

Panchromatic Donor-Acceptor-Donor Conjugated Oligomers For Dye-Sensitized Solar Cell Applications

Stalder, R.¹; Xie, D.¹; Islam, A.²; Han, L.²; Reynolds, J.R.³; Schanze, K.S.¹

¹Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611, United States

²Photovoltaic Materials Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan

³School of Chemistry and Biochemistry, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, United States
reynolds@chemistry.gatech.edu

Table of Contents:

S1.	General	S1
S2.	Synthetic Procedures and Characterization of Products	S2
S3.	Supporting Figures	S6
S4.	References	S8

S1. General

General Synthetic Details. Commercially available reagents were used as received from the chemical suppliers. Reactions that required anhydrous conditions were carried out under an inert atmosphere of argon in flame-dried glassware. Toluene and THF were dried using a Solvent Purification System. Toluene was further degassed by three cycles of freeze-pump-thaw prior to metal-catalyzed couplings. All reactions were monitored using F250 silica gel 60 M analytical TLC plates, with UV detection ($\lambda = 254$ and 365 nm). Silica gel (60\AA , $40\text{--}63\ \mu\text{m}$) was used as stationary phase for column chromatography.

NMR experiments were acquired with working frequencies of 500 MHz for ^1H , and 125 MHz for ^{13}C experiments. The shifts were reported in parts per million (ppm) and referenced to the residual resonance signals of commercially available deuterated chloroform: $\delta_{\text{H}}=7.26$ ppm, $\delta_{\text{C}}=77.23$ ppm. High-resolution mass spectra were recorded on a quadrupole mass analyzer instrument equipped with a direct insertion probe (ionization 70 eV) and an electron spray ionizer. Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida.

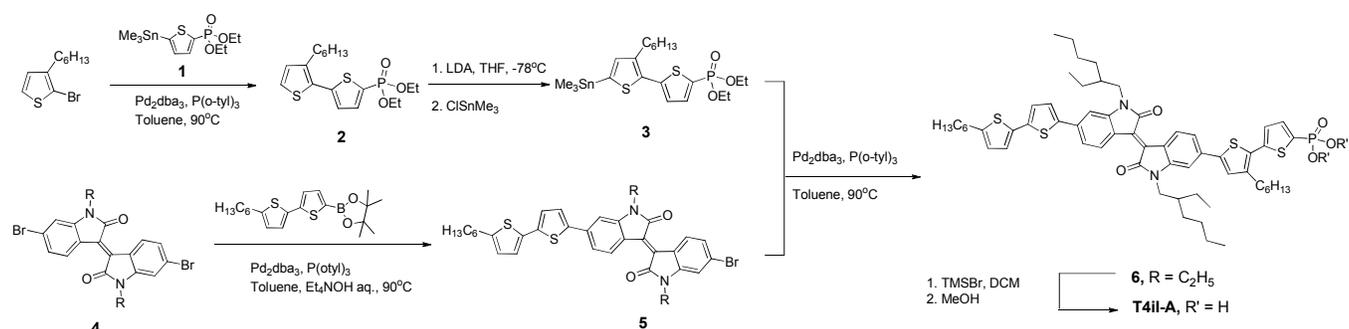
Dye Adsorption Procedure for Solid-State UV-vis Absorption. TiO_2 nanocrystalline paste (20 nm in diameter) was doctor-bladed onto clean FTO-glass slide and sintered at 400°C for 30 min. The absorption of the pristine

films was recorded as background profile. Each sintered films was immersed into a dye solution in DMF (~0.1 mM) for 3 hr to allow for dye adsorption onto the TiO₂ films. The resulting films were first washed with DMF, then EtOH. After drying under a gentle nitrogen flow, the films were set at the same position in the UV-vis spectrometer, and the absorption profiles were recorded. The latter were corrected by the background absorptions to yield the film absorption.

Electrochemistry. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆) was purchased (98%, Acros) and recrystallized from ethanol. The salts were transferred to an argon-filled drybox (OmniLab model, Vacuum Atmospheres). Dichloromethane (DCM) was obtained from an anhydrous solvent system and kept under inert atmosphere before being transferred to the drybox in which the electrolyte solutions were made. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat in the argon-filled drybox. Experiments were carried out in a one compartment electrochemical cell using a platinum disk electrode (0.02 cm²) as working electrode, a Ag/Ag⁺ reference electrode and platinum foil as a counter electrode; all potentials were reported vs. Fc/Fc⁺ redox couple. The following setup parameters were applied for the DPV studies: a step size of 1.4 mV, a step time of 0.035 s, and amplitude of 55 mV.

S2. Synthetic Procedures and Characterization of Products

The synthesis of compounds **1**, **4** and 2-bromo-3-hexylthiophene have been reported elsewhere.¹⁻³



Diethyl (3'-hexyl-[2,2'-bithiophen]-5-yl)phosphonate (2). In a dry, purged Schlenk flask, Pd₂(dba)₃ (322 mg, 0.35 mmol) and P(*o*-tyl)₃ (429 mg, 1.41 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. In a separate purged flask containing diethyl (5-(trimethylstannyl)thiophen-2-yl)phosphonate (**1**, 9 g, 23.5 mmol), 100 mL of degassed toluene were introduced via syringe to dilute **1**. In a separate purged flask containing 2-bromo-3-hexylthiophene (5.8 g, 23.5 mmol), 100 mL of degassed toluene were introduced via syringe. The

afforded solutions of **1** and 2-bromo-3-hexylthiophene (200 mL total volume) were then successively transferred to the Schlenk flask containing the catalyst system. The mixture was stirred and heated to 90°C for 12 hours. After cooling back to room temperature, the mixture was concentrated, and redissolved in 50 mL of hexanes, upon which a white precipitate forms. The solids were filtered off, and the filtrate was concentrated to a dark orange oil. This was purified by column chromatography using 4:1 hexanes:ethyl acetate as eluent. Product-containing fractions were combined and evaporated to dryness. After drying under vacuum in a dessicator overnight, this afforded the title compound (3.4 g, 8.9 mmol, 38%) as a yellow oil. ¹H-NMR (CDCl₃, 500 MHz) δ (ppm): 7.59 (dd, *J*₁ = 3.7 Hz, *J*₂ = 4.2 Hz, 1H), 7.22 (d, *J* = 5.2 Hz, 1H), 7.14 (t, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 5.2 Hz, 1H), 4.26-4.06 (m, 4H), 2.75 (t, *J* = 7.8 Hz, 2H), 1.62 (quintet, *J* = 7.8 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.34-1.24 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR (CDCl₃, 125 MHz) δ (ppm): 144.9, 141.1, 137.1, 130.3, 129.3, 128.2, 126.6, 125.4, 62.9, 62.8, 31.7, 30.6, 29.4, 29.2, 22.7, 16.4, 16.3, 14.2. HRMS (ESI-TOF) Calculated for C₁₈H₂₇O₃PS₂H (M+H)⁺: 387.1210 Found: *m/z* 387.1187. Anal. Calcd for C₁₈H₂₇O₃PS₂: C, 55.79; H, 7.28; Found: C, 55.81; H, 7.42.

Diethyl (3'-hexyl-5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)phosphonate (3). In a dry flask, compound **3** was diluted in anhydrous THF (10 mL) and cooled to -78°C. A lithium diisopropylamine solution was freshly prepared by adding n-BuLi (0.72 mL, 1.15 mmol, 1.6M in THF) dropwise into a dry flask containing a stirred diisopropylamine (0.18 mL, 1.25 mmol, distilled over CaH) solution in anhydrous THF (3 mL) at 0°C. This LDA solution was allowed to stir at 0°C for 30 minutes, and then transferred dropwise using a syringe into the flask containing the solution of **2** cooled to -78°C. After the addition was complete, the reaction mixture was left stirring at -78°C for 2 hours, before trimethyltin chloride (230 mg, 1.15 mmol, solid) was added to the flask in one portion. This was then allowed warm up to room temperature while stirring for 12 hours. The solvent was then evaporated, and the afforded slurry was redissolved in a mixture of chloroform (5 mL) and hexanes (20 mL). This resulted in precipitates, which were filtered off and the filtrate was concentrated to an orange oil. After drying under vacuum overnight, the title compound was obtained in 66% yield as observed by proton NMR and used without further purification. ¹H-NMR (CDCl₃, 500 MHz) δ (ppm): 7.57 (dd, *J*₁ = 3.7 Hz, *J*₂ = 4.2 Hz, 1H), 7.12 (t, *J* = 3.6 Hz, 1H), 7.01 (s, 1H), 4.26-4.06 (m, 4H), 2.75 (t, *J* = 7.8 Hz, 2H), 1.62 (quintet, *J* = 7.8 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.34-1.24 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.38 (s, 9H).

(E)-6-bromo-1,1'-bis(2-ethylhexyl)-6'-(5'-hexyl-[2,2'-bithiophen]-5-yl)-[3,3'-biindolinylidene]-2,2'-dione (5). In a purged Schlenk flask, (E)-6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (**4**, 967 mg, 1.5 mmol) and 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (565 mg, 1.5 mmol), Pd₂(dba)₃ (15 mg) and P(*o*-tyl)₃ (10 mg) were loaded under a flow of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon.

Degassed toluene (10 mL) was then added to flask, followed by a degassed aqueous solution of tetraethylammonium hydroxide (3 mL, 3 mmol, 1M in water). The mixture was stirred and heated up to 90°C for 12 hours, then allowed to cool to room temperature and slowly precipitated in methanol (100 mL). The precipitates were filtered and collected in a 100 mL round-bottom flask, to which a minimum amount of hot chloroform (~20 mL) was added in order to dissolve the solids completely. Silica gel (20 mL) was then added to the flask and swirled to absorb the solution. Careful evaporation of the chloroform adsorbed the crude on the dry silica gel, which was loaded onto a silica gel column packed with 3:2 hexanes:dichloromethane. The latter ratio was used as eluent to separate the remaining starting material and the decoupled by-product from the monocoupled title compound, which was obtained as a dark purple solid (459 mg, 0.56 mmol, 38%). ¹H-NMR (CDCl₃, 500 MHz) δ (ppm): 9.07 (dd, *J*₁ = 0.9 Hz, *J*₂ = 4.2 Hz, 1H), 9.01 (dd, *J*₁ = 0.9 Hz, *J*₂ = 4.2 Hz, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.19 (dd, *J*₁ = 1.8 Hz, *J*₂ = 4.2 Hz, 1H), 7.14 (dd, *J*₁ = 1.8 Hz, *J*₂ = 4.2 Hz, 1H), 7.05 (d, *J* = 3.8 Hz, 1H), 7.02 (d, *J* = 3.5 Hz, 1H), 6.80 (s, 2H), 6.70 (dt, *J*₁ = 0.9 Hz, *J*₂ = 3.5 Hz, 1H), 3.68-3.48 (m, 4H), 2.81 (t, *J* = 7.5 Hz, 2H), 1.82-1.74 (br, 2H), 1.70 (quintet, *J* = 7.8 Hz, 2H), 1.45-1.25 (m, 22H), 1.00-0.85 (m, 15H). ¹³C-NMR (CDCl₃, 125 MHz) δ (ppm): 168.6, 168.2, 146.4, 146.0, 145.9, 141.7, 139.1, 137.9, 134.5, 133.1, 130.9, 130.6, 126.1, 125.2, 125.1, 125.0, 124.1, 124.0, 120.8, 120.7, 118.8, 111.4, 104.5, 44.4, 44.2, 37.9, 37.6, 31.7, 31.0, 30.8, 30.4, 29.1, 29.0, 28.8, 24.4, 24.2, 23.2, 22.7, 14.3, 14.2, 11.0, 10.8. HRMS (ESI-TOF) Calculated for C₄₆H₅₇N₂O₂S₂BrH (M+H)⁺: 815.3106 Found: m/z 815.3117. Anal. Calcd for C₄₆H₅₇N₂O₂S₂Br: C, 67.87; H, 7.06; N, 3.44. Found: C, 68.08; H, 7.67; N, 3.31.

(E)-diethyl(5'-(1,1'-bis(2-ethylhexyl)-6'-(5'-hexyl-[2,2'-bithiophen]-5-yl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)-3'-hexyl-[2,2'-bithiophen]-5-yl)phosphonate (6). In a purged Schlenk flask, compound **5** (450 mg, 0.55 mmol), Pd₂(dba)₃ (9 mg) and P(*o*-tyl)₃ (6 mg) were loaded under a flow of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. To a purged dry flask containing compound **3** (0.66 mmol) was added degassed toluene (10 mL). The afforded solution of **3** was then transferred to the Schlenk flask containing **5** and the catalyst via syringe through a septum. The mixture was stirred and heated up to 90°C for 24 hours, then allowed to cool to room temperature and slowly precipitated in methanol (100 mL). The precipitates were filtered by gravity overnight, discarding the filtrate. The solids were then dissolved in a 100 mL round-bottom flask using pure dichloromethane, and the solution was concentrated to a dark solution. This was loaded onto a silica gel column packed with pure dichloromethane, and flushed with pure dichloromethane to remove low-polarity impurities. The eluent was then switched to 99:1 dichloromethane:acetone, which allowed to collect the pure product-containing fractions (R_f = 0.4). Product containing fractions were combined and evaporated to dryness. After drying under vacuum in a dessicator overnight, this afforded the title compound (380 mg, 0.34 mmol, 62%) as a blue powder. ¹H-NMR (CDCl₃, 500 MHz) δ (ppm): 9.13 (t, *J* = 8.6 Hz, 2H), 7.60 (dd, *J*₁ = 3.7 Hz, *J*₂ = 4.2 Hz, 1H), 7.29 (d, *J* = 3.8 Hz,

1H), 7.27-7.24 (m, 2H), 7.24 (s, 1H), 7.22 (t, $J = 3.5$ Hz, 1H), 7.08 (d, $J = 3.8$ Hz, 1H), 7.04 (d, $J = 3.5$ Hz, 1H), 6.89 (s, 2H), 6.70 (dt, $J_1 = 0.9$ Hz, $J_2 = 3.5$ Hz, 1H), 4.26-4.06 (m, 4H), 3.68-3.48 (m, 4H), 2.85-2.75 (m, 4H), 1.90-1.80 (br, 2H), 1.70 (quintet, $J = 7.8$ Hz, 4H), 1.45-1.25 (m, 34H), 1.00-0.85 (m, 18H). ^{13}C -NMR (CDCl_3 , 125 MHz) δ (ppm): 168.8, 168.7, 146.3, 145.9, 145.9, 145.8, 145.8, 144.4, 142.9, 142.4, 142.0, 139.0, 137.7, 137.2, 137.1, 137.0, 134.6, 132.2, 131.6, 130.4, 130.3, 130.2, 130.2, 127.4, 126.6, 126.5, 125.2, 125.1, 124.2, 124.0, 121.6, 121.1, 119.1, 118.9, 104.8, 104.7, 63.0, 62.9, 44.2, 44.2, 38.0, 31.8, 31.7, 31.7, 31.0, 30.6, 30.4, 29.8, 29.4, 29.1, 29.1, 28.9, 24.5, 24.4, 23.3, 22.8, 22.7, 16.5, 16.5, 14.3, 14.3, 14.2, 11.0. HRMS (ESI-TOF) Calculated for $\text{C}_{64}\text{H}_{83}\text{N}_2\text{O}_5\text{PS}_4\text{H}$ ($\text{M}+\text{H}$) $^+$: 1119.4922 Found: m/z 1119.4930. Anal. Calcd for $\text{C}_{64}\text{H}_{83}\text{N}_2\text{O}_5\text{PS}_4$: C, 68.66; H, 7.47; N, 2.50. Found: C, 68.55; H, 7.35; N, 2.57.

(E)-(5'-(1,1'-bis(2-ethylhexyl)-6'-(5'-hexyl-[2,2'-bithiophen]-5-yl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)-3'-hexyl-[2,2'-bithiophen]-5-yl)phosphonic acid (T4iI-A). In a dry round-bottom flask equipped with a stir bar, compound **6** (300 mg, 0.27 mmol) was added and dissolved in 30 mL of anhydrous dichloromethane. The mixture was stirred under a flow of argon, and trimethylsilylbromide (0.35 mL, 0.27 mmol) was added dropwise at room temperature. The mixture was stirred at room temperature for five hours, after which methanol (10 mL) was added and left to stir at room temperature for 3 hours. The mixture was then diluted with dichloromethane (50 mL) and washed with water (100 mL). After the emulsion decanted, the organic phase was collected and evaporated, and kept under vacuum in a dessicator to afford the title compound as a dark blue solid (240 mg, 0.22 mmol, 84 %). ^1H -NMR (CDCl_3 , 500 MHz) δ (ppm): 9.00-8.95 (br, 2H), 7.64-7.48 (br, 1H), 7.20-7.05 (m, 5H), 6.99-6.96 (m, 2H), 6.67 (t, $J = 3.7$ Hz, 1H), 6.61 (m, 1H), 6.56 (m, 1H), 3.70-3.36 (m, 4H), 2.85-2.75 (m, 4H), 1.90-1.80 (br, 2H), 1.76-1.62 (m, 4H), 1.48-1.22 (m, 28H), 0.96-0.84 (m, 18H). ^{13}C -NMR (CDCl_3 , 125 MHz) δ (ppm): 168.5, 168.4, 146.1, 146.0, 145.5, 145.4, 145.3, 142.7, 142.1, 142.0, 141.9, 138.8, 138.7, 137.2, 137.1, 136.4, 136.3, 134.7, 131.7, 131.1, 130.5, 130.4, 130.2, 127.0, 126.9, 125.1, 124.9, 124.1, 124.0, 123.8, 121.3, 120.9, 120.8, 118.4, 118.3, 118.2, 118.0, 104.5, 104.2, 104.1, 44.1, 44.0, 38.0, 37.9, 31.9, 31.8, 31.7, 31.1, 31.0, 30.6, 30.5, 30.4, 29.9, 29.5, 29.4, 29.2, 29.1, 29.0, 24.5, 23.3, 22.9, 22.8, 14.4, 14.3, 11.0. HRMS (ESI-TOF) Calculated for $\text{C}_{60}\text{H}_{75}\text{N}_2\text{O}_5\text{PS}_4\text{H}$ ($\text{M}+\text{H}$) $^+$: 1063.4369 Found: m/z 1063.4344. Anal. Calcd for $\text{C}_{60}\text{H}_{75}\text{N}_2\text{O}_5\text{PS}_4$: C, 67.76; H, 7.52; N, 2.63. Found: C, 67.75; H, 7.34; N, 2.52.

S3. Supporting Figures

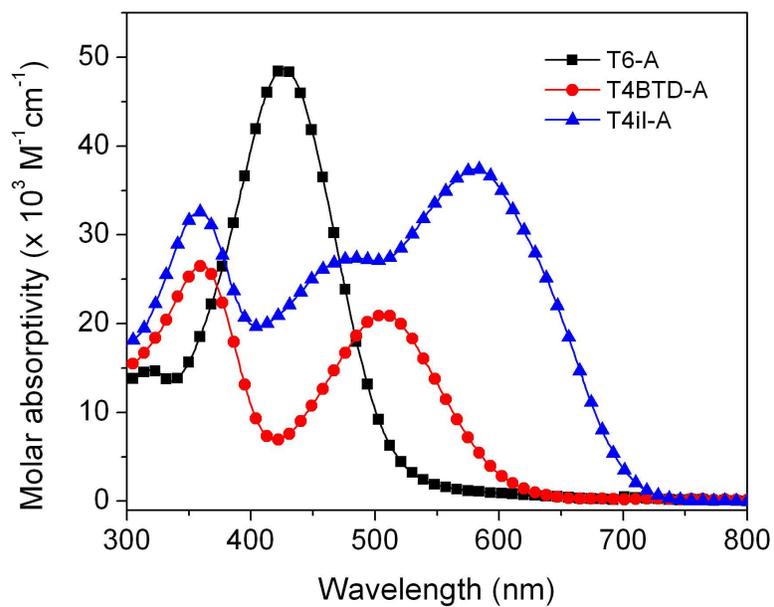


Figure S1. Molar absorptivity of each dye as a function of wavelength, in chloroform solution.

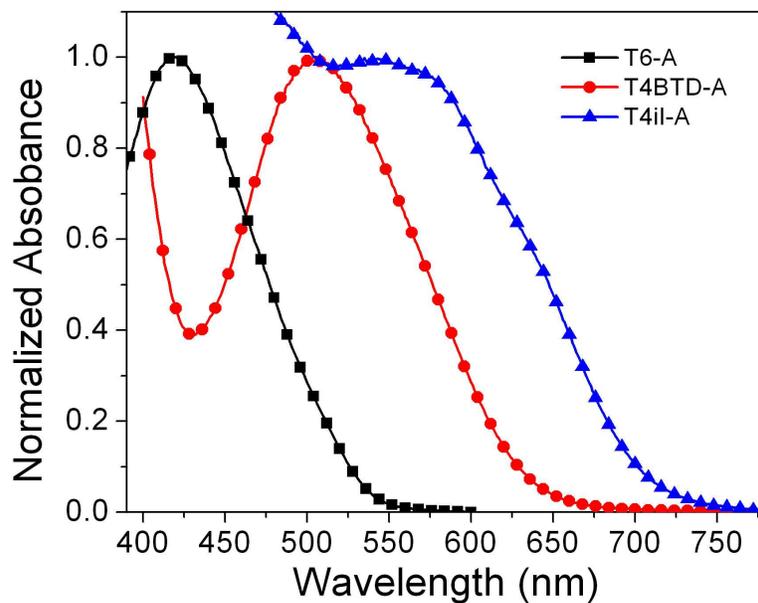


Figure S2. Solid-state absorption spectra (normalized) of the dyes adsorbed on TiO_2 nanoparticles films.

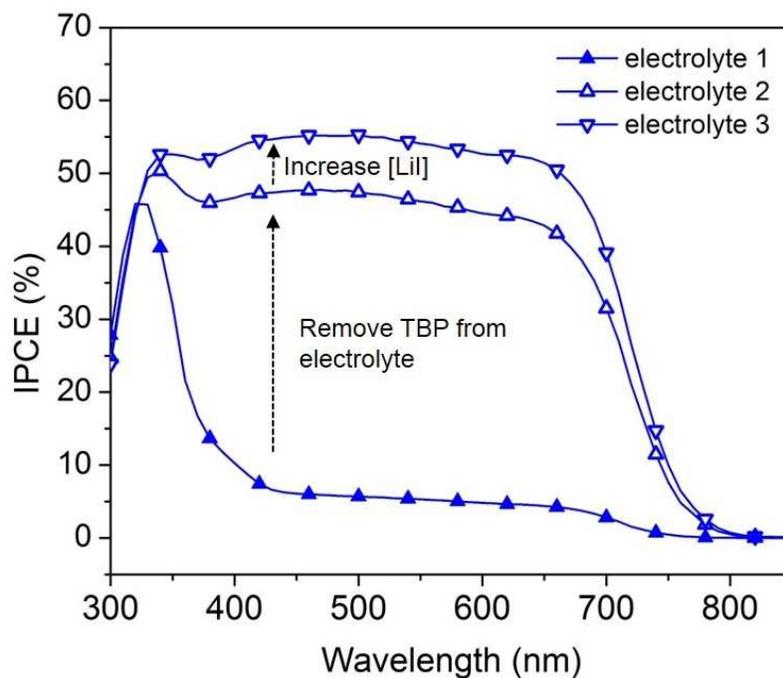


Figure S3. Evolution of the IPCE of the **T4il-A** based DSSCs with electrolytes 1, 2 and 3.

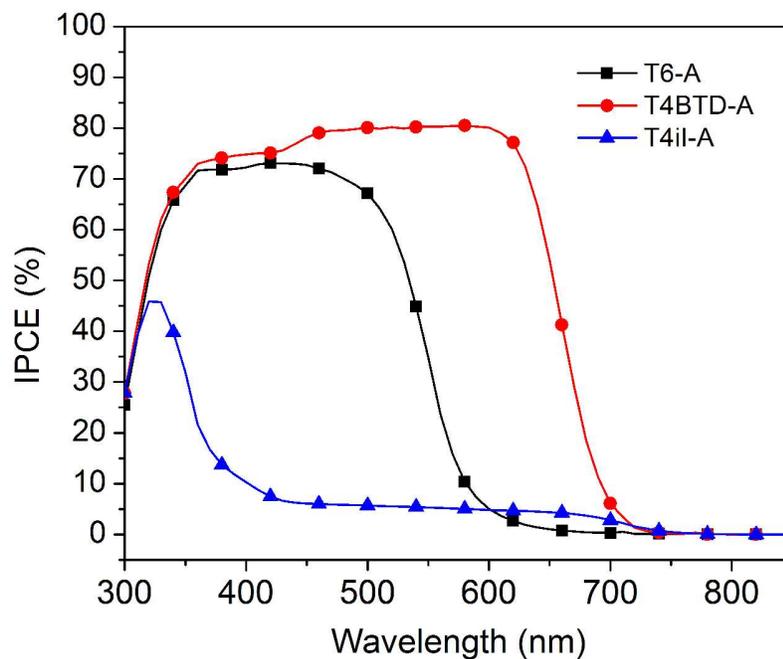


Figure S4. IPCE for the DSSCs based on each dye with electrolyte 1.

S4. References

- (1) Stalder, R.; Xie, D.; Zhou, R.; Xue, J.; Reynolds, J. R.; Schanze, K. S. *Chem. Mater.* **2012**, *24*, 3143.
- (2) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. *Org. Lett.*, **2010**, *12*, 660.
- (3) Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner F.; Gaudl, K.-U. ; Balparda Caro, M.; Fischer P. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 489.