Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Novel Near-Infrared Carboxylated 1,3-Indandione Sensitizers for Highly Efficient Flexible Dye-Sensitized Solar Cells

Naoyuki Shibayama,[a,b] Yukiko Inoue,[c] Masahiro Abe,[b] Shingo Kajiyama,[c] Hironobu Ozawa,[a] Hidetoshi Miura[c] and Hironori Arakawa*[a]

[a] Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, Ichigaya-Funagawara, Shinjuku, Tokyo 162-0826, Japan. E-mail: h.arakawa@ci.kagu.tus.ac.jp

[b] Technical Research Institute, Toppan Printing Co., Ltd., Takanodaiminami, Sugito, Saitama 345-8508, Japan.

[c] R&D center, Chemicrea Inc., 1-133 Ohtsurugi, Shimogawa Izumi-machi, Iwaki, Fukushima, 971-8183, Japan.

Experimental

Materials and measurement

D205 was purchased from Chemicrea Co. Ltd. Titanium isopropoxide and deoxycholic acid (DCA) were purchased from Tokyo Chemical Industry Co. Lid. 1-ethyl-3-methylimidazolium iodide (EMImI) was purchased from Merck. All solvents and reagents were of the highest quality available and were used as received.

NMR spectra were acquired on a JEOL JNM-AL400 spectrometer, where chemical shifts in methanol, acetone, $CDCl_3$ and DMSO-*d6* were referenced to internal standard tetramethylsilane. UV-visible absorption spectra and LHE spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Luminescence spectra were recorded on a JASCO FP-6600 spectrofluorophotometer at room temperature, where the excited wavelength was 530 nm. Each chloroform solution was bubbled with N_2 for at least 15 min prior to the measurement. Electrochemical measurements were carried out in methanol at a sweep rate of 50 mV s^{-1} using a glassy carbon disk working electrode, a Pt wire counter electrode, and an Ag wire reference electrode (*ca*. 200 mV *vs.* SCE). The supporting electrolyte was 0.1 M $LiClO_4$.

Preparation of PDSCs

The TiO_2 paste used in our study comprised a mixture of 10 wt% nanocrystalline TiO_2 and water. Two types of anatase-TiO_2 particles were prepared by autoclave treatment in a basic environment following the hydrolysis of $Ti(OCH(CH_3)_2)_4$, according to the reported procedure.[1] The average particle sizes of the two different TiO_2 particles obtained by SEM were 20 and 100 nm in diameter. After the autoclave treatment, water and any volatiles were removed using a rotary evaporator. Ethanol was added to the TiO_2 residue, the solvent was then removed again. This solvent replacement process was repeated five times. By this method, TiO_2 particles dispersed into ethanol were obtained. These 20 and 100 nm TiO_2 particles were mixed in a weight ratio of 7:3. After homogenization, the dispersion media was replaced again with water by the solvent replacement method. The TiO_2 particle concentration was finally adjusted to 10wt%, resulting in a paste consisting of only TiO_2 particles and water without any binder materials.

The active areas of these TiO_2 films were determined using a KEYENCE VHX-200 digital microscope.

Dye-sensitized TiO_2 photoelectrodes were prepared by immersing the TiO_2 photoelectrodes into the 1-propanol solution of 0.3 mM **DN458**, **DN475**, **DN484** and **D205** and 3 mM DCA for 1 h at room temperature. Photoelectrochemical measurements were performed in a two-electrode sandwich cell configuration composed of the dyeadsorbed TiO_2 photoelectrode, a platinum-sputtered Ti thin substrate (counter electrode), a spacer film (30 µm), and an electrolyte solution (0.05 M I_2, 0.1 M LiI, 0.6 M EMImI and 0.005 M 4-*tert*-butylpyridine (TBP) in acetonitrile).

Photovoltaic measurements

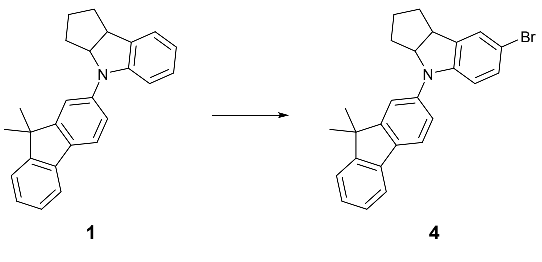
The photocurrent-voltage (J-V) characteristics of the PDSCs were measured on a Keithley 2400 source meter under irradiation of AM 1.5, 100 mW/cm^2 (1 sun) supplied by a solar simulator (Yamashita Denso, YSS-150A). The incident light intensity was calibrated with a grating spectroradiometer (LS-100, EKO Instruments) and a reference Si solar cell equipped with a heat absorbing filter (BS520-BK, Bunko Keiki). Open-circuit voltage decay measurements, irradiation (AM 1.5, 100 mW/cm^2) was carried out under the open circuit condition for 15 seconds, and then simple decay of the *V*oc value of the PDSC was monitored under the dark condition. The incident photon-to-current conversion efficiency (IPCE) was measured on a PEC-S10 (Peccell Technologies).

Synthesis of dyes

Synthesis of 1, 2 and 3

1[2], **2**[2] **and 3**[3] were synthesized following the literature.

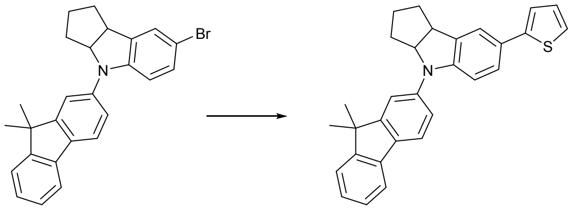
Synthesis of 7-bromo-4-(9,9-dimethyl-9H-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole, 4



An acetone solution (184 mL) of **1** (6.68 g, 19.0 mmol) was added *N*-bromosuccinimide (3.39g, 19.1 mmol) at 5 °C. The mixture was stirred at room temperature for 3 h. The reaction mixture was poured into water (200 mL) and extracted with chloroform (400 mL). The extract was washed with water (200 mL). The solvent was evaporated and the crude residue was purified by silica gel column chromatography (hexane- $CHCl_3$ = 4 : 1) to give **4** (7.75 g, 18.0 mmol, 94.8%) as a grey solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.66-7.63 (m, 2H) , 7.40 (d, *J* = 7.3 Hz, 1H) , 7.33-7.18 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H), 4.83-4.80 (m, 1H), 3.84-3.80 (m, 1H), 2.09-1.95 (m, 2H), 1.88-1.81 (m, 2H), 1.70-1.64 (m, 1H), 1.60-1.45 (m, 1H), 1.48 (s, 6H); ^{13}C-NMR (100

MHz, $CDCl_3$) δ= 155.0, 153.2, 146.7, 142.3, 139.1, 137.4, 133.2, 129.8, 127.6, 127.0, 126.3, 122.4, 120.6, 119.2, 118.4, 113.6, 109.6, 109.3, 69.4, 46.8, 45.3, 34.8, 33.9, 27.3, 27.2, 24.5.

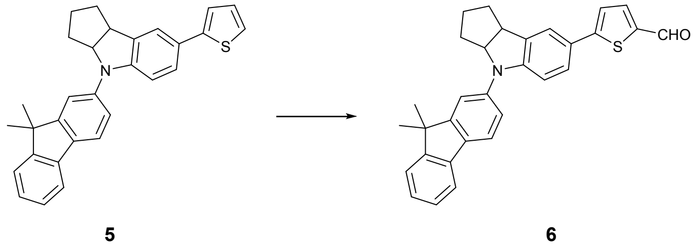
Synthesis of 4-(9,9-dimethyl-9*H*-fluoren-2-yl)-7-(thiophen-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole, 5



4 **5**

A THF solution (100 mL) of **4** (4.30 g, 10.0 mmol) was added 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (2.52 g, 12.0 mmol), tetrakis (triphenyl-phosphine) palladium(0) (0.6 g, 0.50 mmol) and a 2M aqueous potassium carbonate solution (8 mL). The mixture was refluxed for 10 h under N_2. Then, chloroform (200 mL) was added to the reaction mixture and it was then filtered through Celite. The filtrate was washed with water (20 mL). The solvent was evaporated and the crude residue was purified by silica gel column chromatography (hexane-$CHCl_3$ = 4 : 1) to give **5** (3.69 g, 8.51 mmol, 85.1%) as a pale yellow solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.68-7.64 (m, 2H), 7.42-7.23 (m, 7H), 7.18-7.16 (m, 2H), 7.05-7.01 (m, 2H), 4.89-4.86 (m, 1H), 3.90-3.87 (m, 1H), 2.14-1.85 (m, 4H), 1.74-1.56 (m, 2H), 1.50 (s, 3H), 1.49 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ= 155.0, 153.3, 147.1, 145.4, 142.4, 139.2, 135.8, 133.0, 127.8, 127.0, 126.2, 125.4, 125.3, 122.8, 122.6, 122.5, 121.0, 120.6, 119.2, 118.3, 113.5, 108.2, 69.3, 46.9, 45.4, 34.9, 33.9, 27.4, 27.3, 24.5.

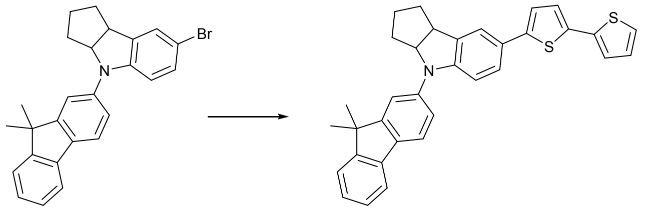
Synthesis of 5-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydro-cyclopenta[*b*]indol-7-yl)thiophene-2-carbaldehyde, 6



5 **6**

To a DMF (4.0 mL) was added phosphorous oxychloride (2.47 g, 16.2 mmol) at 5 °C. To the solution was then added DMF (14 mL) and chloroform (4 mL) solution of **5** (8.07 mmol) at 5 °C. The mixture was stirred at room temperature for 2 h. After the reaction was complete, the reaction mixture was poured into water (56 mL) and chloroform (56 mL), and then alkalinized with aqueous sodium hydroxide. The product was extracted with chloroform (3 × 100 mL). The extract was washed with water (2 × 100 ml), and dried over anhydrous sodium sulfate. The solvent was evaporated and the crude residue was purified by silica gel column chromatography ($CHCl_3$) to give **6** (3.59 g, 7.78 mmol, 96.4%) as an orange solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.70-7.66 (m, 3H), 7.44-7.41 (m, 3H), 7.36-7.23 (m, 5H), 6.97 (d, J = 8.0 Hz, 1H), 4.95-4.92 (m, 1H), 3.91-3.87 (m, 1H), 2.13-2.07 (m, 1H), 1.98-1.86 (m, 3H), 1.62-1.58 (m, 1H), 1.51 (s, 3H), 1.50 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ= 182.4, 156.1, 155.1, 153.3, 149.2, 141.5, 140.1, 139.0, 138.0, 136.1, 134.0, 127.0, 126.5, 126.4, 123.4, 122.9, 122.5, 121.6, 120.7, 119.4, 119.2, 114.5, 107.8, 69.6, 46.9, 45.2, 35.1, 33.7, 27.4, 27.2, 24.5.

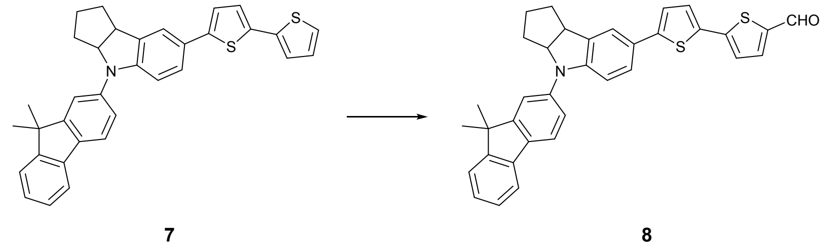
Synthesis of 7-(2,2'-bithiophen-5-yl)-4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole, 7



4 **7**

A THF solution (80 mL) of **4** (3.07 g, 7.1 mmol) was added 5-(4,4,5,5-tetramethyl-1,3,2,-dioxaborolan-2-yl)-2,2'-bithiophen (3.13g, 12.0 mmol), tetrakis (triphenyl-phosphine) palladium(0) (2.22 g, 1.92 mmol) and a 2M aqueous potassium carbonate solution (20 mL). The mixture was refluxed for 24 h under N_2. Then, chloroform (200 mL) was added to the reaction mixture and it was then filtered through Celite. The filtrate was washed with water (20 mL). The solvent was evaporated and the crude residue was purified by silica gel column chromatography (hexane-$CHCl_3$ = 4 : 1) to give **7** (2.95 g, 5.72 mmol, 80.0%) as a pale yellow solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.65(2H, dd, *J*=8.0, 6.4Hz), 7.40(1H, d, *J*=7.6Hz), 7.37(1H, s), 7.35-7.32(2H, m), 7.30(1H, d, *J*=8.4Hz), 7.26(1H, d, *J*=7.2Hz), 7.23(1H, dd, *J*=8.0, 2.0Hz), 7.17(1H, d, *J*=6.0Hz), 7.16(1H, d, *J*=4.0Hz), 7.10(1H, d, *J*=4.0Hz), 7.07(1H, d, *J*=4.0Hz), 7.01(1H, s), 7.00(1H, dd, *J*=3.6, 3.2Hz), 4.89-4.83 (1H, m), 3.88-3.85(1H, m), 2.13-2.04(1H, m), 2.01-1.83(3H, m), 1.73-1.65(1H, m), 1.63-1.54(1H, m), 1.50(3H, s), 1.49(3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ= 155.0, 153.2, 147.2, 144.3, 142.2, 139.1, 137.9, 135.9, 134.5, 133.1, 127.8, 127.0, 126.3, 125.1, 124.9, 124.5, 123.8, 123.0, 122.4, 122.2, 121.5, 120.6, 119.2, 118.4, 113.6, 108.1, 69.4, 46.8, 45.4, 34.9, 33.9, 27.3, 27.2, 24.5.

Synthesis of 5'-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)-2,2'-bithiophene-5-carbaldehyde, 8



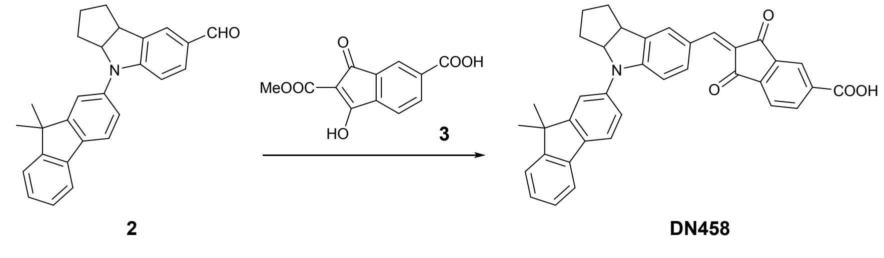
7

8

To a DMF (5.0 mL) was added phosphorous oxychloride (1.99 g, 13.0 mmol) at 0 °C. To the solution was then added chloroform (14 mL) solution of **7** (2.95 g, 5.70 mmol). The mixture was stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was poured into water (56 mL), and then alkalinized with aqueous sodium hydroxide. The product was extracted with chloroform (3 × 100 mL). The extract was washed with water (2 × 100 ml), and dried over anhydrous sodium sulfate.

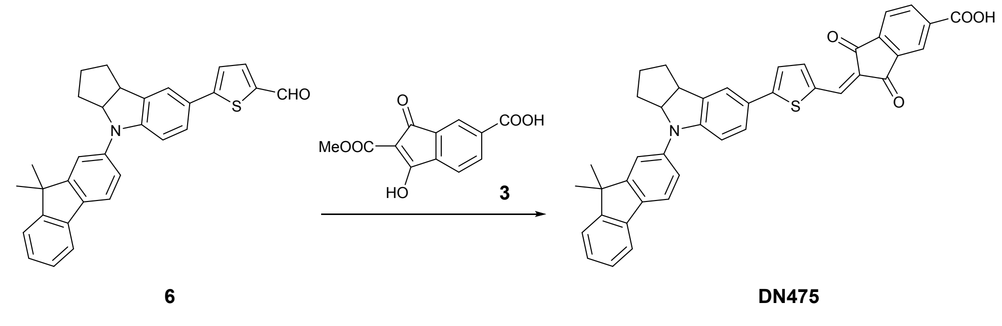
The solvent was evaporated and the crude residue was purified by silica gel column chromatography (hexane-$CHCl_3$ = 1 : 3) to give **8** (1.58 g, 2.91 mmol, 51.0%) as an vermilion solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 9.84(1H, s), 7.69(1H, d, *J*=8.4Hz), 7.67(1H, d, *J*=4.4Hz), 7.66(1H, d, *J*=7.2Hz), 7.42(1H, d, *J*=6.8Hz), 7.38-7.33(3H, m), 7.32(1H, d, *J*=4.0Hz), 7.31(1H, s), 7.27(1H, dd, *J*=7.6, 7.2Hz), 7.24(1H, dd, *J*=8.4, 2.0Hz), 7.21(1H, d, *J*=4.0Hz), 7.13(1H, d, *J*=3.6Hz), 7.00(1H, d, *J*=8.4Hz), 4.93-4.89 (1H, m), 3.91-3.86(1H, m), 2.16-2.07(1H, m), 2.04-1.84(1H, m), 1.75-1.67(1H, m), 1.65-1.57(1H, m), 1.51(3H, s), 1.50(3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ= 182.3, 155.0, 153.3, 148.0, 147.9, 147.7, 141.9, 140.9, 139.1, 137.5, 136.0, 133.5, 132.7, 127.3, 127.0, 126.4, 125.5, 124.1, 123.3, 122.5, 122.4, 121.9, 120.7, 119.3, 118.8, 114.1, 108.0, 69.5, 46.9, 45.3, 35.0, 33.8, 27.4, 27.2, 24.5.

Synthesis of 2-((4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)methylene)-1,3-dioxo-2,3-dihydro-1*H*-indene-5-carboxylic acid, DN458



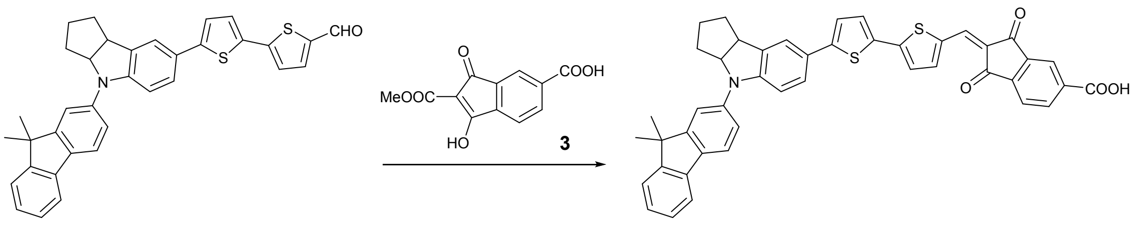
A solution of **2** (0.76 g, 2.0 mmol) in acetic acid (5.0 mL) was added **3** (496 mg, 2.0 mmol). The mixture was stirred at 100 °C for 4 h. After cooling to room temperature, the precipitate was filtrated, washed with MeOH, and dried in *vacuo* and purified by silica gel column chromatography ($CHCl_3$- MeOH = 100 : 1 → 50 : 1) to give **DN458** (0.86 g, 1.46 mmol, 73%) as a black solid: ^{1}H-NMR (400 MHz, DMSO-*d6*) δ= 13.63(1H, br. s), 8.72(1H, br.s), 8.35(1H, d, *J*=8.0Hz), 8.28(1H, br.s), 8.25(1H, d, *J*=11.6Hz), 7.95(1H, dd, *J*=8.0, 7.6Hz), 7.90(1H, d, *J*=8.4Hz), 7.83(1H, d, *J*=7.2Hz), 7.69(1H ,s), 7.67(1H, d, *J*=1.6Hz), 7.56(1H, d, *J*=7.2Hz), 7.41(1H, dd, *J*=8.0, 1.2Hz), 7.36(1H, dd, *J*=8.0, 7.2Hz), 7.32(1H, dd, *J*=8.4, 7.2Hz), 6.87(1H, d, *J*=8.4Hz), 5.27-5.24(1H, m), 3.94-3.90(1H, m), 2.18-2.08(1H, m), 1.88-1.74(3H, m), 1.73-1.64(1H, m), 1.50(3H, s), 1.47(3H, s), 1.53-1.37(1H, m); ^{13}C-NMR (100 MHz,DMSO-*d6*) *δ*= 189.8, 188.2, 166.2, 155.0, 153.8, 153.4, 146.9, 144.3, 141.7, 140.0, 139.2, 138.7, 138.0, 136.3, 136.2, 135.6, 135.4, 131.4, 127.2, 127.2, 124.2, 122.8, 122.5, 121.7, 121.4, 121.2, 120.0, 117.0, 106.9, 70.1, 46.7, 43.7, 35.2, 32.4, 26.9, 26.7, 23.8; HRMS (ESI, *m/z*, [M+H]$^+$) Calcd For $C_{37}H_{30}NO_4$: 552.2175. Found: 552.2170.

Synthesis of 2-((5-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-7-yl)thiophen-2-yl)methylene)-1,3-dioxo-2,3-dihydro-1*H*-indene-5-carboxylic acid, DN475



A solution of **6** (0.69 g, 1.5 mmol) in acetic acid (10 mL) was added **3** (372 mg, 1.5 mmol). The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, the precipitate was filtrated, washed with MeOH, and dried in *vacuo* and purified by silica gel column chromatography ($CHCl_3$- MeOH = 100 : 1 → 50 : 1) to give **DN475** (0.68 g, 1.07 mmol, 71%) as a glossy black solid: ^{1}H-NMR (400 MHz, DMSO-*d6*) *δ*= 13.66(1H, br.s), 8.35(1H, d, *J*=8.0Hz), 8.25(1H, br.s), 8.24(1H, d, J=8.4Hz), 8.20(1H, d, *J*=4.4Hz), 7.98(1H, s), 7.94（1H, d, *J*=8.0Hz), 7.81(1H, d, *J*=8.4Hz), 7.76(1H, d, *J*=7.2Hz), 7.63-7.62(1H, m), 7.62(1H, s), 7.61-7.58(1H, m), 7.54(1H, s), 7.53(1H, d, *J*=6.8Hz), 7.33(1H, dd, *J*=8.0, 6.8Hz), 7.28(1H, dd, *J*=7.6, 6.4Hz), 6.98(1H, dd, *J*=8.4, 8.4Hz), 5.07-5.04(1H, m), 3.91-3.86(1H, m), 2.16-2.05(1H, m), 1.92-1.73(3H, m), 1.70-1.60(1H, m), 1.48(3H, s), 1.47(3H, s), 1.52-1.37(1H, m); ^{13}C-NMR (100 MHz,DMSO-*d6*) δ= 188.9, 188.2, 166.0, 159.6, 154.8, 153.1, 149.0, 147.1, 143.9, 142.5, 141.3, 140.6, 139.8, 138.4, 136.5, 136.3, 135.6, 133.8, 133.3, 127.1, 127.0, 126.6, 123.6, 122.9, 122.6, 122.6, 122.4, 121.3, 120.9, 119.5, 119.1, 114.6, 107.6, 68.8, 46.6, 44.3, 34.9, 32.9, 27.0, 26.8, 24.0; HRMS (ESI, *m/z*, $[M+H]^+$) Calcd For $C_{41}H_{32}NO_4S$: 634.2052. Found: 634.2050.

Synthesis of 2-((5'-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydro-cyclopenta[*b*]indol-7-yl)-2,2'-bithiophen-5-yl)methylene)-1,3-dioxo-2,3-dihy-dro-1*H*-indene-5-carboxylic acid, DN484



8

DN484

A solution of **8** (0.54 g, 1.0 mmol) in acetic acid (10 mL) was added **3** (248 mg, 1.0 mmol). The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, the precipitate was filtrated, washed with MeOH, and dried in *vacuo* and purified by silica gel column chromatography ($CHCl_3$- MeOH = 100 : 1 → 50 : 1 → 30 : 1) to give **DN484** (0.49 g, 0.69 mmol, 69%) as a glossy black solid: ^{1}H-NMR (400 MHz, DMSO-*d6*) δ= 13.58(1H, br.s), 8.27(1H, dd, *J*=10.0, 8.4Hz), 8.18(1H, d, *J*=14.8Hz), 8.08(1H, d, *J*=3.6Hz), 7.90(1H, s), 7.87（1H, dd, *J*=7.2, 7.2Hz), 7.73(1H, d, *J*=8.4Hz), 7.69(1H, d, *J*=7.2Hz), 7.53(1H, dd, *J*=4.0, 4.0Hz), 7.49(1H, d, *J*=7.2Hz), 7.45(1H, s), 7.44(1H, d, *J*=5.6Hz), 7.40(1H, s), 7.33-7.21(5H, m), 6.90(1H, d, *J*=8.0Hz), 4.94-4.91(1H, m), 3.81-3.77(1H, m), 2.09-2.00(1H, m), 1.91-1.71(3H, m), 1.66-1.57(1H, m), 1.44(6H, s), 1.47-

1.34(1H, m); ^{13}C-NMR (100 MHz,DMSO-*d6*) δ= 188.6, 188.1, 165.9, 154.7, 153.0, 150.7, 147.6, 147.2, 146.3, 143.8, 142.4, 141.2, 141.1, 139.7, 138.5, 136.4, 135.9, 135.5, 134.8, 132.5, 132.0, 128.9, 127.0, 126.3, 125.4, 124.7, 123.3, 122.9, 122.6, 122.5, 122.1, 122.0, 120.8, 119.3, 118.2, 113.6, 107.6, 68.5, 46.5, 44.5, 34.6, 33.1, 27.0, 26.8, 24.1; HRMS (ESI, *m/z*, [M+H]$^+$) Calcd For $C_{45}H_{34}NO_4S_2$: 716.1929. Found: 716.1927.

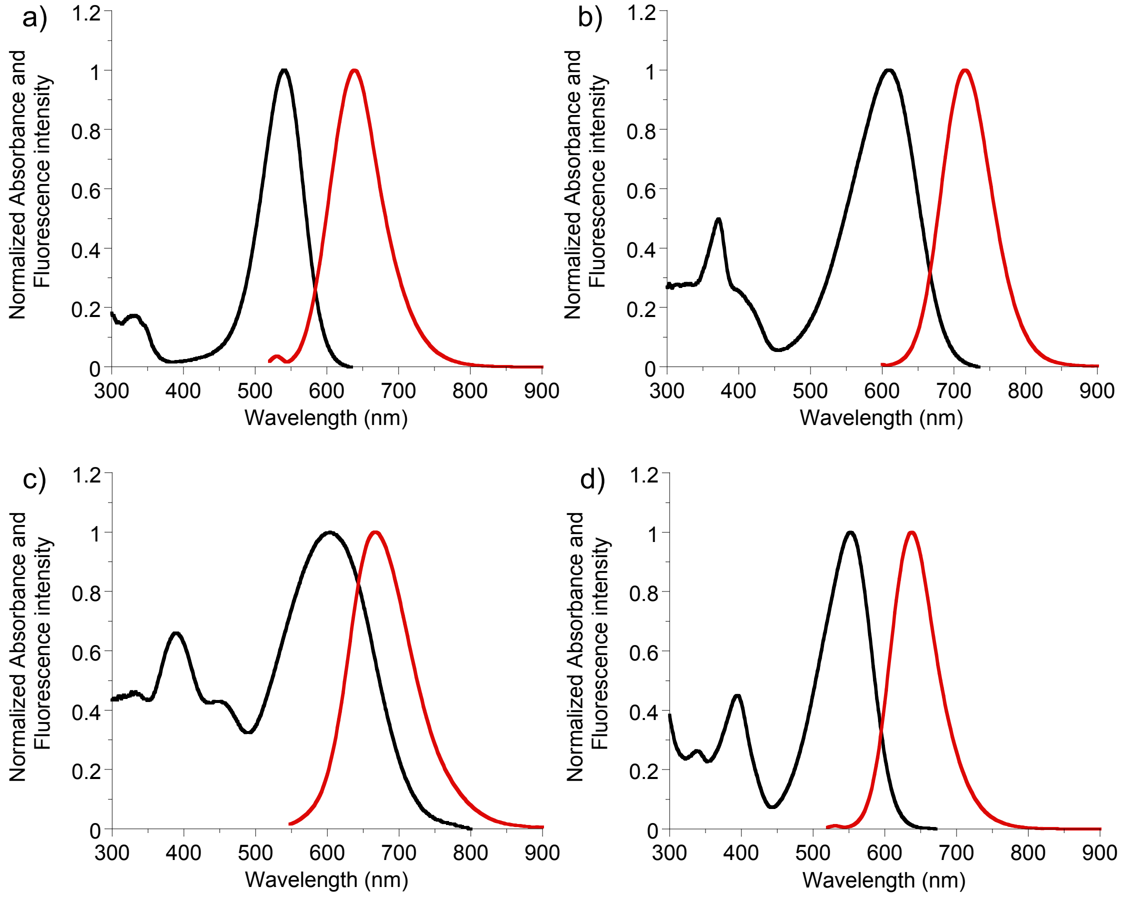


Fig. S1 Normalized absorption and Fluorescence spectra of (a) **DN458**, (b) **DN475**, (c) **DN484** and (d) **D205** in chloroform.

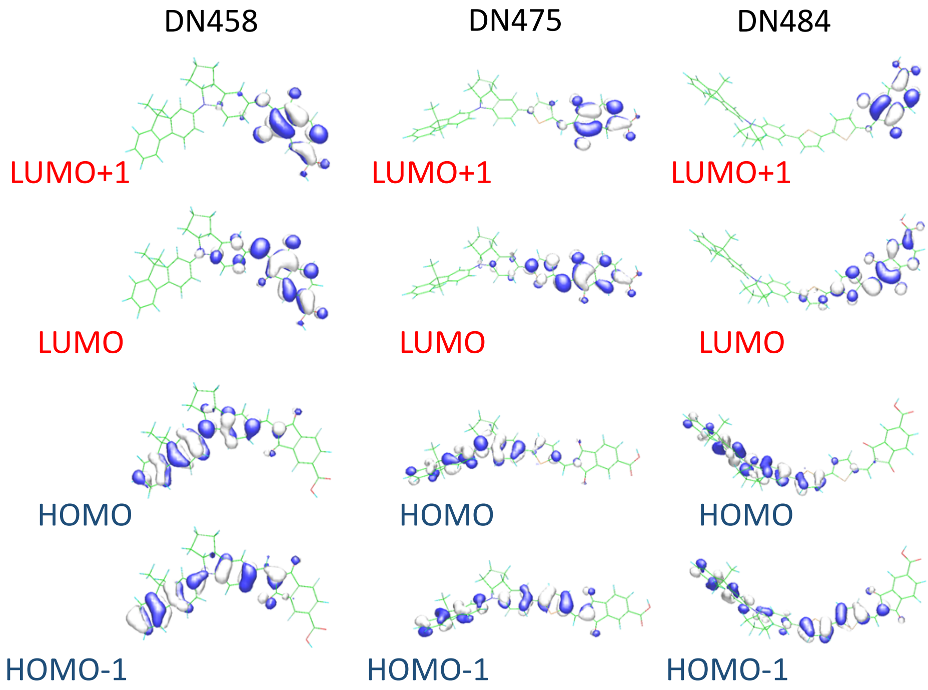


Fig. S2 Frontier molecular orbitals of **DN458**, **DN475** and **DN484** calculated by DFT/B3LYP/6-31+G*.

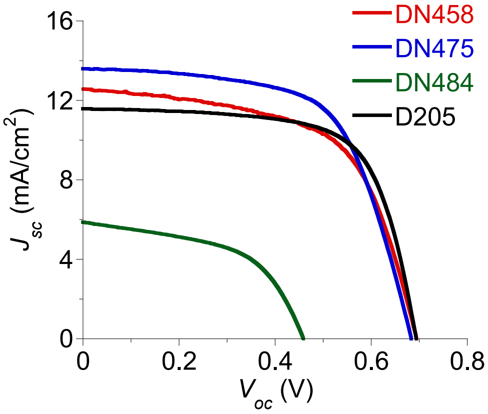


Fig. S3 J-V curves of the PDSCs based on **DN458**, **DN475**, **DN484** and **D205**.

References

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