were used as received from chemical companies without further purification. Anhydrous solvents were degassed by Ar bubbling for 20 min before use. Compounds **1**,[1] **4**[2] and **LJ-1**[3] were synthesized according to the reported methods. Column chromatography was performed using with Wakogel-C300 as a stationary phase. HPLC analyses were performed by CBM-20A HPLC system (SHIMADZU) with a column of phenomenex Fusion RP (4.5 mm I.D × 150 mm L., 4 μm). UV-Vis-NIR spectra were measured in CH_2Cl_2 solution or TiO_2 film using UV-3600 UV-VIS-NIR Spectrophotometer (SHIMADZU). Photoluminescence spectra were measured using a F-7000 Fluorescent spectrometer (HITACHI High-Technologies Corporation). Cyclic voltammetry (CV) was performed on a CH Instruments 624D potentiostat/galvanostat system. All CV measurements were carried out in CH_2Cl_2 containing 0.1 M TBAHFP as a supporting electrolyte, purging with argon prior to conduct the experiment. Platinum electrode was used as a working electrode, $Ag/AgNO_3$ as a reference electrode, and a platinum wire as a counter electrode. Mass spectra were measured on a Shimadzu Biotech matrix-assisted laser desorption ionization (MALDI) mass spectrometer. The ^{1}H- and ^{13}C-NMR measurements were performed by a DRX-600 spectrometer (Bruker BioSpin). Incident photon-to-current conversion efficiency spectra were measured by a CEP-200BX spectrometer (Bunko Keiki). The current-voltage (*I*-*V*) curves were obtained by a WXS-90S-L2 Super solar simulator (WACOM).

Synthesis Procedure and characterization data



Scheme S1. Synthetic routes of **LJ-2** and **LJ-3**.

Synthesis of compound 2

To a stirred solution of compound **1** (400 mg, 0.57 mmol) in THF (40 mL) was added 5-Formyl-2-thiopheneboronic acid (89 mg, 0.57 mmol), potassium carbonate (236 mg, 1.71 mmol), H_2O (10 mL), followed by $Pd(PPh_3)_4$ (33 mg, 0.028 mmol). The resulting mixture was stirred at 50 °C under argon atmosphere for 3 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (40 mL), extracted with CH_2Cl_2 (50 mL × 2). The organic layers were combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with hexane/EA (10/1, v/v) as eluent to afford the desired compound **2** as an yellow solid (127 mg, 31%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.79 (s, 1H), 7.58 (d, *J* = 4.2 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.05 (s, 1H), 7.00 (d, *J* = 4.2 Hz, 1H), 6.76 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 4.09-4.11 (m, 4H), 3.72-3.76 (m, 4H), 1.52-1.55 (m, 4H), 1.22-1.25 (m, 4H), 0.97-0.99 (m, 4H), 0.88-0.91 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 182.34, 158.66, 148.19, 140.72, 137.53, 135.09, 134.15, 132.80, 132.42, 132.00, 131.19, 130.86, 128.75, 123.06, 115.15, 111.81, 106.82, 69.78, 30.34, 27.72. ESI (m/z): Calcd for $C_{37}H_{35}BrO_5S_3$, 734.08 (M^+); found, 735.09 $[M+H]^+$.

Synthesis of compound 3

To a stirred solution of compound **2** (120 mg, 0.163 mmol) in 1,4-dioxane (20 mL) was added 4-diphenylaminophenylboronic acid (71 mg, 0.245 mmol), potassium carbonate (68 mg, 0.49 mmol), H_2O (5 mL), followed by $Pd(PPh_3)_4$ (15 mg, 0.01 mmol). The resulting mixture was stirred at 90 °C under argon atmosphere for 12 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (30 mL), extracted twice with CH_2Cl_2 (40 mL × 2). The organic layers were combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with hexane/EA (5/1, v/v) as eluent to afford the desired compound **3** as an orange solid (106 mg, 72%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.79 (s, 1H), 7.58 (d, *J* = 4.8 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 8.4 Hz, 1H), 7.28-7.30 (m, 4H), 7.22-7.24 (m, 2H), 7.08-7.10 (m, 5H), 7.00-7.02 (m, 6H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 4.09-4.11 (m, 4H), 3.71-3.77 (m, 4H), 1.50-1.55 (m, 4H), 1.22-1.25 (m, 8H), 0.97-0.99 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 182.30, 158.81, 148.56, 147.50, 146.88, 141.30, 140.41, 137.62, 136.03, 134.00, 132.39, 131.93, 131.19, 130.86, 129.30, 129.04, 128.57, 125.86, 125.09, 124.46, 123.63, 123.05, 122.83, 116.30, 115.90, 69.79, 30.34, 27.63. FAB (m/z): Calcd for $C_{55}H_{49}NO_5S_3$, 899.28 (M^+); found, 899.28.

Synthesis of compound 5

To a stirred solution of compound **4** (400 mg, 0.673 mmol) in DME (40 mL) was added 5-Formyl-2-thiopheneboronic acid (105 mg, 0.57 mmol), potassium carbonate (278 mg, 2.02 mmol), H_2O (10 mL), followed by $Pd(PPh_3)_4$ (39 mg, 0.034 mmol). The resulting mixture was stirred at 50 °C under argon atmosphere for 3 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (40 mL), extracted with CH_2Cl_2 (50 mL × 2). The organic layers were combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with hexane/EA (10/1, v/v) as eluent to afford the desired compound **5** as an orange solid (135 mg, 32%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 9.82 (s, 1H), 7.62 (d, *J* = 3.6 Hz, 1H), 7.12-7.18 (m, 4H), 6.84 (s, 1H), 6.39-6.45 (m, 4H), 3.58 (s, 6H), 3.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz):

δ 182.44, 158.14, 147.81, 141.25, 137.42, 135.50, 134.78, 133.94, 132.80, 131.86, 131.45, 130.53, 129.22, 123.77, 112.67, 110.28, 103.96, 55.60. ESI (m/z): Calcd for $C_{29}H_{23}BrO_5S_3$, 625.99 (M^+); found, 648.98 $[M+Na]^+$.

Synthesis of compound 6

To a stirred solution of compound **5** (130 mg, 0.208 mmol) in 1,4-dioxane (20 mL) was added 4-diphenylaminophenylboronic acid (90 mg, 0.312 mmol), potassium carbonate(86 mg, 0.624 mmol), H_2O (5 mL), followed by $Pd(PPh_3)_4$ (15 mg, 0.01 mmol). The resulting mixture was stirred at 90 °C under argon atmosphere for 12 h. Evaporation of the solvent under reduced pressure and the residue was treated with water (30 mL), extracted twice with CH_2Cl_2 (40 mL × 2). The organic layers were combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with hexane/EA (5/1, v/v) as eluent to afford the desired compound **6** as an orange solid (121 mg, 74%). ^1H NMR ($CDCl_3$, 600 MHz): δ 9.82 (s, 1 H), 7.62 (d, *J* = 3.6 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.18-7.24 (m, 2H), 7.17 (s, 1H), 7.14-7.16 (m, 4H), 7.08-7.11 (m, 4H), 7.01-7.04 (m, 6H), 6.41 (d, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 2H), 3.60 (s, 6H), 3.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 182.42, 157.87, 148.17, 147.50, 146.97, 141.33, 140.83, 137.50, 136.90, 132.28, 132.06, 131.04, 130.89, 129.29, 128.82, 128.56, 126.95, 126.23, 124.45, 123.60, 123.34, 123.03, 113.79, 113.20, 104.04, 55.77. FAB (m/z): Calcd for $C_{47}H_{37}NO_5S_3$, 791.18 (M^+); found, 791.18.

Synthesis of LJ-2

A solution of the aldehyde **6** (40 mg, 0.051 mmol), cyanoacetic acid (13 mg, 0.153 mmol), piperidine (26 mg, 0.31) in $CHCl_3$ (20 mL) was stirred at reflux for 12 h. The reaction mixture was cooled to room temperature, then treated with water (30 mL) and acidified with 1 M aqueous hydrochloric acid (10 mL), extracted twice with $CHCl_3$ (40 mL × 2). The organic layers were combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with CH_2Cl_2/CH_3OH (15/1, v/v) as eluent to afford the desired dye **LJ-2** as a black solid (35 mg, 80%). ^1H NMR (DMSO-d_6, 600 MHz): δ 8.37 (s, 1H), 7.88 (d, *J* = 3.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.30-7.33 (m, 6H), 7.24 (s, 1H), 7.06-7.08 (m, 3H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 4H); 6.92 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.60 (s, 6H), 3.59 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.15, 158.10, 147.03, 146.93, 145.93, 140.73, 135.43, 134.00, 133.10, 132.38, 131.78, 130.84, 130.65, 130.24, 130.10, 129.85, 127.59, 127.02, 126.25, 124.85, 124.43, 123.62, 123.36, 117.23, 113.07, 112.54, 104.60, 104.52, 55.69. ESI (m/z): Calcd for $C_{50}H_{38}N_2O_6S_3$, 857.19 $(M\text{-}H)^-$; found, 857.19.

Synthesis of LJ-3

A solution of the aldehyde **3** (50 mg, 0.056 mmol), cyanoacetic acid (14 mg, 0.167 mmol), piperidine (28 mg, 0.324) in $CHCl_3$ (20 mL) was stirred at reflux for 12 h. The reaction mixture was cooled to room temperature, then treated with water (30 mL) and acidified with 1 M aqueous hydrochloric acid (10 mL), extracted twice with $CHCl_3$ (40 mL × 2). The organic layer was combined and washed twice with water and once with brine, dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with CH_2Cl_2/CH_3OH (15/1, v/v) as eluent to afford the desired dye **LJ-3** as a purple solid (44 mg, 82%). ^1H NMR (DMSO-d_6, 600 MHz): δ 8.36 (s, 1H), 7.86 (d, J = 3.0 Hz, 1H), 7.49 (s, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.30-7.35 (m, 6H), 7.26 (s, 1H), 7.24 (d, J = 4.8 Hz, 1H), 7.13 (s, 1H), 7.07 (t, J = 7.2 Hz, 2H), 7.03 (d, J = 8.4 Hz, 4H); 6.91 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 7.2 Hz, 2H), 6.82 (d, J = 7.2 Hz, 2H), 4.07-4.10 (m, 4H), 3.71-3.74 (m, 4H), 1.38-1.50 (m, 8H), 1.10-1.14 (m, 4H), 0.84-0.87 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 158.68, 158.57, 147.28, 147.09, 140.83, 135.62, 134.69, 133.65, 133.21, 131.68, 131.60, 131.53, 130.97, 130.08, 129.82, 128.14, 126.09, 125.98, 124.57, 124.14, 123.88, 123.81, 115.94, 115.52, 107.52, 107.43, 69.52, 30.32, 27.55. ESI (m/z): Calcd for $C_{58}H_{50}N_2O_6S_3$, 965.28 $(M\text{-}H)^-$; found, 965.28.

Cell Fabrication

The DSC devices were fabricated as follows. A 14 μm main transparent layer with ca. 20 nm sized titania particles and a 6 μm scattering layer with ca. 400 nm sized titania particles were screen printed on the fluorine-doped tin oxide (FTO) conducting glass substrate. Coating of the titania film was carried out by immersing in 3×10^{-4} M acetonitrile/*tert*-butyl alcohol (1/1, v/v) solution of sensitizers for 45 h. The dye adsorbed titania film was clipped with a platinized FTO glass used as counter electrode. Finally, the sandwich-type solar cell could be obtained after the injection of an electrolyte consisting of 0.6 M 1-methyl-3-propylimidazolium iodide, 0.1 M LiI, 0.5 M *tert*-butylpyridine and 0.05 M I_2 in acetonitrile.

Absorption and emission spectra

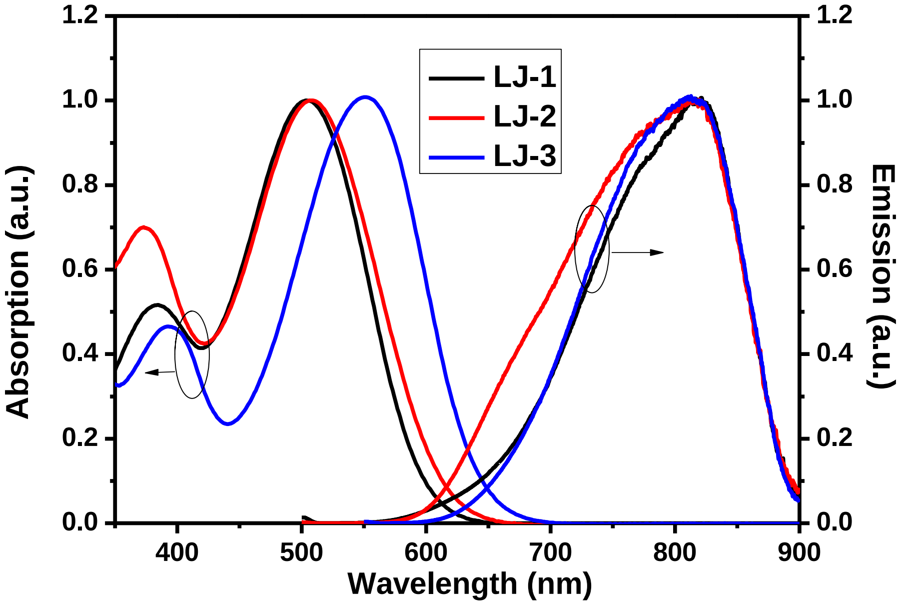


Fig. S1 UV-vis and emission spectra of dyes **LJ-1**, **LJ-2** and **LJ-3** in CH_2Cl_2.

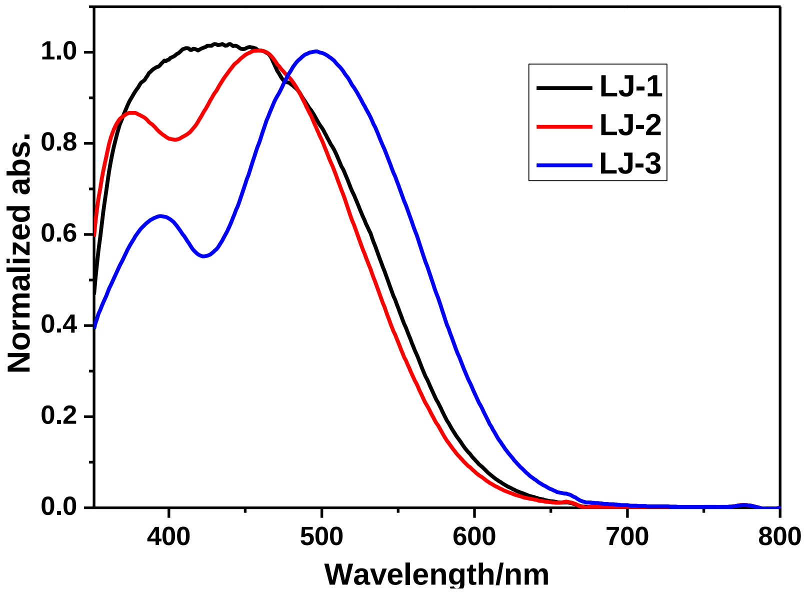


Fig. S2 Normalized UV-vis spectra of dyes **LJ-1**, **LJ-2** and **LJ-3** anchored on TiO_2 film.

Cyclic voltammogram

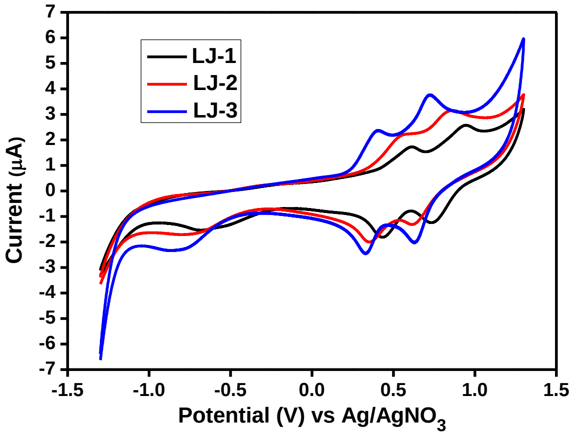


Fig. S3 Cyclic voltammograms of dyes in DCM/TBAHFP (0.1 M), [c] = 1×10^{-4} mol L^{-1}, 293 K, scan rate = 100 mV s^{-1}, vs. Ag/AgNO$_3$.

Table S1: Spectral and electrochemical properties of **LJ-1**, **LJ-2** and **LJ-3**.

Dye	$^a\lambda_{max}$ (nm)	$^a\varepsilon_{max}$ (L mol^{-1} cm^{-1})	$^b\lambda_{max}$ (nm)	$^cS^{+/0}$/V (vs NHE)	$^dS^{+/*}$/V (vs NHE)	$^eE_{0\text{-}0}$ (V)
LJ-1	504	31090	453	0.97	–1.05	2.02
	385	16050				
LJ-2	506	33440	459	0.90	–1.01	2.01
	373	23410				
LJ-3	551	50420	496	0.81	–1.10	1.91
	393	23250				

[a] Measured in CH_2Cl_2 solution (2×10^{-5} M). [b] Measured on TiO_2 films. [c] The $S^{+/0}$ corresponding to the ground-state oxidation potential (vs NHE) in CH_2Cl_2 internally calibrated with ferrocene (0.63 V vs NHE). [d] $S^{+/*} = S^{+/0} - E_{0\text{-}0}$, where $E_{0\text{-}0}$ is the zero-zero transition energy. [e] $E_{0\text{-}0}$ values were estimated from the intersection between the absorption and emission spectra in CH_2Cl_2.

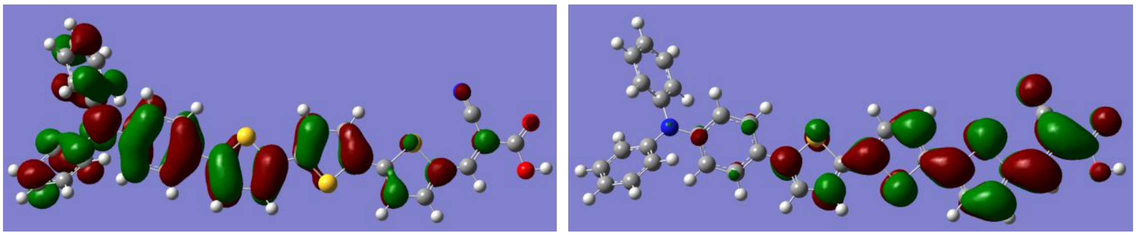
Table S2: Photovoltaic performance of DSCs based on **LJ-1**, **LJ-2** and **LJ-3**.[a]

Dye	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
LJ-1	13.95	0.68	0.73	6.98
LJ-2	13.48	0.75	0.76	7.77
LJ-3	15.03	0.74	0.75	8.34

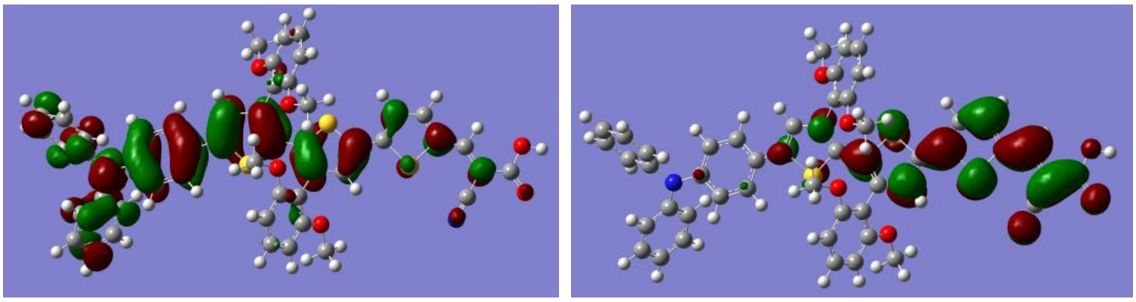
[a] Measurements were performed under the following conditions: AM 1.5 irradiation; DSC active surface area, 0.25 cm^2; electrolyte: 0.6 M 1-propyl-2,3-dimethylimidazolium iodide, 0.05 M I_2, 0.1 M LiI and 0.5 M *tert*-butylpyridine in acetonitrile. Abbreviations: J_{SC}, short-circuit current; V_{OC}, open-circuit voltage; FF, fill factor; η, overall conversion efficiency.

DFT Calculation

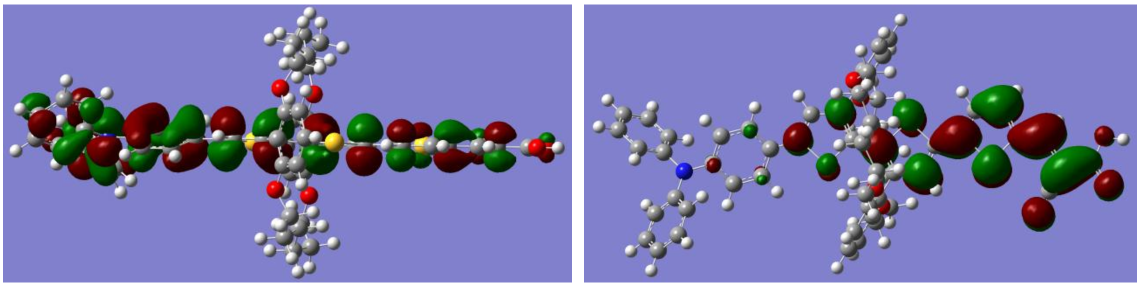
Geometry optimization and Molecular orbital distributions of three dyes were performed using B3LYP functional and 6-31G (d,p) basis set implemented in the Gaussian 09 program package.[4]



HOMO (LJ-1) **LUMO (LJ-1)**



HOMO (LJ-2) **LUMO (LJ-2)**



HOMO (LJ-3) **LUMO (LJ-3)**

Fig. S4 The HOMO and LUMO of dyes **LJ-1**, **LJ-2** and **LJ-3** optimized at B3LYP/6-31G** level

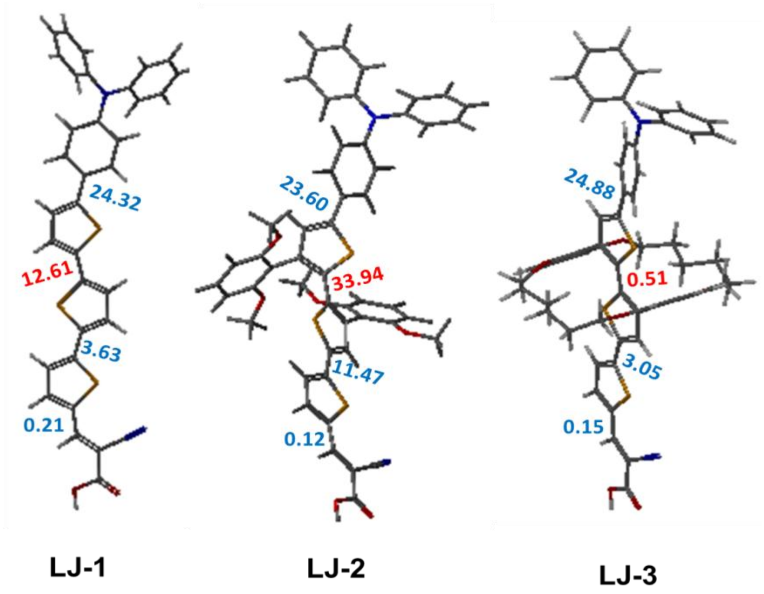


Fig. S5 Optimized ground-state geometries and dihedral angles between the π-planes of **LJ-1**, **LJ-2** and **LJ-3**.

HPLC analysis and ^{1}H NMR spectra

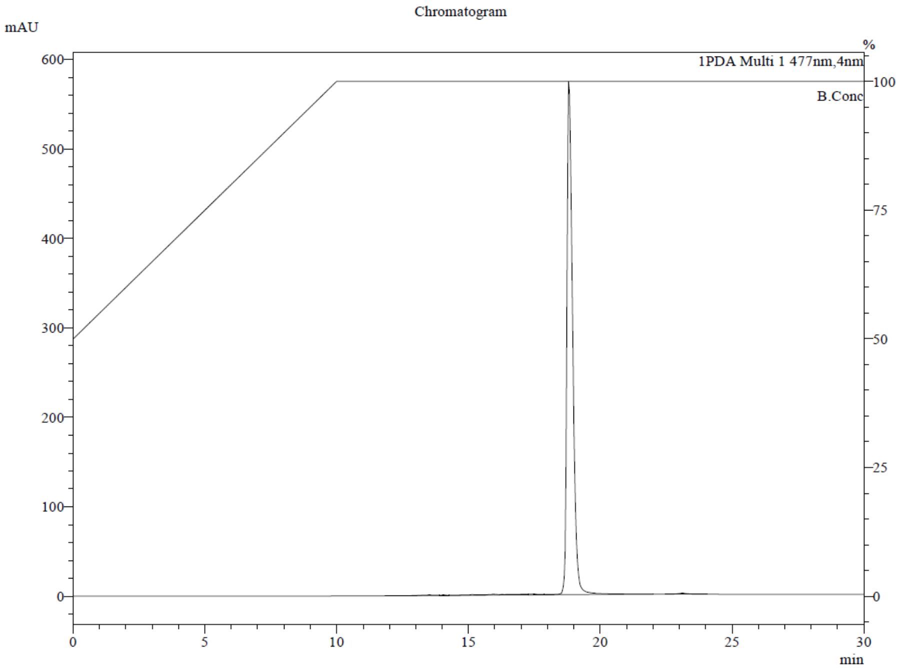


Fig. S6 HPLC analysis of dye **LJ-1** (purity: 97.9%); mobile phase A: 1% formic acid in water; mobile phase B: methanol, gradient program: B: 50% (0 min)→ B: 0% (10-30 min).

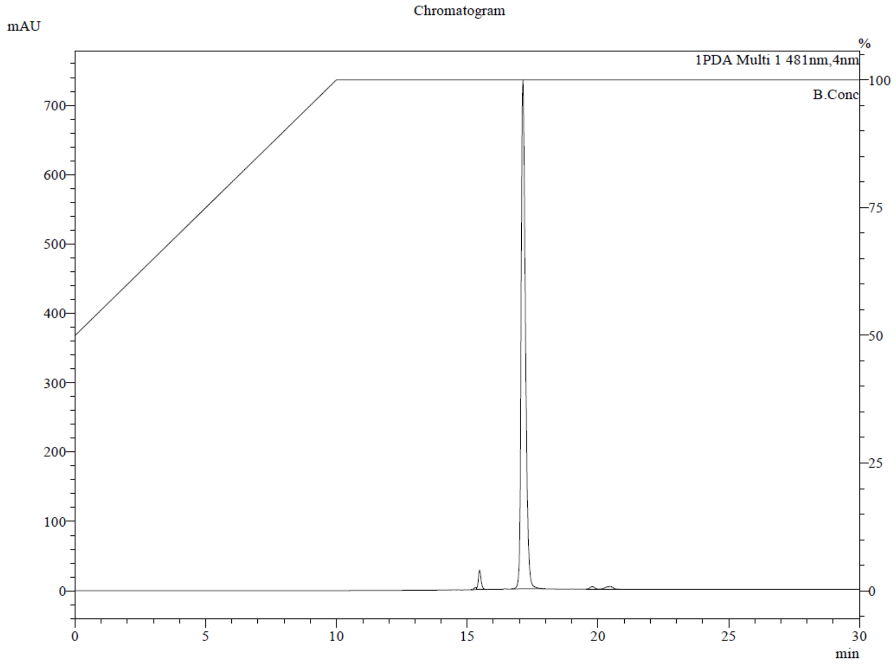


Fig. S7 HPLC analysis of dye **LJ-2** (purity: 96.1%); mobile phase A: 1% formic acid in water; mobile phase B: methanol, gradient program: B: 50% (0 min)→ B: 0% (10-30 min).

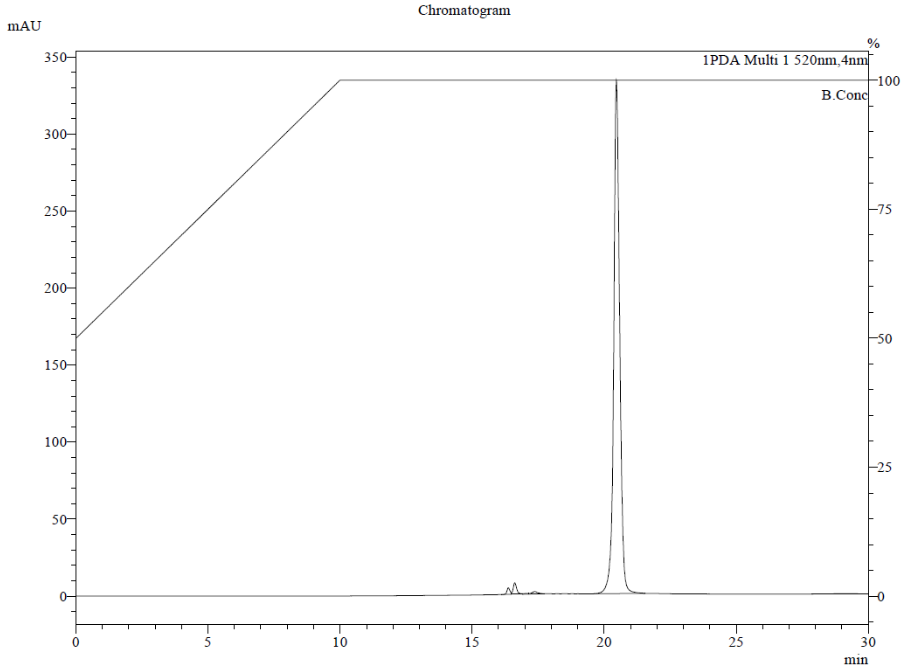


Fig. S8 HPLC analysis of dye **LJ-3** (purity: 97%); Mobile phase A: 1% formic acid in water; mobile phase B: methanol, gradient program: B: 50% (0 min)→ B: 0% (10-30 min).

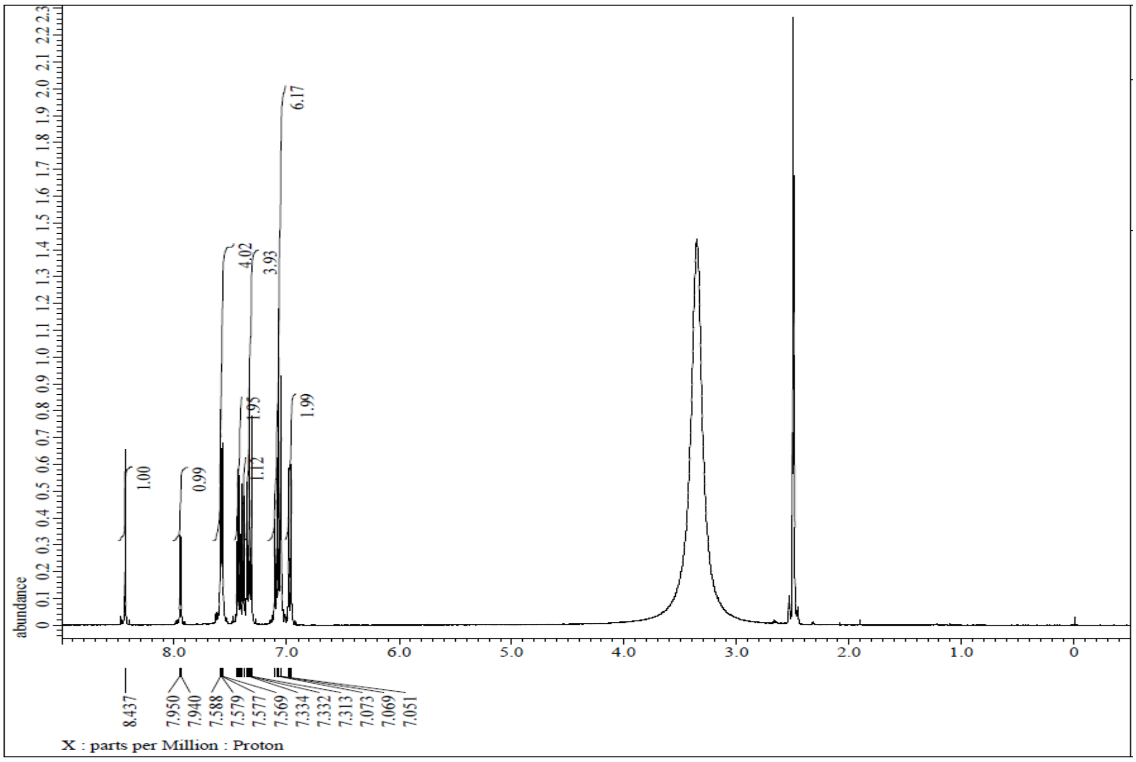


Fig. S9 ^{1}H NMR spectra of dye **LJ-1**.

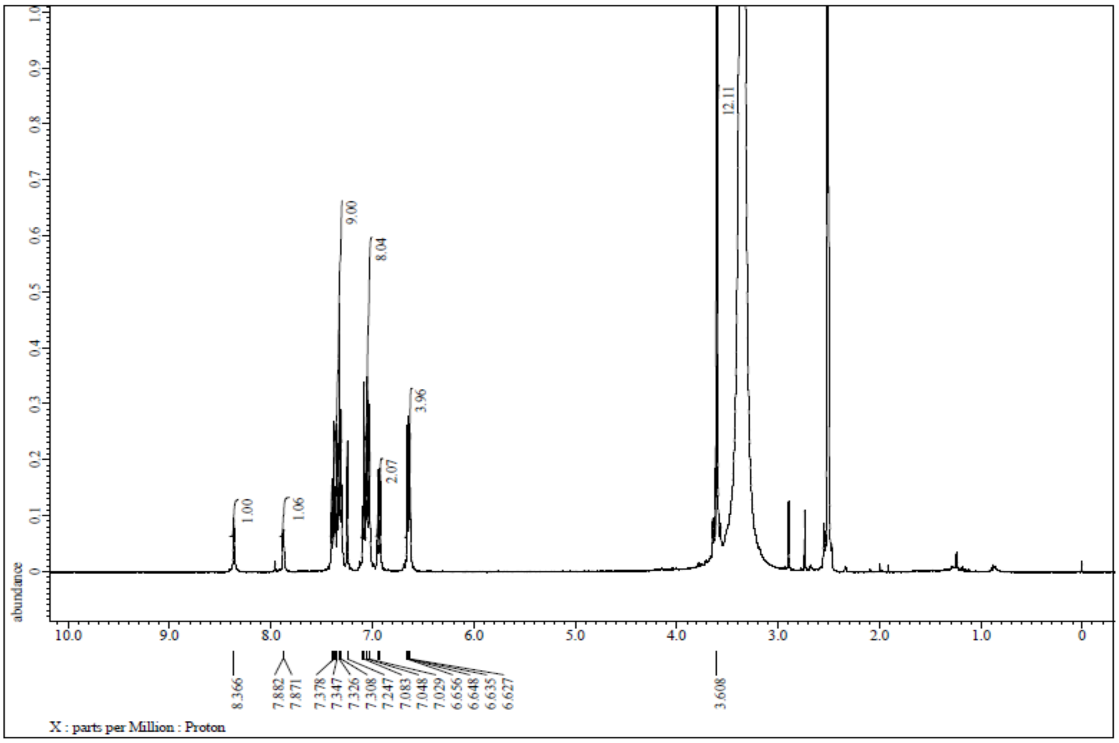


Fig. S10 ^{1}H NMR spectra of dye **LJ-2**.

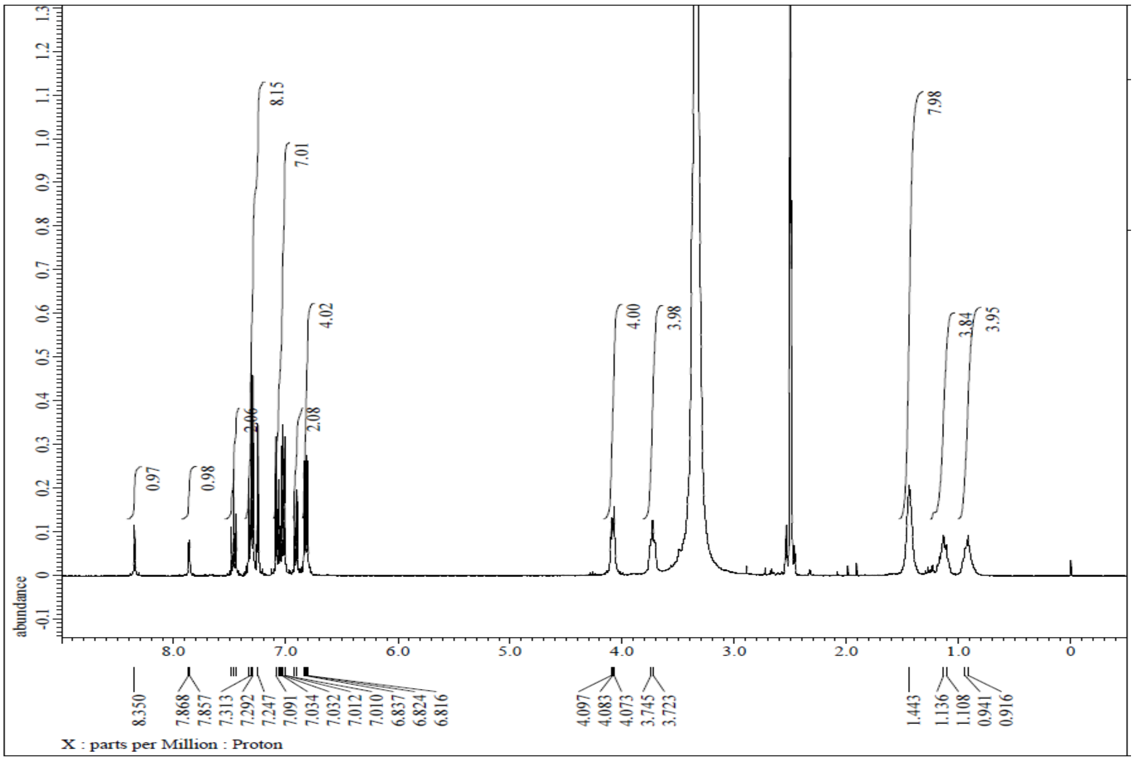


Fig. S11 ^{1}H NMR spectra of dye **LJ-3**.

Reference

1. K. Sugiyasu, Y. Honsho, R. M. Harrison, A. Sato, T. Yasuda, S. Seki, M. Takeuchi, *J. Am. Chem. Soc.* **2010**, *132*, 14756.

2. R. Shomura, K. Sugiyasu, T. Yasuda, A. Sato, M. Takeuchi, *Macromolecules* **2012**, *45*, 3759.

3. K. R. Justin Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng, P.-T. Chou, *Chem. Mater.* **2008**, *20*, 1830.

4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg,

S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, **2009**.