

Supporting Information

Novel TPD-based organic D- π -A dyes for dye-sensitized solar cells

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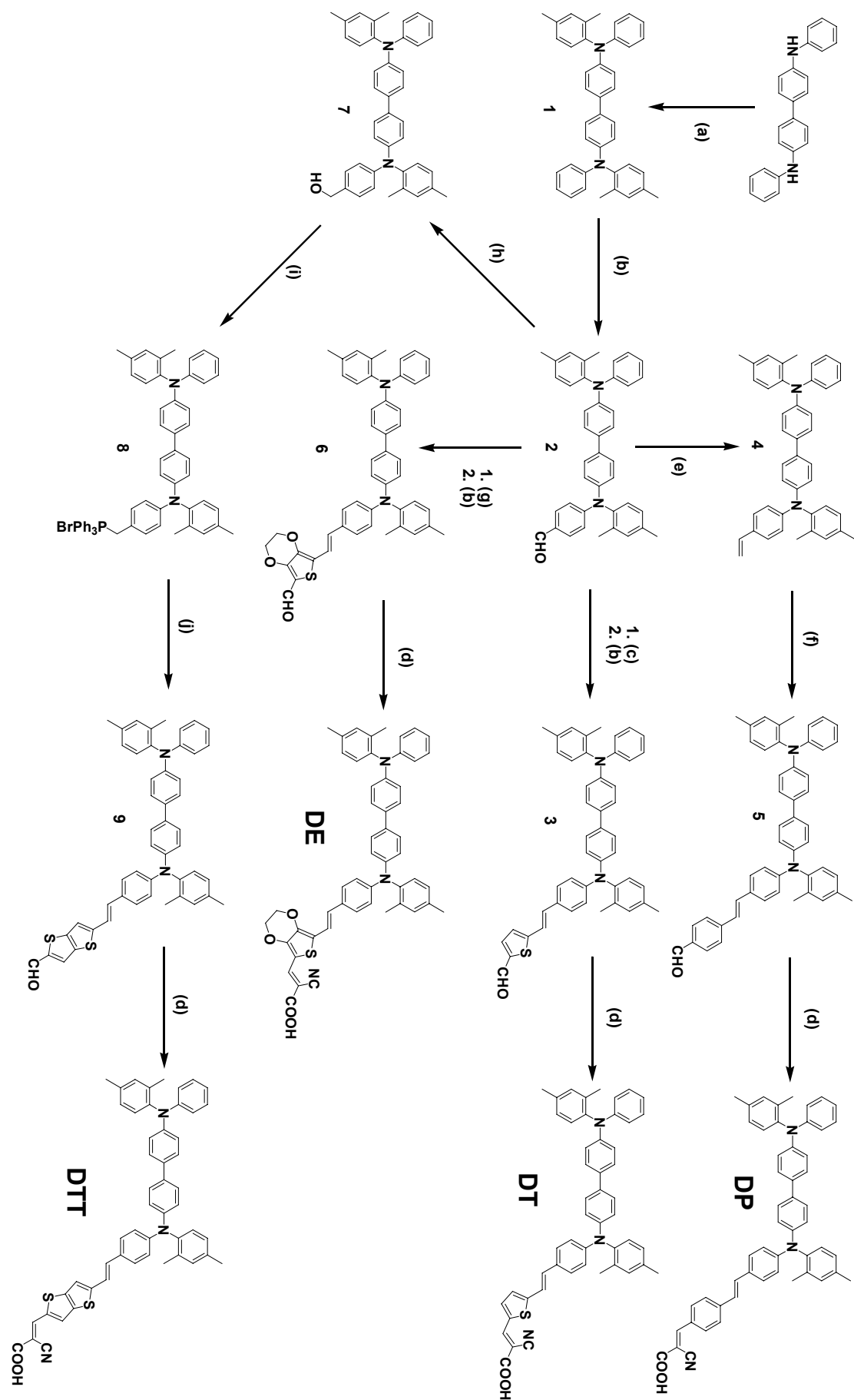
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General procedures

All reactions were performed under N₂ atmosphere. Solvents were distilled from appropriate drying agents prior to use, and other common reagents were obtained from commercial sources and used without further purification. *N,N'*-Diphenylbenzidine, 4-iodo-*m*-xylene, potassium *tert*-butoxide, 18-crown-6 ether, piperidine, cyanoacetic acid, tetrabutylammonium hexafluorophosphate, deoxychenocholic acid (DCA), Triton X-100, 4-*tert*-butylpyridine (TBP) are commercially available and used as received. The N3 dye was purchased from Solaronix Company. Thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde¹ was synthesized according to the literature. ¹H NMR spectra were obtained on a Bruker Advance DPS-400 or 300 spectrometer using tetramethylsilane as internal standard. EI-MS spectra were recorded on a Micromass GCT-MS spectrometer. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. UV-vis spectra of the dyes in THF solutions were recorded in a quartz cell with 1 cm path length on an HP-8453 spectrometer. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV₂₅₄). All chromatographic separations were carried out on silica gel (200–300 mesh).

1. Synthesis of materials

A general picture for the synthesis of the four TPD-based organic dyes is presented in Scheme S1. The detailed procedures are followed.



Scheme S1. Synthetic routes to the TPD-based organic dyes. *Reagents and conditions:* (a) Cu/K₂CO₃/18-Crown-6 ether, 1,2-dichlorobenzene, 190°C. (b) DMF/POCl₃, ClCH₂CH₂Cl, reflux. (c) THF/*t*-BuOK, 2-thienylmethyl triphenylphosphonium bromide, rt. (d) CNCH₂COOH, Piperidine, MeCN, reflux. (e) THF/*t*-BuOK, CH₃PPh₃I, rt. (f) DMF/Et₃N, Pd(PPh₃)₄/P(*o*-tolyl)₃, 4-bromobenzaldehyde, reflux. (g) THF/*t*-BuOK, 3,4-ethylenedioxy-2-thienylmethyl triphenylphosphonium bromide, rt. (h) NaBH₄/THF/EtOH, rt. (i) CH₃Cl/PPh₃•HBr, reflux. (j) DMF/K₂CO₃/18-Crown-6 ether, thieno[3,2-*b*]thiophene-2,5-dicarbaldehyde, rt; I₂/THF, reflux.

***N,N'*-bis(2,4-dimethylphenyl)-*N,N'*-diphenylbenzidine (TPD) (1)**

To a solution of *N,N'*-diphenylbenzidine (3.5 g, 10.4 mmol) and 4-iodo-*m*-xylene (6.96 g, 30 mmol) in *o*-dichlorobenzene (50 mL) was added copper (7.0 g, 109.4 mmol), K₂CO₃ (15 g, 108 mmol) and 18-crown-6 (100 mg) at room temperature, and the resultant mixture was stirred at 190°C for 24 h. Then inorganic solids were removed by filtration. These solids were washed with THF four times. After removal of solvent, the crude product was purified by column chromatography on silica gel using toluene–hexane (7:3) as eluent to yield the pure product **1** as a white powder (4.8 g, 85 %). Mp: 130–132 °C. ¹H NMR (400 MHz, *d*₆-DMSO): δ 1.98 (s, 6H), 2.29 (s, 6H), 6.83–6.93 (m, 10H), 6.98 (d, 2H, *J* = 7.9 Hz), 7.07 (d, 2H, *J* = 7.9 Hz), 7.13 (s, 2H), 7.23 (t, 4H, *J* = 7.5 Hz), 7.46 (d, 4H, *J* = 7.8 Hz). MS-EI: *m/z* 544 (M⁺).

TPD-carbaldehyde (2)

POCl₃ (3.07 g, 20 mmol) was added dropwise with stirring to a solution of dried 1,2-dichloroethane (20 mL) and anhydrous DMF (1.46 g, 20 mmol) at 0–5 °C. After stirring for 20 min, a solution of TPD (**1**) (10.6 g, 19.4 mmol) in 1,2-dichloroethane (40 mL) was added slowly whereupon the mixture was heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) with stirring for 2 h, and then extracted with CH₂Cl₂ (100 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄. Solvents were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with CH₂Cl₂–petroleum ether (1:2) as eluent to yield the product **2** as a yellow solid (5.35 g, 48%). ¹H NMR (300 MHz, CDCl₃): δ 2.02 (s, 3H), 2.05 (s, 3H), 2.34 (s, 3H), 2.36 (s, 3H), 6.90–7.23 (m, 17H), 7.40 (d, 2H, *J* = 8.7 Hz), 7.48 (d, 2H, *J* = 8.7 Hz), 7.67 (d, 2H, *J* = 8.7 Hz), 9.78 (s, 1H). MS-EI: *m/z* 572 (M⁺).

5-(TPD-vinyl)thiophene-2-carbaldehyde (3)

2-Thienylmethyl triphenylphosphonium bromide (0.87 g, 2 mmol) and **2** (0.8 g, 1.39 mmol) were dispersed in anhydrous THF (30 mL) and stirred at ambient temperature for 10 min. *t*-BuOK (0.36 g, 3 mmol) was dissolved in anhydrous THF and added dropwise to the solution, and then the mixture was stirred overnight at ambient temperature. Then 20 mL of water was added, and the mixture was extracted with CH₂Cl₂ (50 mL × 3). The combined extract was dried over anhydrous Na₂SO₄ and filtered. Purification by column chromatography over silica gel with CH₂Cl₂–petroleum ether (1:8) as eluent yielded a yellow solid (0.5 g). Then the solid was dissolved in anhydrous CH₂Cl₂ (20 mL) and anhydrous DMF (0.47 g, 6.35 mmol)

at 0–5 °C. POCl₃ (0.168 g, 1.09 mmol) was added dropwise with stirring to the solution. Then the mixture was heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) and stirred for 2 h, and extracted with CH₂Cl₂ (50 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄. Solvents were removed and the residue was purified by silica-gel column chromatography with CH₂Cl₂–petroleum ether (1:1) as eluent to yield **3** (0.25 g, 27%). ¹H NMR (300 MHz, CDCl₃): δ 2.02 (s, 6H), 2.34 (s, 3H), 2.35 (s, 3H), 6.92 (d, 2H, *J* = 8.5 Hz), 6.98–7.23 (m, 17H), 7.32 (d, 2H, *J* = 8.6 Hz), 7.40 (m, 5H) 7.63 (d, 1H, *J* = 3.8 Hz), 9.82 (s, 1H). MS-EI: *m/z* 680 (M⁺).

2-cyano-3-[5-(TPD-vinyl)thienyl]acrylic acid (DT).

An acetonitrile (30 mL) solution of **3** (0.15 g, 0.22 mmol) and cyanoacetic acid (0.05 g, 0.66 mmol) was refluxed in the presence of piperidine (0.1 mL) for 6 h. Solvent removal by rotary evaporation followed by purification by column chromatography over silica gel with a CH₂Cl₂–acetic acid (50:1) yielded the product **DT** as a purple solid (0.15 g, 91%). Mp: 205–210 °C. ¹H NMR (400 MHz, *d*₆-DMSO): δ 2.02 (s, 3H), 2.03 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 6.82 (d, 2H, *J* = 8.4 Hz), 6.83–7.26 (m, 15H), 7.19 (d, 1H, *J* = 16.5 Hz), 7.37 (d, 1H, *J* = 16.0 Hz), 7.38 (d, 1H, *J* = 3.8 Hz), 7.49 (d, 2H, *J* = 8.9 Hz), 7.51–7.54 (m, 4H), 7.90 (d, 1H, *J* = 3.6 Hz), 8.42 (s, 1H). MALDI-TOF: *m/z* 747.5 (M⁺).

***N,N'*-bis(2,4-dimethylphenyl)-*N*-phenyl-*N'*-(4-vinylphenyl)benzidine (TPD-vinyl) (**4**)**

Methyltriphenylphosphonium iodide (1.12 g, 2.78 mmol) and **2** (0.8 g, 1.39 mmol) were dispersed in anhydrous THF (30 mL) and stirred at ambient temperature for 10 min. *t*-BuOK (0.31 g, 2.78 mmol) dissolved in anhydrous THF was added dropwise to the mixture and then the reaction mixture was stirred for 4 h. 20 mL of water was added. The mixture was extracted with CH₂Cl₂ (50 ml × 3), and the combined extract was dried over anhydrous Na₂SO₄. Solvent removal by rotary evaporation followed by column chromatography over silica gel with CH₂Cl₂–petroleum ether (1:7) as eluent, yielded **4** as a white solid (0.45 g, 56%). ¹H NMR (300 MHz, *d*₆-DMSO): δ 1.96 (s, 6H), 2.29 (s, 6H), 5.10 (d, 1H, *J* = 11.0 Hz), 5.65 (s, 1H, *J* = 17.0 Hz), 6.62 (t, 1H, *J*₁ = 17.0 Hz, *J*₂ = 11.0 Hz), 6.83 (d, 2H, *J* = 8.3 Hz), 6.86–6.94 (m, 7H), 6.98 (d, 2H, *J* = 7.9 Hz), 7.07 (d, 2H, *J* = 7.9 Hz), 7.14 (s, 2H), 7.23 (t, 2H, *J*₁ = 7.9 Hz, *J*₂ = 7.3 Hz), 7.32 (d, 2H, *J* = 8.3 Hz), 7.45–7.48 (m, 4H). MS-EI: *m/z* 570 (M⁺).

4-(TPD-vinyl)benzaldehyde (5**)**

A DMF (10 mL) solution of **4** (0.25g, 0.438 mmol), 4-bromobenzaldehyde (0.1 g, 0.54 mmol), triethylamine (0.3 mL), Pd(PPh₃)₄ (20 mg, 0.016 mmol) and P(*o*-tolyl)₃ (10 mg, 0.032 mmol) was stirred at reflux for 24 h. After cooling, the solution was poured into 100 mL of water and the mixture extracted with CH₂Cl₂ (20 mL × 3), the organic phase was removed by rotary evaporation to give the crude product. Then the solid was purified by column chromatography using silica gel and CH₂Cl₂–petroleum ether (1:2) as eluent gave the pure **5** as a dark yellow solid (0.12 g, 34%). ¹H NMR (400 MHz, CDCl₃): δ 2.02 (s, 3H), 2.03 (s, 3H), 2.34 (s, 3H), 2.35 (s, 3H), 6.89–7.08

(m, 16H), 7.17–7.21(m, 3H), 7.36–7.42 (m, 6H), 7.60 (d, 2H, $J = 8.0$ Hz), 7.83 (d, 2H, $J = 8.0$ Hz), 9.96 (s, 1H). MS-EI: m/z 674 (M^+).

2-cyano-3-[4-(TPD-vinyl)phenyl]acrylic acid (DP)

An acetonitrile (30 mL) solution of **5** (0.4 g, 0.59 mmol) and cyanoacetic acid (0.1 g, 1.17 mmol) was refluxed in the presence of piperidine (0.25 ml, 2.5 mmol) overnight. Solvent removal by rotary evaporation followed by purification by column chromatography over silica gel with a CH_2Cl_2 –acetic acid (50:1) yielded the product **DP** as a red solid (0.18 g, 41%). Mp: 275–280 °C. ^1H NMR (300 MHz, d_6 -DMSO) : δ 1.97 (s, 3H), 1.98 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 6.84–7.27 (m, 18H), 7.47–7.52 (m, 6H), 7.38 (d, 1H, $J = 16.5$ Hz), 7.71 (d, 2H, $J = 8.1$ Hz), 7.97 (s, 2H, $J = 8.1$ Hz), 8.16 (s, 1H). MALDI-TOF: m/z 741.6 (M^+).

3,4-ethylenedioxy-5-(TPD-vinyl)thiophene-2-carbaldehyde (6)

(3,4-Ethylenedioxy-2-thienylmethyl)triphenylphosphonium bromide (1.0 g, 2 mmol) and **2** (0.8 g, 1.39 mmol) were dispersed in anhydrous THF (30 ml) and stirred at ambient temperature for 10 min. *t*-BuOK (0.34 g, 3 mmol) dissolved in anhydrous THF was added dropwise to the solution, with being stirred 6 h at ambient temperature. Then 20 mL water was added, followed by extraction with CH_2Cl_2 (50 mL \times 3). The combined extracts were dried over anhydrous Na_2SO_4 and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel with a mixture of CH_2Cl_2 –petroleum (1:4) as eluent yielded a yellow intermediate compound (0.5 g). The intermediate compound was dissolved in anhydrous CH_2Cl_2 (20 mL) containing anhydrous DMF (0.5 g, 7.71 mmol). POCl_3 (0.168 g, 1.09 mmol) was added dropwise with stirring at 0–5 °C. After stirring for 20 min, the mixture was heated to reflux for 12 h. After cooling to room temperature, the reaction mixture was poured into an aqueous solution of sodium acetate (1 M, 200 mL) and stirred for 2 h, and then extracted with CH_2Cl_2 (50 mL \times 3). The combined organic phases were dried over anhydrous Na_2SO_4 . Solvents were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with CH_2Cl_2 –petroleum ether (2:1) as eluent to yield **6** as a yellow solid (0.41 g, 40%). ^1H NMR (300 MHz, CDCl_3): δ 2.01 (s, 6H), 2.34 (s, 3H), 2.35 (s, 3H), 4.33–4.37 (m, 4H), 6.91 (d, 2H, $J = 8.3$ Hz), 6.92–7.08 (m, 15H), 7.20 (t, 2H, $J = 7.5$ Hz), 7.31 (d, 2H, $J = 8.1$ Hz), 7.36–7.42 (m, 4H), 9.86 (s, 1H). MS-EI: m/z 738 (M^+).

2-cyano-3-[3,4-ethylenedioxy-5-(TPD-vinyl)thienyl]acrylic acid (DE)

An acetonitrile (30 mL) solution of **6** (0.18 g, 0.24 mmol) and cyanoacetic acid (0.05 g, 0.66 mmol) was refluxed in the presence of piperidine (0.1 mL) overnight. Solvent removal by rotary evaporation followed by purification by column chromatography over silica gel with a CH_2Cl_2 –acetic acid (100:1) yielded the product **DE** as a purple solid (0.15 g, 77%). Mp: 215–217 °C. ^1H NMR (400 MHz, d_6 -DMSO): δ 1.97 (s, 6H), 2.30(s, 6H), 4.41–4.47 (m, 4H), 6.76 (d, 2H, $J = 8.32$ Hz), 6.87–6.95 (m, 5H), 6.99–7.07 (m, 4H), 7.09–7.16 (m, 6H), 7.24 (s, 1H), 7.25 (d, 1H, $J = 15.3$ Hz), 7.48–7.53 (m, 6H), 8.16 (s, 1H). MALDI-TOF: m/z 805.5 (M^+).

TPD-methanol (7)

To a solution of **2** (1.0 g, 1.74 mmol) in THF (30 mL) and anhydrous ethanol (10 mL)

was added slowly a solution of NaBH₄ (0.16 g, 4.2 mmol) in NaOH aq (10%), and the mixture was stirred at room temperature for 2 h. Then the solution mixture was poured into 100 mL of water with vigorously stirring, and extracted with CH₂Cl₂ (50 mL × 3). The organic layer was dried with anhydrous Na₂SO₄ and then rotary evaporated to remove the solvent to give a white solid product **7** (0.96 g, 96%). ¹H NMR (300 MHz, *d*₆-DMSO): δ 1.96 (s, 6H), 2.29 (s, 6H), 3.6 (s, 1H), 4.41 (s, 2H), 6.82–6.98 (m, 9H), 7.04–7.12 (m, 5H), 7.18–7.24 (m, 4H), 7.42–7.45 (m, 5H). MS-EI: *m/z* 574 (M⁺).

(TPD-methyl)triphenylphosphonium bromide (8)

Compound **7** (0.96 g, 1.67 mmol) and PPh₃•HBr (0.68 g, 2 mmol) was dissolved in chloroform (20 mL) and refluxed for 3 h. After removing the solvent, the residue was solidified with diethyl ether and filtrated to obtain the product **8** as a white solid (1.47 g, 98 %). MS-EI: *m/z* 898 (M⁺).

5-(TPD-vinyl)thieno[3,2-b]thiophene-2-carbaldehyde (9)

Thieno[3,2-b]thiophene-2,5-dicarbaldehyde (0.196 g, 1 mmol), anhydrous K₂CO₃ (0.276 g, 2 mmol), 18-crown-6 ether (15 mg) were charged sequentially in a three-necked flask and then dried in vacuo for 30 min. Dried DMF (40 mL) was added. Then a solution of **8** (0.95 g, 1 mmol) in dried DMF (10 mL) was added dropwise to the above solution with stirring. The mixture was stirred for another 3 h at ambient temperature and then poured into ice–water (200 g), leading to a precipitate of yellow solids. The precipitate was filtered off and the dried solid was dissolved in 20 mL of anhydrous THF to reflux in the presence of iodine (10 mg) for 6 h. The mixture was added to a dilute solution of sodium hydroxide to remove iodine, extracted with CH₂Cl₂ and dried with anhydrous Na₂SO₄. Then purified by silica-gel column chromatography with CH₂Cl₂–petroleum ether (1:1) as eluent to yield the product **9** as a yellow solid (0.4 g, 54%). ¹H NMR (300 MHz, CDCl₃): δ 2.02 (s, 6H), 2.34 (s, 3H), 2.35 (s, 3H), 6.88–7.12 (m, 17H), 7.18–7.23 (m, 3H), 7.31–7.43 (m, 6H), 7.83 (s, 1H), 9.91 (s, 1H). MS-EI: *m/z* 736 (M⁺).

2-cyano-3-[5-(TPD-vinyl)thieno[3,2-b]thienyl]acrylic acid (DTT)

An acetonitrile (30 mL) solution of **9** (0.3 g, 0.41 mmol) and cyanoacetic acid (0.15 g, 1.98 mmol) was refluxed in the presence of piperidine (0.2 mL) overnight. Solvent removal by rotary evaporatory followed by purification by column chromatography over silica gel with a CH₂Cl₂–acetic acid (50:1) yielded the product **DTT** as a purple solid (0.18 g, 56%). Mp: 220–225 °C. ¹H NMR (400 MHz, *d*₆-DMSO): δ 1.93 (s, 3H), 1.96 (s, 3H), 2.29 (s, 3H), 2.30 (s, 3H), 6.81 (d, 2H, *J* = 8.6 Hz), 6.86–7.09 (m, 12H), 7.13 (d, 2H, *J* = 8.2 Hz), 7.21–7.25 (m, 2H), 7.38 (d, 1H, *J* = 16 Hz), 7.46–7.51 (m, 6H), 7.59 (s, 1H), 8.23 (s, 1H), 8.52 (s, 1H). MALDI-TOF: *m/z* 803.4 (M⁺).

2. Fabrication of the dye-sensitized nanocrystalline TiO₂ electrodes

For fabrication of the devices, two layers of TiO₂, main layer and scattering layer, were prepared by screen-printing TiO₂ pastes on FTO glass substrate (10 Ω/sq, Nippon Sheet Glass). The main layer (thickness: 6 μm; TiO₂ particle size: 18 nm) and scattering layer (thickness: 3 μm; TiO₂ particle size: 400 nm) were prepared from

these two different TiO₂ colloids (PST-18NR and PST-400C from Catalysts & Chemicals Ind. Co., Ltd, CCIC in Japan). After screen-printing, the TiO₂ film was heated at 500 °C for 30 minutes, and treated with 0.04 M TiCl₄ aqueous solution as reported by Ito.² The four dyes and N3 solutions were prepared in THF at a concentration of 0.5 mM; 3 mM of chenodeoxy cholic acid in *tert*-butyl alcohol/acetonitrile (1:1, v/v) was added as reported in order to effectively prevent unfavorable dye aggregation on the TiO₂ surface.³ The TiO₂ films were left in the solution at room temperature for 12 h. A Pt-sputtered FTO glass was used as a counter electrode. The electrolyte was composed of 0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.05 M I₂, and 0.75 M 4-*tert*-butylpyridine in a co-solvent of acetonitrile and valeronitrile (1:1, v/v). Afterwards, the dye-sensitized TiO₂ electrode was rinsed with absolute ethanol and dried in air.

3. Photovoltaic measurements

The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were performed by using a commercial setup for IPCE measurement (PV-25 DYE, JASCO) under 5 mW/cm² monochromic light illumination. The irradiation source for the photocurrent–voltage (J–V) measurement is an AM 1.5 solar simulator (YSS-50A, Yamashita Denso Co. Ltd.). A 500-W Xe lamp serves as the light source in combination with a band-pass filter (400–800 nm) to remove the ultraviolet and infrared light and to give a light power of 100 mW/cm². The current–voltage curves were obtained by a linear sweep voltammetry method using an electrochemical workstation using a PC-controlled voltage–current source meter (R6246, Advantest) under a solar simulator illumination (Yamashita Denso, Yss-80) of Air Mass 1.5 (100 mW/cm²) conditions at 25 °C. The active electrode area was 0.2 cm².

4. Molecular Orbital Calculation

All calculations were performed on the Gaussian 03 program package by using Density Functional Theory (DFT).⁴ B3LYP and the 6-31 G (D) basis set were used. Before optimizing ground state geometries by B3LYP/6-31G(D), the molecular structures were initially optimized in a HF/ST0-3G calculation method. All the geometries and electronic properties were calculated by assuming that the target molecules would be isolated in gas phase.

5. Emission spectra of TPD dyes.

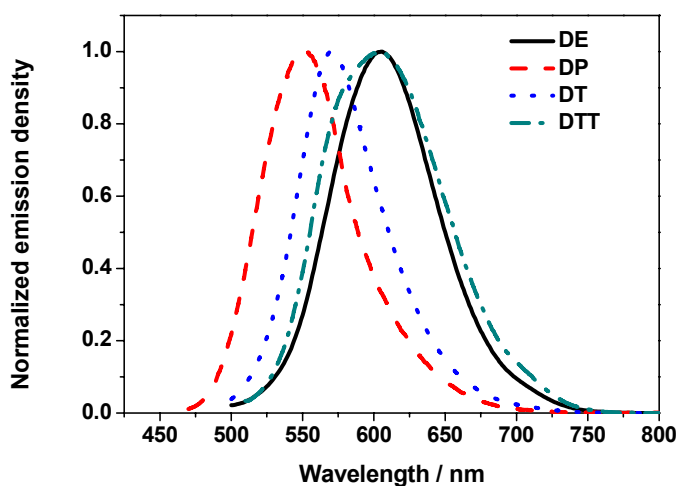


Figure S1. Normalized emission spectra of the as-synthesized dyes in THF solutions.

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