

Supporting information

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Experimental Section

Materials and Methods.

Solvents were dried by standard procedures. All other chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were recorded with a Varian INOVA 400 NMR instrument (USA) with the chemical shifts by using TMS as standard. MS data were obtained with GCT CA156 (UK) LC/Q-TOF MS (UK) or HP1100 LC/MSD (USA) mass spectrometer. UV-vis and emission spectra of the dyes in solution were recorded in a quartz cell with 1 cm path length on a HP 8453 (USA) and PTI700 (USA) spectrophotometer, respectively. Electrochemical redox potentials were obtained by cyclic voltammetry using a three electrode cell and an electrochemical workstation (BAS100B, USA). The working electrode was a glass carbon electrode, the auxiliary electrode was a Pt wire, and Ag/Ag⁺ was used as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M was used as supporting electrolyte in CH₂Cl₂. Ferrocene was added to each sample solution at the end of the experiments, and the ferrocenium/ferrocene (Fc/Fc⁺) redox couple was used as an internal potential reference. The potentials versus NHE were calculated by addition of 440 mV to the potentials versus Fc/Fc⁺. Electrochemical impedance spectroscopy (EIS) for DSCs with forward bias -0.7 V under dark was measured with an impedance/gain-phase analyzer (PARSTAT 2273, USA). The spectra were scanned in a frequency range of 10⁻² -10⁵ Hz at room temperature. The alternate current (AC) amplitude was set at 10 mV.

DSC Fabrication.

The DSCs were fabricated as reported in literature.¹ A layer of 13 nm (DHS-TPP3, Heptachroma, China) paste (ca. 2 μm) was coated on the F-doped tin oxide conducting glass (TEC15, 15 Ω/square, Pilkington, USA) by screen printing and then dried for 6 min at 125 °C. This procedure was repeated for 6 times (ca. 12 μm) and coated by a layer of 300 nm (DHS-SLP1, Heptachroma, China) titania paste (ca. 4 μm) as scattering layer. The double-layer TiO₂ electrodes (area: 6×6 mm) were gradually

heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The sintered film was further treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, then washed with ethanol and water, and annealed at 500 °C for 30 min. After the film was cooled to 40 °C, it was immersed into a dye solution in CH₂Cl₂ and maintained under dark. The sensitized TiO₂ electrode was then rinsed with the solvent of dye-bath and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and Pt-coated conducting glass as the counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont). The electrolyte was introduced into the cell via vacuum backfilling by the hole in the back of the counter electrode. Finally, the hole was also sealed using Surlyn 1702 film and cover glass.

Photovoltaic Properties Measurements.

The irradiation source for the photocurrent-voltage (J-V) measurement is an AM 1.5 solar simulator (16S-002, Solar Light Co. Ltd., USA). The incident light intensity was 100 mW·cm⁻² calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.159 cm². The photocurrent-voltage curves were obtained by the linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermonolight (SM-25, Jasco Co. Ltd., Japan). The J_{sc} was calibrated by integrating the IPCE value tuned light density of AM 1.5 against wavelength.²

Theoretical Calculation Methods.

The geometrical structures of the three dyes were optimized by performed density functional theory (DFT) calculations and time-dependent DFT (TDDFT) calculations of the excited states at the B3LYP/6-31+G(d) level with the Gaussian 03W program package.³ Polarizabilities and dipole moments were calculated at the B3LYP/6-31+G(d) level of theory. Optimized 3D structures were generated with the ChemBio3D ultra 11.0 program.

Synthesis.

(E)-ethyl

3-(6-(2-(3-(dicyanomethylene)-5,5-dimethylcyclohex-1-enyl)vinyl)-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoate (10)

10 was prepared by the similar procedure of synthesizing **12**. GCT/TOF HRMS-EI (m/z): [M]⁺ calcd for C₃₁H₃₉N₃O₂, 485.3042; found: 485.3063.

ethyl

3-(6-((E)-2-((Z)-3-(1-cyano-2-ethoxy-2-oxoethylidene)-5,5-dimethylcyclohex-1-enyl)vinyl)-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoate (11)

11 was prepared by the similar procedure of synthesizing **12**. API-ES MS (Positive, m/z): calcd. for C₃₁H₄₀N₂O₄, 504; found, 504.

(E)-ethyl

2-cyano-2-(5,5-dimethyl-3-((E)-2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)cyclohex-2-enylidene)acetate (12)

D0 (492.6 mg, 2.27 mmol) and ethyl 2-cyano-2-(3,3,5-trimethylcyclohexylidene)acetate **9** (1.06 g, 4.54 mmol), and piperidine (18 mg, 0.23 mmol) were refluxed in acetonitrile (20 mL) for 12 h under nitrogen atmosphere. After cooling to room temperature, the solvent was removed by vacuum. The resulting coarse product was purified by chromatography (silica gel, dichloromethane: hexane = 2:1) to provide **12** of the title product as dark red solid. API-ES MS (Positive, m/z): calcd. for C₂₈H₃₆N₂O₂, 432; found, 432.

(E)-3-(6-(2-(3-(dicyanomethylene)-5,5-dimethylcyclohex-1-enyl)vinyl)-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (HY102)

The ester **10** (145 mg, 0.3 mmol) was hydrolyzed in 2 M LiOH in equal volume of ethanol and water by room temperature over night. The reaction mixture was diluted by water and the solution pH was adjusted to 6 by adding 1 M HCl at room temperature. The precipitate was then filtered, and purified by silica gel chromatography using methanol and methylene chloride (1:15) gave pure **HY102** as a dark red powder (yield 40%). ¹H NMR (400 MHz, Acetone) δ 7.65 (s, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.17 (d, *J* = 15.8 Hz, 1H), 6.77 (s, 1H), 6.52 (s, 1H), 3.05 (m, 2H), 2.92 (s, 3H), 2.86 (m, 1H), 2.58 (m, 2H), 1.84 (dd, *J* = 12.9, 4.4 Hz, 1H), 1.42 (t, *J* = 12.8 Hz, 1H), 1.27 (m, 13H), 0.87 (d, *J* = 6.5 Hz, 6H). GCT/TOF HRMS-EI (m/z): [M]⁺ calcd for C₂₉H₃₅N₃O₂, 457.2729; found: 457.2737.

3-(6-((E)-2-((Z)-3-(carboxy(cyano)methylene)-5,5-dimethylcyclohex-1-enyl)vinyl)-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (HY102-2)

HY102-2 was prepared by the similar procedure of synthesizing **HY102**. ¹H NMR (400 MHz, Acetone) δ 7.68 (s, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.14 (d, *J* = 15.8 Hz, 1H), 6.76 (s, 1H), 6.52 (s, 1H), 3.05 (m, 2H), 2.92 (s, 3H), 2.86 (m, 1H), 2.58 (m, 2H), 1.84 (dd, *J* = 12.9, 4.4 Hz, 1H), 1.40 (t, *J* = 12.8 Hz, 1H), 1.23 (m, 13H), 0.87 (d, *J* = 6.5 Hz, 6H). API-ES MS (Negative, m/z): calcd. for C₂₉H₃₆N₂O₄, 476; found, 476.

(E)-2-cyano-2-(5,5-dimethyl-3-((E)-2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)vinyl)cyclohex-2-enylidene)acetic acid (HY102-1)

The ester **12** (173 mg, 0.4 mmol) was hydrolyzed in 2 M LiOH in equal volume of ethanol and water by heating at 50 °C for 5 h. The reaction mixture was diluted by water and the solution pH was adjusted to 6 by adding 1 M HCl at room temperature. The precipitate was then filtered, and purified by silica gel chromatography using methanol and methylene chloride (1:20) gave pure **HY102-1** as a dark red powder (yield 55%). ¹H NMR (400 MHz, Acetone) δ 7.89 (s, 1H), 7.41 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.10 (m, 1H), 6.94 (d, *J* = 16.1 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 2.86 (m, 4H), 2.62 (s, 2H), 2.50 (s, 2H), 1.87 (dd, *J* = 13.0, 4.3 Hz, 1H), 1.47 (t, *J* = 12.8 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H), 1.32 (s, 3H), 1.24 (s, 3H), 1.07 (s, 6H). API-ES MS (Negative, m/z): calcd. for C₂₆H₃₂N₂O₂, 404; found, 404.

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