

A novel organic chromophore for dye-sensitized nanostructured solar cells

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Supporting Material

Experimental

General methodology. All reactions were carried out under N₂ with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by standard procedures.

Proton (¹H) and carbon (¹³C) NMR spectra were recorded on a 400 or 500 MHz instrument using the residual signals from THF, δ (3.57 and 1.71) ppm and δ (67.4 and 25.3) ppm or CHCl₃, δ 7.26 ppm and δ 77.0 ppm as internal references for ¹H and ¹³C respectively.

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene¹

4-Diphenylamino-benzaldehyde (7.37 mmol, 2 g) THF (22 mL) and t-BuOK (8.84 mmol, 0.99 g) was stirred at ambient temperature under nitrogen atmosphere for 1 h. 2-thienylmethyl triphenylphosphonium chloride (10.2 mmol, 4.05 g) was dissolved in THF and added drop wise to the solution, and the reaction mixture was stirred for 1 h at ambient temperature, whereupon the mixture was heated to reflux for 24 h. The reaction mixture was allowed to cool to ambient temperature and a molar excess of water was added. The mixture was concentrated by rotary evaporator and the water phase was extracted with DCM. The organic phase was dried over MgSO₄, filtered through a plug of silica gel (DCM) and a crude intermediate was obtained (7.52 mmol, 2.65 g). The crude product was used in the next step without further purification.

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene-2-carbaldehyde¹

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene (7.52 mmol, 2.65 g) was dissolved in THF (20 mL) and was cooled to -78 °C under nitrogen atmosphere. n-Butyl Lithium (3.3 mL, 2.5 M hexane solution) was added drop wise over 10 min and the mixture was stirred at -78 °C for 1 h. The mixture was allowed to warm to 0 °C and stirred for 30 min. The mixture was once again cooled to -78 °C and DMF (0.64 ml, 8.27 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The

reaction was quenched by the addition of aqueous HCl (10 %, 100 mL) and extracted with DCM (3 × 30 mL). The combined organic extract was dried over anhydrous MgSO₄ and filtered. Solvent removal by rotary evaporation and column chromatography over silica gel using hexane/DCM mixture (1:1) yielded an orange solid (1.1 g, 39%). ¹H NMR (400 MHz, CDCl₃): 9.85 (s, 1 H), 7.67 (d, 1 H), 7.40-7.15 (m, 6 H), 7.16-7.05 (m, 11 H)- ¹³C NMR (100 MHz, CDCl₃): 182.8, 153.6, 148.9, 147.6, 141.4, 137.8, 133.0, 130.0, 128.3, 126.3, 125.4, 124.0, 123.7, 123.0, 119.1.

3-(5-(4-(diphenylamino)styryl)thiophen-2-yl)-2-cyanoacrylic acid (D5)

A 50 mL acetonitrile solution of 5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (1 g, 2.6 mmol) and cyanoacetic acid (0.29 g, 3.4 mmol) was refluxed in the presence of piperidine (0.2 mmol, 17 mg) for 4 h under nitrogen atmosphere. Solvent removal by rotary evaporator followed by purification by column chromatography over silica gel (1% acetic acid in DCM) yielded the product as dark purple solid, **D5** (78 mg, 72%), mp 236-238°C. ¹H NMR (500 MHz, d₈-THF): δ 11.81 (s, 1H), 8.29 (s, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 16.1 Hz, 1H), 7.25 (m, 3H), 7.21 (d, *J* = 16.1 Hz, 1H), 7.20 (d, *J* = 4.0 Hz, 1H), 7.07 (m, 4H), 7.03 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, d₈-THF): 163.6, 153.5, 148.9, 147.8, 145.9, 139.6, 134.7, 132.8, 130.5, 129.6, 128.3, 126.6, 125.2, 123.7, 122.8, 119.1, 116.1, 98.4. MS (API-ES) *m/z*: 447.0 [M-H]⁻.

1. Hu, Z. Y.; Fort, A.; Barzoukas, M.; Jen, A. K. Y.; Barlow, S.; Marder, S. R. *Journal Of Physical Chemistry B* **2004**, 108, (25), 8626-8630.

