

Efficient Near Infrared D- π -A

Sensitizers with Lateral Anchor Group for Dye-Sensitized Solar Cells

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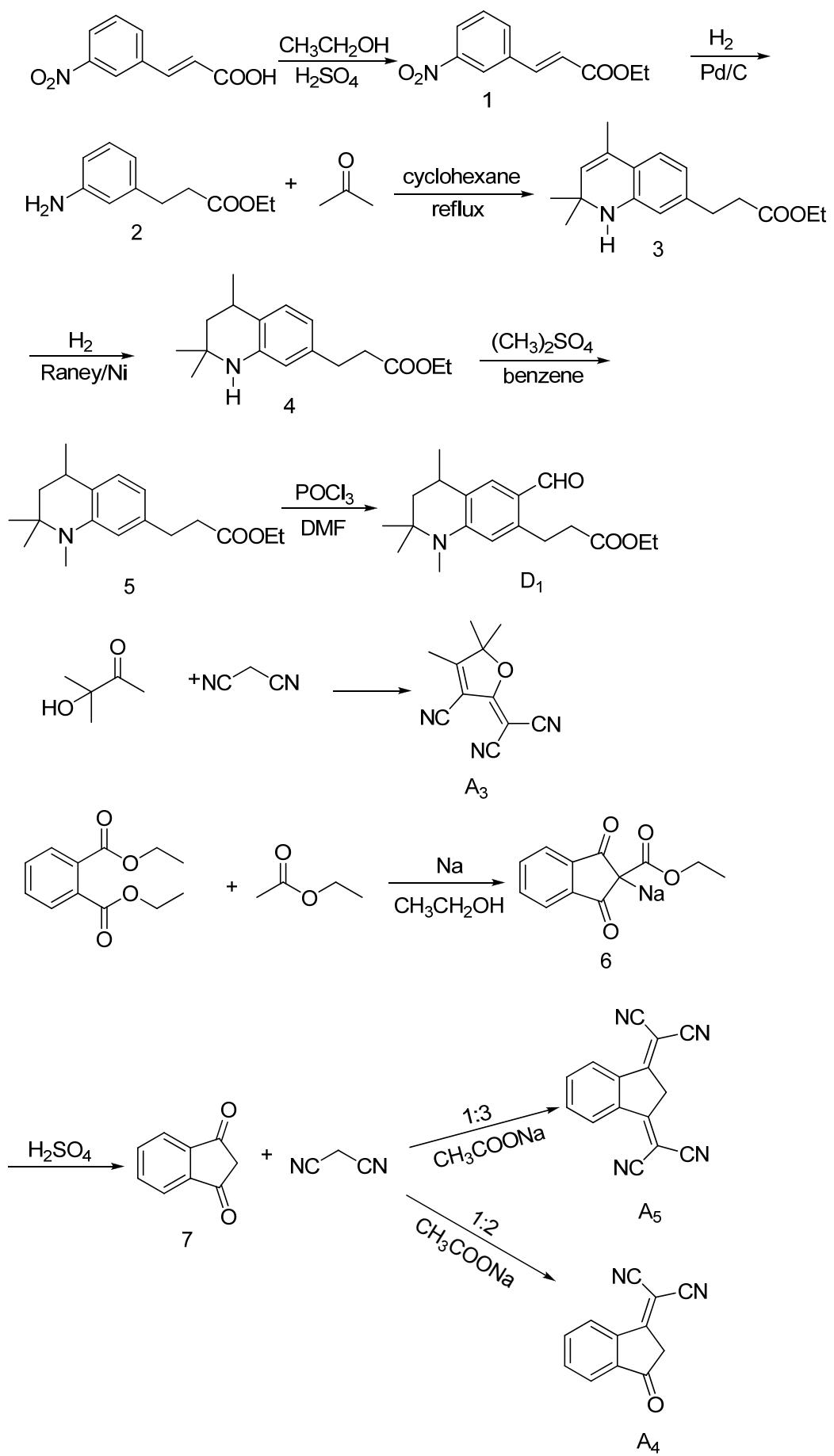
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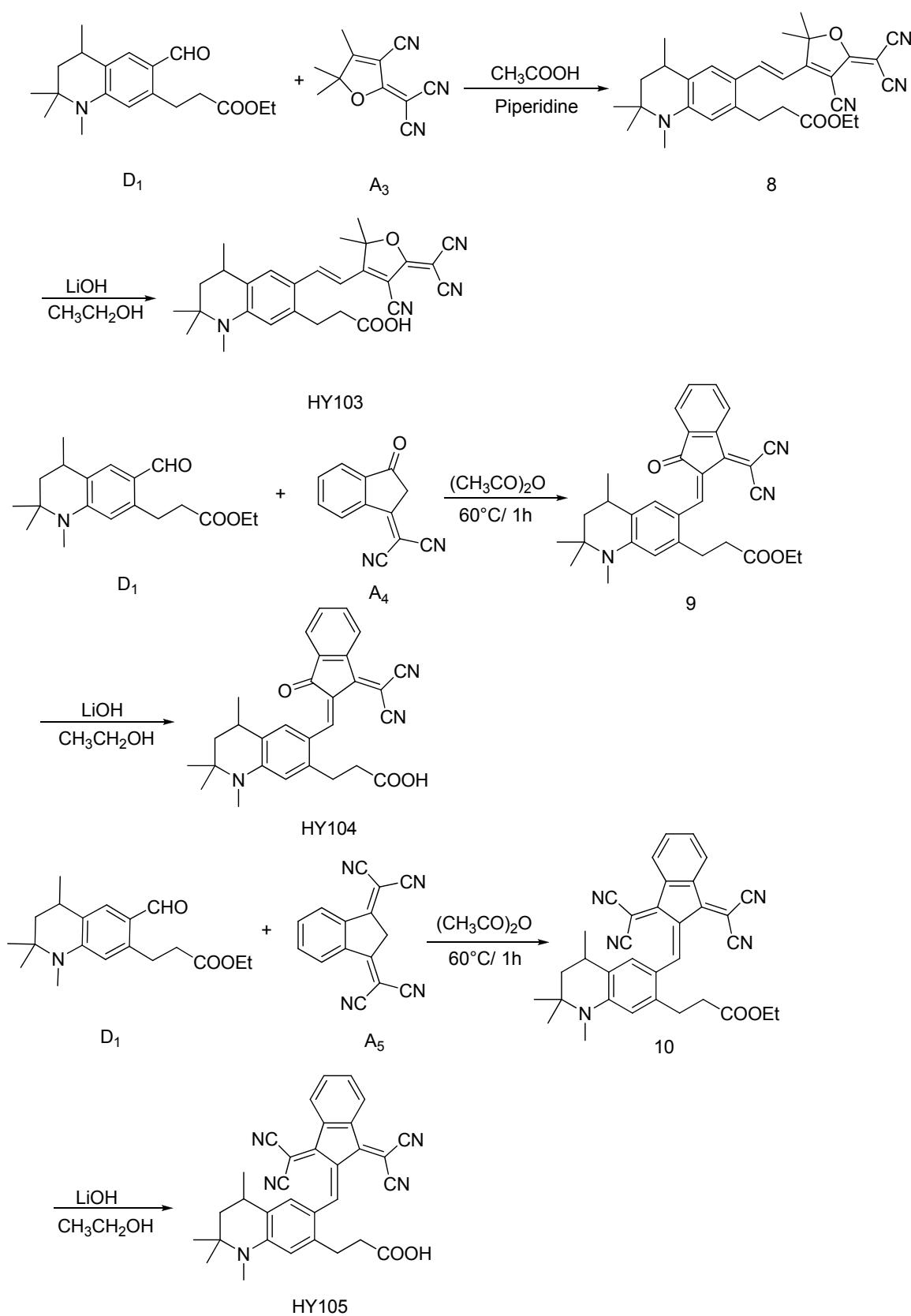
Supporting Material

Experimental

General methodology. 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. MS data were obtained with GCT CA156 (UK) high-resolution mass spectrometer (HRMS) or HP1100 LC/MSD (USA) mass spectrometer. UV-vis spectra of the dyes in solutions were recorded in a quartz cell with 1 cm path length on a HP 8453 spectrophotometer. Electrochemical redox potentials were obtained by cyclic voltammetry using a threeelectrode 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 CH₃CN. 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 calibrated by addition of 630 mV to the potentials versus Fc/Fc⁺.

1. Synthesis of HY103, HY104 and HY105:





Scheme S1. Synthetic route of HY103, HY104 and HY105.

The electron-donating moiety tetrahydroquinoline was obtained from aniline as precursor based on improved literature procedures.^{1,2} **D₁** was obtained in 6 steps from 3-Nitrocinnamic acid. First, compound **2** as intermediate was synthesized in 2 steps according to the already reported procedures.³ Then compound **2** was reacted with acetone, hydrogen gas and dimethyl sulfate under cycliation, hydrogenation and methylation to get compound **5**.⁴ Formylation of **D₁** was achieved by treatment of the compound **5** with 2-3 equiv of POCl₃, followed by addition of DMF and hydrolysis. The residue was purified by chromatography (silica gel, dichloromethane) to provide the title product **D₁**: light yellow oil (yield 79%): ¹H NMR (CDCl₃, 400MHz, ppm): δ 0.88 (m, 3H), 1.34 (s, 6H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.81 (dd, *J₁* = 4.26 Hz, *J₂* = 4.27 Hz, 2H), 2.64 (m, 2H), 2.80-2.86 (m, 1H), 2.91 (s, 3H), 3.27(m, 2H), 4.14(m, 2H), 6.40 (s, 1H), 7.53 (s, 1H), 9.92(s, 1H).

Acceptors **A₃**, **A₄** and **A₅** was synthesized according to the already reported procedures respectively.^{5,6}

The **HY103**, **HY104** and **HY105** sensitizers were synthesized under Knoevenagel Condensation and hydrolyzation conditions.^{5,6} After chromatography purification procedure (silica gel, CH₂Cl₂: MeOH=20:1 as eluent), the target compounds were obtained as dark solids as following. (The specific synthesis and characterization details of intermediate will be introduced in the later article.)

(E)-3-(6-(2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)-1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (**HY103**): Black solid (yield 90%). ¹H-NMR (Acetone-d₆, 400MHz, ppm): δ 1.33 (s, 6H), 1.38 (s, 6H), 1.40 (d, *J* = 5.39 Hz, 3H), 1.94 (dd, *J₁* = 4.207 Hz, *J₂* = 4.213 Hz, 2H), 2.65 (m, 2H), 2.80 (m, 1H), 3.07(s, 3H), 3.11(m, 2H), 6.68 (s, 1H), 6.94 (d, *J* = 15.48Hz, 1H), 7.79 (s, 1H), 8.43 (d, *J* = 15.50 Hz, 1H). HRMS-EI (*m/z*): [M]⁺ calcd for C₂₈H₃₀N₄O₃, 470.2318; found, 470.2338.

(Z)-3-((1-(dicyanomethylene)-3-oxo-1H-inden-2(3H)-ylidene)methyl)-1,2,2,4-tetra methyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (**HY104**): Black solid (yield 88%). ¹H-NMR (Acetone-d₆, 400MHz, ppm): δ 1.27 (s, 3H), 1.33 (d, *J* = 6.25 Hz, 6H), 1.86 (dd, *J₁* = 3.89 Hz, *J₂* = 4.04 Hz, 2H), 2.54 (m, 2H), 2.98 (m, 1H), 3.02(s, 3H), 3.09(m, 2H), 6.60 (s, 1H), 7.70 (m, 3H), 8.43 (d, *J* = 7.71 Hz, 1H), 8.61 (s, 1H), 8.75(s, 1H). HRMS-EI (*m/z*): [M]⁺ calcd for C₂₉H₂₇N₃O₃, 465.2052; found, 465.2058

3-((1,3-bis(dicyanomethylene)-1H-inden-2(3H)-ylidene)methyl)-1,2,2,4-tetramethyl -1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (**HY105**): Black solid (yield 80%) ¹H-NMR (Acetone-d₆, 400MHz, ppm): δ 1.37 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 6H), 1.95 (dd, *J₁* = 5.75 Hz, *J₂* = 5.83 Hz, 2H), 2.62 (m, 2H), 3.03 (m, 1H), 3.11(s, 3H), 3.18(m, 2H), 6.76 (s, 1H), 7.98 (m, 2H), 8.58 (d, *J* = 8.05 Hz, 2H), 8.74 (s, 1H), 8.95(s, 1H). HRMS-EI (*m/z*): [M]⁺ calcd for C₂₉H₂₇N₃O₃, 513.2165; found, 513.2160

2. DSCs fabrication process of HY103, HY104 and HY105:

The DSCs were fabricated as the reported literature procedure.⁷ A layer of 13 nm (D/SP, Solarnix, Switzerland) 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 5 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 2×10^{-4} M dye solution in CH₂Cl₂ with CDCA (2×10^{-4} M) and maintained under dark for 3 h. 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). Under optimized test conditions, the electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) which is synthesized as the reported literature,⁸ 0.06M LiI, 0.02 M I₂, and 0.1 M tetrabutyl ammonium iodide (TBAI) in acetonitrile:valeronitrile (AN:VN)=85:15 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.

3. Photochemical and Electrochemical Properties of HY103.

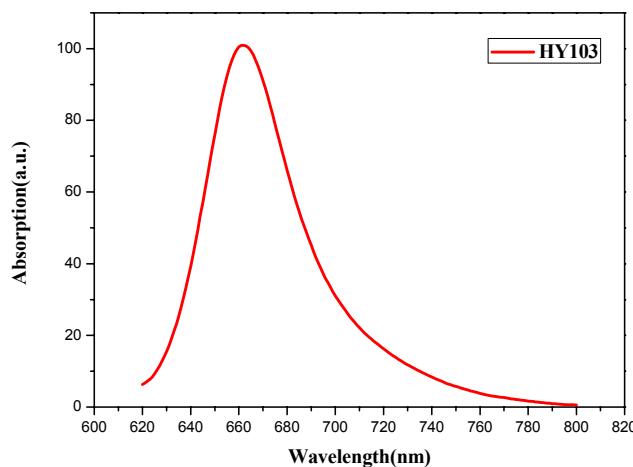


Figure S1. Emission spectrum of HY103 dye in CH₃CN (2×10^{-5}).

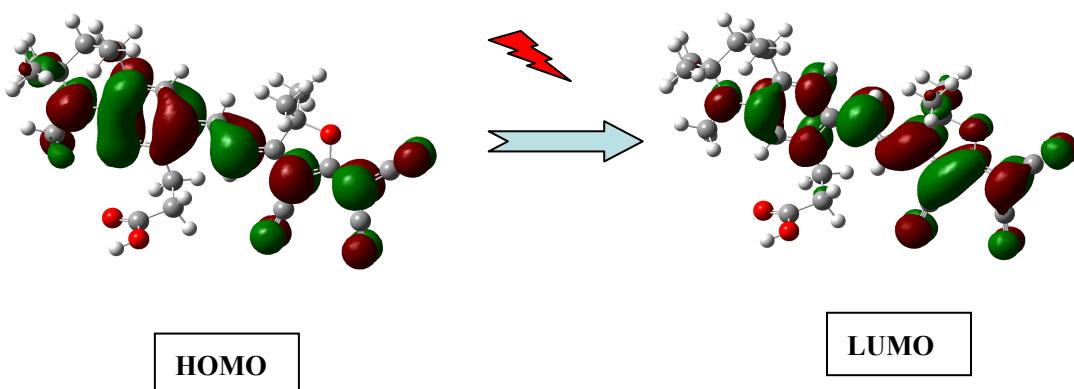


Figure S2. HOMO and LUMO of **HY103** in DFT

4. Photovoltaic Properties of dyes.

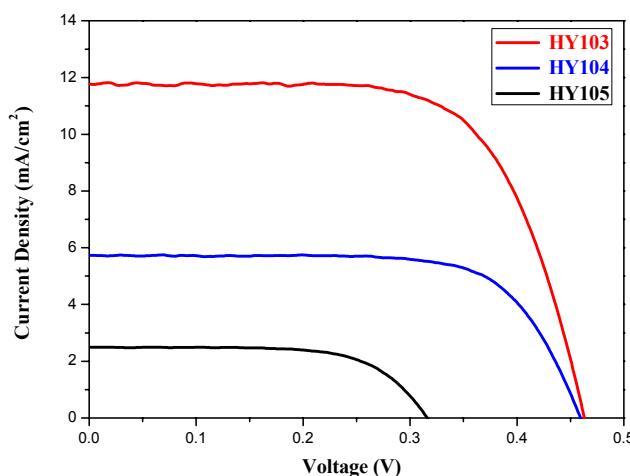


Figure S3. Comparison of J-V curves of **HY103**, **HY104** and **HY105** dye sensitized TiO_2 solar cells.

Table S1. Photoelectrochemical properties of TiO_2 semiconductor solar cells sensitized with **HY103**, **HY104** and **HY105**.^[a]

dyes	Solvents	J_{SC} (mA/cm ²)	V_{OC} (mV)	Fill factor (FF)	η (%)
HY103	CH_2Cl_2	11.76	464	0.674	3.7
HY104	CH_2Cl_2	5.74	460	0.702	1.9
HY105	CH_2Cl_2	2.49	317	0.662	0.5

^[a] irradiated light: AM 1.5G (100 mW·cm⁻²); Working area: 0.159 cm²; Electrolyte: DMPII/0.6 M, LiI/0.5 M, I₂/0.02 M, TBAI/0.1 M in AN; VN=85:15.

5. References:

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