

Functionalizing Organic Dye with Cross-linked Electrolyte-blocking Shell as a New Strategy for Improving DSSC Efficiency

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Electronic Supplementary Information

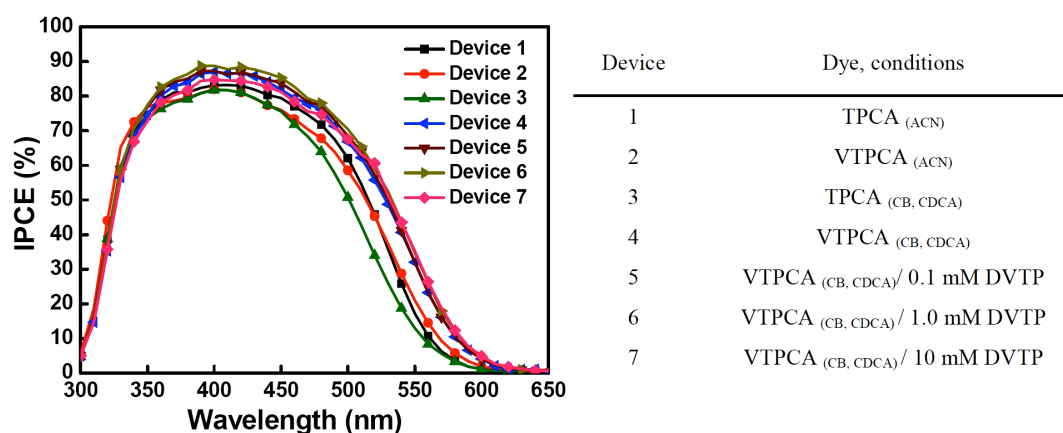


Fig. S1 IPCE spectra of various devices in this report.

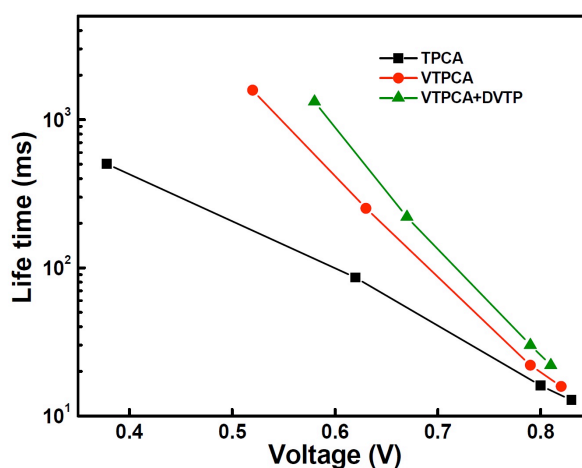


Fig. S2 The semilogarithmic plot of electron lifetime of device 3 (TPCA), device 4 (cross-linked VTPCA), and device 5 (cross-linked VTPCA+DVTP) under different V_{oc} conditions. All of three devices gain higher V_{oc} from new TiO_2 paste (Solaronix, T, 15-20 nm, 20 nm) because original TiO_2 paste (Solaronix, T20) was unavailable.

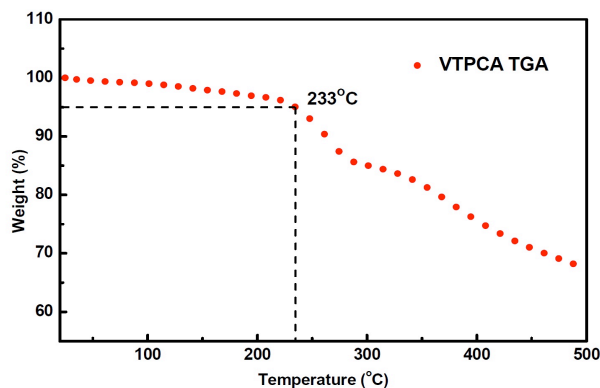


Fig. S3 The thermogravimetric analysis of VTPCA.

Experimental

Fabrication of dye-sensitized solar cells

The TiO₂ working electrode of DSSCs was composed of a 12- μ m-thick 20-nm anatase TiO₂ nanoparticle layer and a 4- μ m-thick 400-nm anatase TiO₂ light scattering layer on FTO glass plates, coated by doctor-blading. The nanoporous TiO₂ electrodes were then heated at temperatures ramping from 150 °C to 500 °C. After cooling, the nanoporous TiO₂ electrodes were immersed into the 0.5 mM dye solution in acetonitrile or into the 0.5 mM dye + 0.5 mM chenodeoxycholic acid solution in chlorobenzene at room temperature for 24 hours. 40-nm-thick Pt films on the FTO glass plates deposited by e-beam evaporation were used as counter electrodes. For cross-linkable dyes, dye-loaded TiO₂ electrodes were heated at 150 °C for 20 min for thermal polymerization before cell assembly. The electrolyte solution used (0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M LiI, 0.03 M I₂, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate) in a mixture of acetonitrile–valeronitrile (85:15, v/v). A mask with an aperture area of 0.125 cm² was placed on the cell during photovoltaic measurements.

Repair Modification of dye-loaded TiO₂ films

For the devices being subjected to “repair modification”, after the dye adsorption step, the dye-loaded TiO₂ films were dipped in the DVTP (4,4'-divinyltriphenylamine) solutions for 30 min, followed by heating at 150 °C for 20 min for the thermal polymerization reaction. The concentrations of the DVTP solutions in cyclohexane were 0.1, 1.0, and 10 mM.

Photocurrent-voltage Measurement

The photocurrent-voltage characteristics of the DSSCs were measured under illumination of AM1.5G solar light from a 300-W xenon lamp solar simulator. The incident light intensity was calibrated as 100 mW/cm². Photocurrent-voltage curves were obtained by applying an external bias voltage to the cell and measuring the generated photocurrent.

Electrochemical Impedance Spectroscopy Measurement

The electrochemical impedance spectroscopy (EIS) of the cells was measured by using an impedance analyzer with a frequency range of 20 Hz to 1 MHz. In this study, during the impedance measurement, the cell was under the constant AM 1.5G 100 mW/cm² illumination. The impedance of the cell (throughout the frequency range of 20 Hz to 1MHz) was then measured by applying a bias at the open-circuit voltage V_{OC} of the cell (namely, under the condition of no dc electric current) and by using an ac amplitude of 10 mV.

Synthesis

All reactions were performed under argon and were magnetically stirred unless otherwise stated. Solvents were distilled from appropriate drying agent prior to use: THF and Et₂O from sodium and benzophenone, toluene and CH₂Cl₂ from P₂O₅. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated aluminum foil sheets (0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV light at 254 nm and 365 nm. Column chromatography was carried out using flash silica gel from Merck (230-400 mesh). Infrared (IR) spectra were recorded within KBr on a Nicolet FT-IR spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a TA Instrument DSC-2920 Low-Temperature Difference Scanning Calorimeter, the sample were recorded at a heating rate of 10 °C/min. ¹H NMR and ¹³C NMR in CDCl₃, DMSO-d₆ or Acetone-d₆ were

recorded using a Bruker (Avance 4000) or Varian (Unity Plus 400) spectrometer at 400 MHz and 100 MHz respectively. Low and high-resolution mass spectra were recorded using a Jeol SX-102A spectrometer in ESI mode.

General Procedure for the Synthesis of VTPCA derivatives

The diphenylamine starting materials **1** and **2** were synthesized following the reported literature method¹. It should be noted that after a period of storage, the starting material **2** should be purified by recrystallization from ethanol before use. The synthesis of VTPCA was described in detail below.

N-phenyl-4-vinylaniline (**1**)

¹H NMR (400 MHz, CDCl₃, δ): 7.33-7.25 (m, 4H), 7.08 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.67 (dd, J = 18.0, 11.2 Hz, 1H), 5.75 (s, 1H), 5.62 (d, J = 18.0 Hz, 1H), 5.13 (d, J = 11.2 Hz, 1H)

(E)-1-bromo-4-(4-(diethoxymethyl)styryl)benzene (**2**)

¹H NMR (400 MHz, CDCl₃, δ): 7.51-7.45 (m, 6H), 7.39-7.35 (m, 2H), 7.07 (ABq, Δν = 21.10 Hz, J = 16.2 Hz, 2H), 5.51 (s, 1H), 3.67-3.52 (m, 4H), 1.26 (t, J = 7.2 Hz, 6H)

(E)-4-(4-(phenyl(4-vinylphenyl)amino)styryl)benzaldehyde (**4**)

A mixture of freshly prepared *N*-phenyl-4-vinylaniline **1** (1.953 g, 10.0 mmol, 1.0 equiv.), freshly recrystallized **2** (3.61 g, 10.0 mmol, 1.0 equiv.), Pd₂(dba)₃ (458 mg, 0.50 mmol, 0.05 equiv.), NaO^tBu (2.88 g, 10.0 mmol, 3.0 equiv.), tri(*tert*-butyl)phosphine (20.0 mL, 0.05 M in toluene, 1.0 mmol, 0.1 equiv.) in toluene (200 mL) was heated at 70 °C and was monitored by TLC for 8 to 12 hours. After cooling to room temperature, the mixture was filtrated with celite and was washed twice with 50 mL ether. The combined organic solutions were then evaporated under reduced pressure to afford crude **3** as a pale yellow solid. To a solution of crude **3** (4.180 g, ~8.8 mmol), water (10.0 mL) and THF (40.0 mL), boron trifluoride diethyl etherate (1.0 mL, 2% vol) was dropwisely added. The resulting solution was stirred at ambient temperature for an hour. After reaction was completed, both 20 mL of brine and 3 M NaOH_(aq) were added into the solution to quench boron trifluoride diethyl etherate. The mixture was then extracted with ether (3 × 30 mL); the combined organic layers were dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel using hexanes/ethyl acetate (20:1 to 10:1) as the eluent to afford **4** as yellow to orange solid (3.05 g, 76% yield). mp: 130.4 °C (DSC); IR (KBr): ν = 3368 (w), 3178 (w), 3029 (m), 2824 (w), 2735 (w), 1687 (s), 1587 (s), 1500 (s), 1421 (m), 1325 (s), 1281 (s), 1164 (s), 965 (m), 903 (s), 832 (s), 797 (s), 754 (s), 697 (s), 536 (s) cm⁻¹ (m); ¹H NMR (400 MHz, CDCl₃, δ): 9.97 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.33-7.27 (m, 4H), 7.21 (d, J = 16.4 Hz, 1H), 7.13 (dd, J = 8.8, 1.0 Hz, 2H), 7.10-7.00 (m, 6H), 6.68 (dd, J = 17.6, 11.2 Hz, 1H), 5.67 (dd, J = 17.6, 0.8 Hz, 1H), 5.19 (dd, J = 11.2, 0.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ): 190.6, 147.3, 146.5, 146.3, 143.2, 135.6, 134.5, 132.1, 131.2, 130.1, 129.8, 129.0, 127.4, 126.8, 126.2, 125.0, 124.5, 123.9, 123.2, 122.8, 122.3; ESIMS (m/z, [M + H]⁺): 402, HRMS (ESI, m/z, [M + H]⁺): calcd for C₂₉H₂₄NO, 402.1858; found, 402.1881.

VTPCA

A mixture of **4** (401.5 mg, 1.0 mmol, 1.0 equiv.), cyanoacetic acid (255.2 mg, 3.0 mmol, 3.0 equiv.), ammonium acetate (231.2 mg, 3.0 mmol, 3.0 equiv.), in acetonitrile (10 mL) was refluxed for 6 hours. After cooling to ambient temperature, the precipitate was collected, sonicated and washed with acetonitrile, ethyl acetate, dichloromethane, ether, and hexanes, respectively. The solid residue was then suspended in 20 mL cold dichloromethane and poured into cold HCl_(aq) (50 mL, 10% vol) solution. After the residue was fully dissolved, the aqueous layer was removed from resulting mixture and the organic layer was washed carefully with brine (3 × 50 mL). The remained organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure to give VTPCA as dark red solid (218.1 mg, 60% yield). T_d: 233 °C (TGA, 5% weight loss); ¹H NMR (400 MHz, DMSO-d₆, δ): 8.25 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 7.44-7.39 (m, 3H), 7.33 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 16.0 Hz, 1H), 7.11-7.05 (m, 3H), 6.99-6.96 (m, 4H), 6.67 (dd, J = 18.4, 11.2 Hz, 1H), 5.71 (d, J = 18.4 Hz, 1H), 5.18 (d, J = 11.2 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆, δ): 163.2, 151.4, 146.8, 146.3, 146.2, 141.4, 135.7, 131.9, 130.8, 130.7, 130.6, 130.4, 129.5, 127.9, 127.2, 126.8, 126.6, 125.4, 124.4, 123.6, 123.5, 122.6, 117.1, 112.8; IR (KBr): ν = 3028 (w), 2924 (w), 2853 (w), 2223 (w), 1696 (m), 1579 (vs), 1506 (s), 1421 (m), 1319 (s), 1280 (s), 1210 (m), 1176 (s), 958 (m), 901 (w), 834 (m), 755 (w), 697 (w) cm⁻¹ (m); ESIMS (m/z, [M + H]⁺): 469, HRMS (ESI, m/z, [M + H]⁺): calcd for C₃₂H₂₅N₂O₂, 469.1916; found, 469.1909.

¹ a) H. L. Ngo, N. A. Zafiroopoulos, T. A. Foglia, E. T. Samulski, W. Lin, *Energy & Fuels*, 2008, **22**, 626. b) L. Viau, O. Maury, H. Le Bozec, *Tetrahedron Lett.*, 2004, **45**, 125.