

Supplementary Information for Publication

Photoelectrochemical Properties and Interfacial Charge Transfer

Kinetics of BODIPY-sensitized TiO₂ electrodes

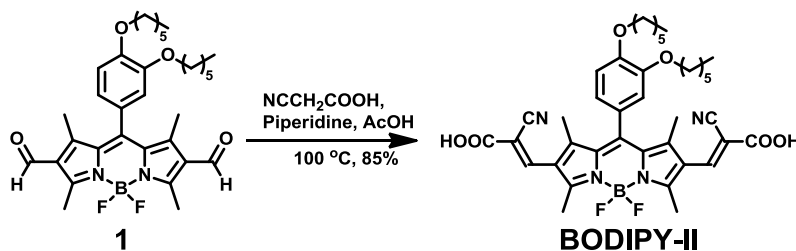
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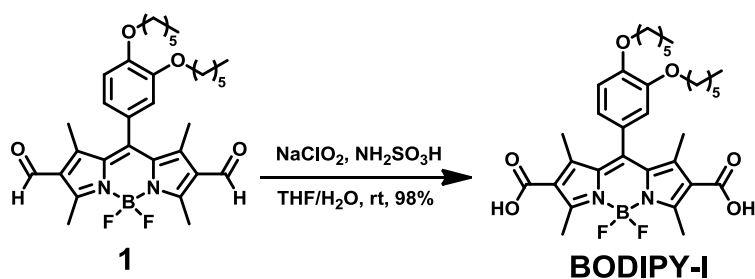
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Synthesis of BODIPY-1 and 2



4,4-Difluoro-8-(3,4-dihexyloxyphenyl)-1,3,5,7-tetramethyl-2,6-bis[(E)-2-carboxy-2-cyanovinyl]-4-bora-3a,4a-diaza-s-indacene (BODIPY-II).

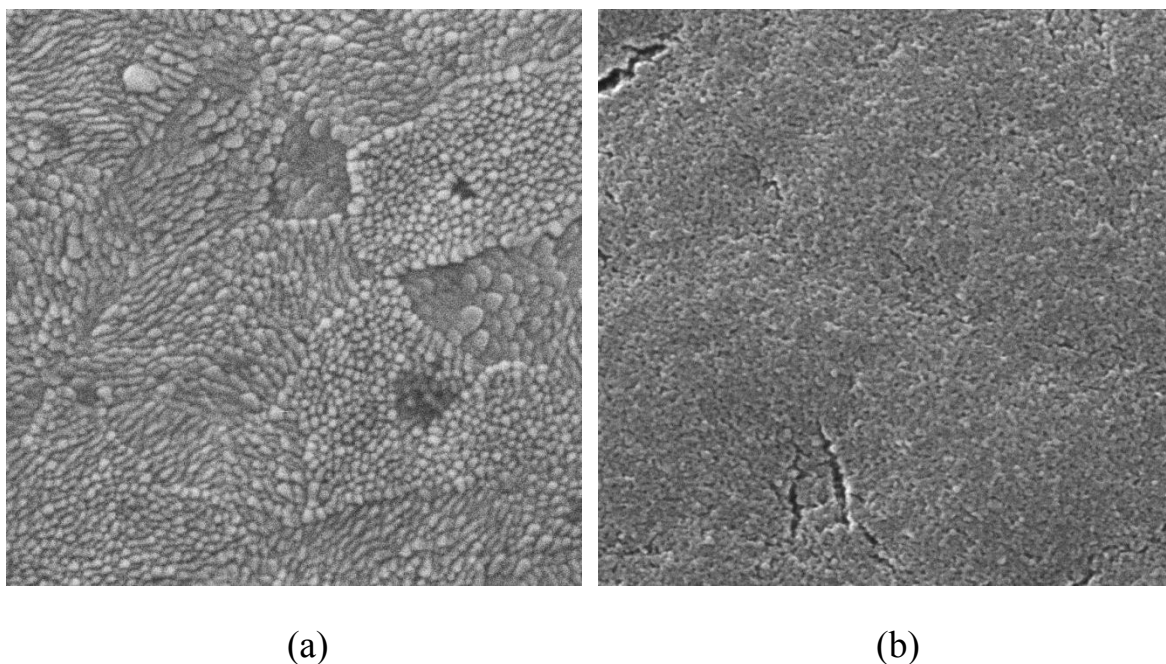
BODIPY dye 1 (58 mg, 0.1 mmol) and cyanoacetic acid (85 mg, 1.0 mmol) were refluxed in a mixture of benzene (15 mL), toluene (5 mL), piperidine (0.2 mL) and AcOH (0.1 mL). Any water formed during the reaction was removed using Dean-Stark apparatus. After 3 h, the mixture was diluted with EtOAc and then was washed with water and brine, respectively. The organic layer was collected, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by precipitation with CH₂Cl₂ and MeOH. The precipitated solid was collected and washed by CH₂Cl₂ to obtain BODIPY dye (BODIPY-II) as red-purple solid (60 mg, 85%). ¹H NMR (400 MHz, CD₃OD): δ 8.10 (s, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.61 (s, 6H), 1.85-1.72 (m, 4H), 1.61 (s, 6H), 1.56-1.44 (m, 4H), 1.39-1.30 (m, 8H), 0.94-0.87 (m, 6H).

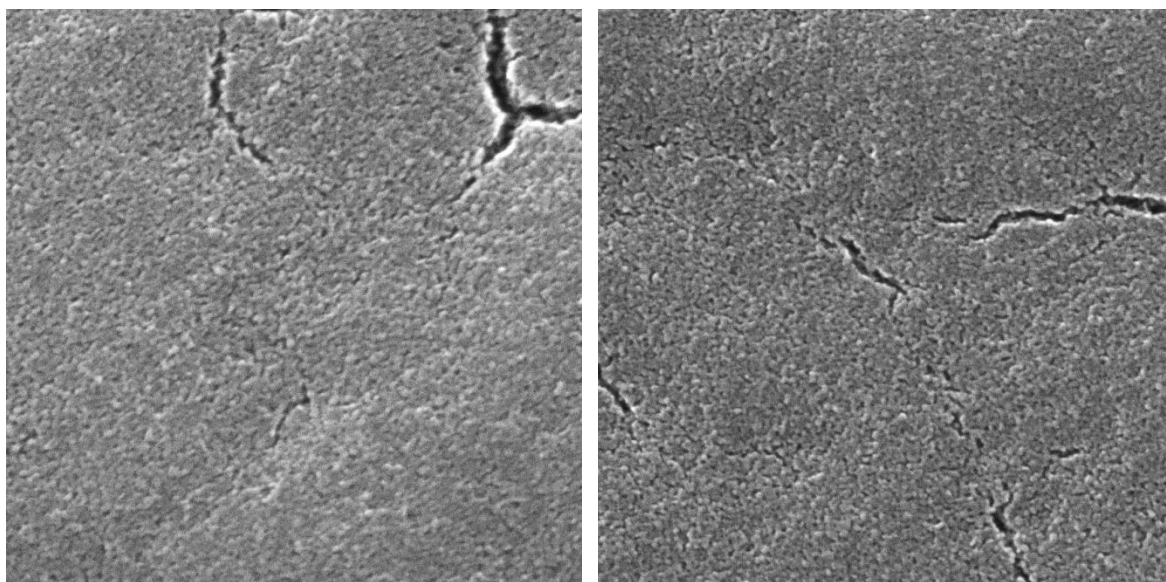


4,4-Difluoro-8-(3,4-dihexyloxyphenyl)-1,3,5,7-tetramethyl-2,6-dicarboxy-4-bora-3a,4a-diaza-s-indacene (BODIPY-1).

To BODIPY **1** (58 mg, 0.1 mmol) in mixed solution of THF (6 mL) and water (2 mL) was added NaClO₂ (90 mg, 1.0 mmol) and NH₂SO₃H (97 mg, 1.0 mmol). The mixture was stirred at room temperature for one hour, diluted with EtOAc and washed by aqueous Na₂S₂O₃. The organic layer was collected, dried over Na₂SO₄ and concentrated to form red-orange powder. The powder was washed twice by CH₂Cl₂ to yield BODIPY dye (**BODIPY-I**) (60 mg, 98%) as red-orange powder. ¹H NMR (400 MHz, DMSO-d₆): δ 7.09 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.68 (s, 6H), 1.71-1.41 (m, 10H), 1.39-1.34 (m, 4H), 1.29-1.22 (m, 8H), 0.85-0.79 (m, 6H).

Fig. S1. SEM images of (a) bare ITO, (b) ITO coated with TiO₂ (ITO/TiO₂), (c) ITO/TiO₂/BODIPY-1, (d) ITO/TiO₂/BODIPY-2. All SEM images have size of 1 μm × 1 μm.





(c)

(d)

Fig. S2. Current-Voltage characteristics of ITO/TiO₂/BODiPY electrodes in an electrochemical cell as the white light illumination was turned on or off. 0.05 M LiI and 0.05 M I₂ in acetonitrile was used as an electrolyte.

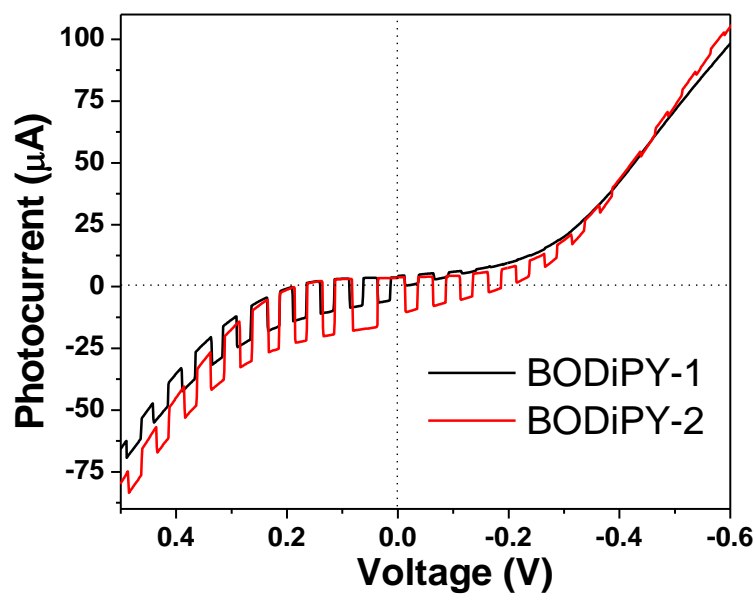
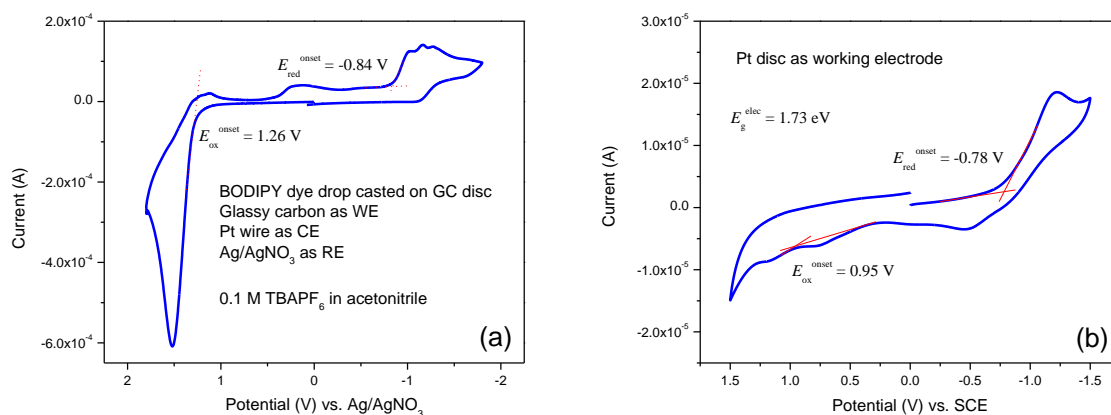


Fig. S3. Cyclic voltammograms of (a) BODIPY-1 dye drop-casted on glassy carbon working electrode, 0.1 M TBAPF₆ in acetonitrile as electrolyte, Pt wire as counter electrode, and Ag/AgNO₃ as the reference electrode and (b) BODIPY-2 dye in DMF solution (1.5 mM) with 0.1 M TBAPF₆, Pt disc working electrode, Pt wire counter electrode, and SCE as reference electrode, respectively. Scan rate: 50 mV/s.



The electrochemical properties of the two BODIPY dyes were also studied by cyclic voltammetry. The BODIPY-1 dye was drop-casted on a glassy carbon electrode from DMF solution, using a Pt wire and Ag/AgNO₃ (10 mM Ag⁺ in acetonitrile) as counter electrode and reference electrode, respectively. As shown in Figure S2(a), the onset points of n-doping and p-doping process of BODIPY-1 dye are at -0.84 V and 1.26 V, and the band-gap of the BODIPY-1 dye was calculated by $E_g^{elec} = (E_{red}^{onset} + 4.7) - (E_{ox}^{onset} + 4.7) = 2.10$ eV. The CV curve for the BODIPY-2 dye is shown in Figure S2 (b). The onset points of n-doping and p-doping process of BODIPY-1 dye are at -0.78 V and 0.95 V, and the electrochemistry band-gap of BODIPY-2 dye is 1.73 eV, which calculated according the same equation.