

## Supporting Information

### Variable Gap Reactive Conjugated Oligomer / CdSe Nanocrystal Hybrids

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#### **1. Experimental Section**

##### **1.1. Materials and Methods**

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. The Et<sub>4</sub>NOH (1M) aqueous solution was degassed by three freeze-pump-thaw cycles. Anhydrous solvents were obtained from an anhydrous solvent system. All <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75.5 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts were referenced to residual signals from CHCl<sub>3</sub> (<sup>1</sup>H 7.26 ppm and <sup>13</sup>C 77.23 ppm). Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida.

The ground state absorption measurements were recorded on a Cary100 UV-vis absorption spectrometer and corrected for background due to solvent (HPLC grade) absorption. Fluorescence emission spectra and PL quenching data were collected on a Photon Technology International (PTI) photon counting fluorescence spectrometer. Fluorescence lifetime measurements were conducted on a PicoQuant Picoharp-300 TCSPC instrument. Thermogravimetric analysis (TGA) was performed using dynamic scans under nitrogen.

### 1.2. Electrochemical Studies

Tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) 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 cm<sup>2</sup>) as working electrode, a Ag/Ag<sup>+</sup> reference electrode and platinum foil as a counter electrode; all potentials were reported vs. Fc/Fc<sup>+</sup> 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.

### 1.3. Hybrid Oligomer-CdSe Photovoltaic Device Fabrication

Glass substrates pre-coated with patterned indium tin oxide (ITO) were cleaned with successive sonication in soap, deionized water, acetone, and isopropanol for 15 min each, followed by UV-

ozone treatment for another 15 min. A layer of 40-nm-thick Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin-coated upon the ITO substrates, and annealed at 150°C for 15 min at the air. The oligomer-CdSe hybrids (30 mg/mL in chlorobenzene) were spin-coated upon the PEDOT:PSS layer with thickness of ~ 80-90 nm, followed by the spin-coating of a layer of 40-nm-thick ZnO NPs. The hybrid active layer and ZnO NP layer were co-annealed at 120°C for 20 min under inert atmosphere in a glove box. The devices were completed by vacuum deposition of an Al layer as cathode.

To measure the incident photon-to-electron conversion efficiency (IPCE), the white light emission from a Xe-arc lamp was shined through an Oriel monochromator. The monochromatic light was chopped at 400 Hz by a mechanical chopper prior to incidence onto the devices. The photocurrent response was measured using a Stanford Research Systems 830DSP lock-in amplifier and a Keithley 428 current amplifier. The monochromatic light intensity was measured using a calibrated Newport 818-UV Si detector.

## 2. Synthetic Procedures and Characterizations of Products

**1,4-bis(octyloxy)benzene (1)**<sup>1</sup> 8.6 g KOH powder and 50 mL DMSO were added to a 200 mL round bottom flask, the mixture was degassed for 15 min before 5.5 g (0.05 mol) hydroquinone was added. The system was heated to 80°C. When hydroquinone dissolved, 19.3 g (0.1 mol) 1-bromooctane was added via syringe. The reaction was then allowed to run for 12 hours. After cooling down, the mixture was poured into 600 mL ice-cold water and the crude product was precipitated as tan solid. The crude product was recrystallized by ethanol and then dried as colorless crystals. Yield 89% <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  6.82 (s, 4H), 3.90 (t, 4H,

J=6.6Hz), 1.75 (pentet, 4H J=7.0Hz), 1.45-1.30 (m, 20H), 0.88(t, 6H, J=6.6Hz)  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  153.15, 115.34, 68.61, 31.80, 31.49, 29.37, 29.24, 26.03, 22.64, 14.09

**1,4-diiodo-2,5-bis(octyloxy)benzene (2)<sup>2</sup>** 14.5 g (0.043 mol) **1** and a mixture of 200 mL acetic acid and 40 mL DI water was heated to 80°C in a 500 mL 3-necked round bottom flask with a condenser fitted on. After half an hour, compound **1** was well mixed with acetic/H<sub>2</sub>O (the melting point of **1** was around 60°C, so they actually melted while heating). Then 13 g (0.05 mol) I<sub>2</sub> and 6.9 g KIO<sub>3</sub> was added while the system was kept stirring. After attaining reflux, a solution of sulfuric acid (4 mL in 10 mL water) was added slowly to the reaction. The reaction was then allowed to run 24 hours while the color of the iodine (purple) faded. After cooling down, saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> was added until the color of the reaction mixture turned pale yellow. The mixture was poured into ice-cold water and crude product precipitated as light yellow solid. The crude product was dissolved in DCM and washed with DI water twice. DCM was then evaporated and the crude product was recrystallized in ethanol as white solid, yield 18.8g (75%)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.17 (s, 2H), 3.93 (t, 4H, J=6.4Hz), 1.80 (pentet, 4H, J=6.9Hz), 1.45-1.30 (m, 20H), 0.89 (t, 6H, J= 6.8Hz)  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  152.79, 122.68, 86.29, 70.29, 31.77, 29.21, 29.10, 25.98, 22.63, 14.10

**3-(4-(phenylethynyl)phenyl)prop-2-yn-1-ol (3)<sup>3</sup>** 1,4 diiodobenzene (5g, 15.2 mmol) was dissolved in a mixture of 50 mL THF and 15 mL diisopropylamine (DIPA) in a 250 mL round bottom flask. The solution was degassed under argon flow for 40 min before 20 mg Pd(PPh<sub>3</sub>)<sub>4</sub> and 15 mg CuI were charged. Under the protection of argon, propargyl alcohol (15 mmol) was injected slowly via syringe. The reaction mixture turned cloudy after 30 min, and then phenylene

acetylene (15.2 mmol) was added to the mixture under argon. The reaction was allowed to run overnight before the mixture was filtered, the filtrate was concentrated to remove free amines. The crude product was dissolved in DCM and washed by saturated ammonium chloride (20 mL  $\times$  2) and brine (20 mL  $\times$  3). The organic layer was combined and dried, and the crude product was purified by flash chromatography. (DCM: Hexane v/v 2:1) Yield 2.2g, 45%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.52 (m, 5H), 7.42 (m, 4H), 4.52 (d, 2H), 1.63 (t, 1H)  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  131.62, 131.48, 128.44, 128.37, 123.43, 122.93, 122.28, 91.24, 88.87, 85.37, 51.64.

**1-ethynyl-4-(phenylethynyl)benzene (4)**<sup>4</sup> 500 mg (2.2 mmol) of compound **3** was dissolved by 50 mL diethyl ether in a 200 mL round bottom flask. The system was degassed for 30 min. Then, 10 equivalents of  $\text{MnO}_2$  (22 mmol) and KOH (22 mmol) powder were well mixed and divided into three portions. One portion was added every one hour with vigorous stirring of the reaction. The reaction was allowed to run for another 2h after the addition of the last portion of  $\text{MnO}_2/\text{KOH}$ . The reaction mixture was filtered and passed through a short column by DCM and dried by vacuo. Compound **4** was obtained as pale white solid. Yield 89%  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.55 (m, 2H), 7.49 (s, 4H), 7.37 (m, 3H), 3.19 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  132.15, 131.72, 131.56, 128.62, 128.46, 123.85, 122.99, 91.46, 88.91, 83.35, 78.96

**Diethyl-(4-iodophenyl)phosphonate (5)** 16.5 g (50 mmol) 1,4-diiodobenzene and 0.33 g (2.5 mmol) anhydrous  $\text{NiCl}_2$  was charged into a 100 mL 3-necked round bottom flask with an argon

inlet and outlet. The mixture was degassed for 20 min and then melted under 145°C. While stirring, 10.4 mL (60 mmol) P(OEt)<sub>3</sub> was slowly added into the flask via syringe with argon flow. 30 min later, the reaction mixture turned brown. The product was purified by flash chromatography. Hexane was employed first to remove free P(OEt)<sub>3</sub> and 1,4-diiodobenzene, and then the product was eluted by DCM. Evaporation of solvent provided pure product as light yellow oil. Yield 70% <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.83 (m, 2H), 7.52 (m, 2H), 4.10 (m, 4H), 1.30 (m, 6H) <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 138.02, 133.30, 128.35, 100.21, 62.40, 16.34. <sup>31</sup>P NMR (CDCl<sub>3</sub>, against H<sub>3</sub>PO<sub>4</sub>, ppm): 19.1

**3-(4-ethynylphenyl)prop-2-yn-1-ol (6)**<sup>5</sup> This compound was synthesized in a two-step reaction. Step 1 was Sonogashira cross-coupling reaction that was carried out under similar condition with compound **3**, except that trimethylsilyl acetylene (instead of phenylene acetylene) was installed. The intermediate was subsequently deprotected in step 2, where mild basic condition was employed: 500 mg intermediate (3-(4-((trimethylsilyl)ethynyl)phenyl)prop-2-yn-1-ol) was dissolved in DCM (20 mL) and MeOH (20 mL) mix solvent and the system was degassed for 30 min. Excess amount of K<sub>2</sub>CO<sub>3</sub> (3.5 g) solid was added and the reaction was vigorously stirred for 4h. The reaction mixture was filtered and the filtrate was concentrated under vacuo to yield the title compound as a white solid. Yield for 2 steps 40% <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.47-7.35 (m, 4H), 4.51 (d, 2H), 3.18 (s, 1H), 1.69 (t, 1H) <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 132.23, 131.68, 123.15, 122.32, 89.25, 85.30, 83.34, 79.13, 51.65.

**Diethyl-(4-((4-ethynylphenyl)ethynyl)phenyl)phosphonate(7)** This compound was synthesized in a two-step reaction. Step 1: compounds **5** (150 mg, 0.44 mmol) and **6** (68.8 mg, 0.44 mmol) were dissolved by a mix solvent of 15 mL THF and 5 mL DIPA in a 50 mL round bottom flask. The system was degassed by argon for 25 min before 8 mg Pd(PPh<sub>3</sub>)<sub>4</sub> and 5 mg CuI were charged. The reaction was gently heated to 50°C and let run for 12 hours. The reaction mixture was filtered and the filtrate was concentrated and redissolved in DCM. Washed by saturated ammonium chloride (20 mL × 2) and brine (20 mL × 3), the crude product was dried under vacuo and purified by flash chromatography. (DCM: MeOH v/v 20:1) Step 2: the intermediate was deprotected at propargyl alcohol site under the same condition described for compound **4**. The deprotected product was obtained as pale yellow powder. Yield for 2 steps 68% <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 7.80 (m, 2H), 7.60 (m, 2H), 7.49 (s, 4H), 4.16 (m, 4H), 3.19 (s, 1H), 1.35 (t, 3H) <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ 132.00, 131.89, 131.78, 131.58, 129.65, 127.40, 122.89, 91.73, 82.42, 62.57, 51.77, 16.60 <sup>31</sup>P NMR (CDCl<sub>3</sub>, against H<sub>3</sub>PO<sub>4</sub>, ppm):19.0 ESI-TOF-MS calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub>PNa (M+Na) 361.0970 found 361.0958 Anal. calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub>P: C, 71.00; H, 5.66 found: C, 69.85; H, 5.70

**OPE-E (8)** In a 100 mL round bottom flask, compounds **2** (176 mg 0.3 mmol) and **7** (100 mg, 0.296 mmol) were dissolved by a mix solvent of 20 mL THF and 10 mL DIPA in a 50 mL round bottom flask. The system was degassed by argon for 40 min before 10 mg Pd(PPh<sub>3</sub>)<sub>4</sub> and 8 mg CuI were charged. The mixture was stirred under room temperature for 1h and then **4** (60.7 mg 0.3 mmol) was quickly added to the system under argon. The reaction was then gently heated to 50°C and allowed to run overnight. The reaction mixture was filtered and the filtrate was concentrated and redissolved in DCM. Washed by saturated ammonium chloride (20 mL × 2)

and brine (20mL  $\times$  3), the crude product was dried under vacuo and purified by flash chromatography using DCM as eluent. Yield 80mg, 31%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.80 (m, 2H), 7.62 (m, 2H), 7.54 (m, 9H), 7.35 (m, 4H), 7.03 (s, 2H), 4.15 (m, 4H), 4.05 (t, 4H), 1.86 (pentet, 4H), 1.50-1.30 (m, broad, 20H), 1.31 (t, 6H), 0.88 (t, 6H)  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  14.1, 16.4, 23.1, 26.0, 29.3, 29.6, 33.2, 61.8, 67.9, 96.0, 120.0, 128.4, 124.0, 133.1, 134.4  $^{31}\text{P}$  NMR (300 MHz  $\text{CDCl}_3$ , ppm)  $\delta$  19.5 ppm. HRMS (APCI):  $m/z$  calcd for  $\text{C}_{58}\text{H}_{63}\text{O}_5\text{PH}$  ( $\text{MH}^+$ ) 871.4491 found 871.4482; Anal. calcd for  $\text{C}_{58}\text{H}_{63}\text{O}_5\text{P}$ : C, 79.97; H, 7.29 found C, 79.80; H, 7.36.

**OPE-A (9)** In a round bottom flask equipped with stirring bar, **OPE-E** was dissolved in DCM. Upon stirring, excess amount of trimethylsilyl bromide (TMSBr) was added via syringe. The reaction was allowed to run for 30 min before nitrogen inlet and outlet were set up. After all the DCM and free TMSBr were evaporated under nitrogen flow, MeOH was added and the mixture was kept stirring for another 30 min. The crude product was dried under vacuo and dissolved in a few drops of  $\text{CHCl}_3$ . 10 mL MeOH was added to obtain the title compound as yellow precipitate, which is collected by centrifuge. Yield (95%)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  10.25 (broad, 2H) 7-8 (broad, 16H), 4.20 (broad, 4H), 1.0-1.8 (broad, 22H)  $^{31}\text{P}$  NMR (300 MHz  $\text{CDCl}_3$ , ppm)  $\delta$  22ppm. Anal. calcd for  $\text{C}_{54}\text{H}_{55}\text{O}_5\text{P}$ : C, 79.58; H, 6.80 found C, 79.57; H, 6.95.

**3,3'''-bis(hexyl)-2,2':5',2'':5'',2'''-quaterthiophene (10).**<sup>6</sup> To a suspension of magnesium turnings (319 mg, 13.1 mmol) in anhydrous diethyl ether (20mL) is added compound 2-bromo-3-hexylthiophene (3.10 g, 12.54 mmol) dropwise while heating gently. After refluxing for 2 hours,



the Grignard reagent is transferred dropwise to a solution of 5,5'-dibromo-2,2'-bithiophene (1.62g, 5.02 mmol) and Ni(dppp)Cl<sub>2</sub> (35 mg, 0.07 mmol) in a mixture of toluene and diethyl ether (50mL, 3:2). The reaction mixture was refluxed at 55~60°C overnight, then quenched with a saturated aqueous solution of ammonium chloride (100mL) and extracted twice with chloroform. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate, brine and water, and then dried over magnesium sulfate. The solvent was evaporated and the residue, an orange-brown oil, was purified by column chromatography on silica gel with pure hexanes as eluent to yield the title compound (2.15g, 4.31 mmol, 86%) as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.18 (d, J = 5.2 Hz, 1H), 7.13 (d, J = 3.8 Hz, 1H), 7.03 (d, J = 3.8 Hz, 1H), 6.94 (d, J = 5.2 Hz, 1H), 2.79 (t, J = 7.7 Hz, 2H), 1.66 (m, 2H), 1.36 (m, 6H), 0.89 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 140.08, 137.00, 135.53, 130.52, 130.30, 126.73, 124.06, 124.03, 31.88, 30.86, 29.50, 29.44, 22.84, 14.32. HRMS (ESI-TOF): *m/z* calcd for C<sub>28</sub>H<sub>34</sub>S<sub>4</sub> (MH<sup>+</sup>) 499.1616 found 499.1645. Anal. calcd for C<sub>28</sub>H<sub>34</sub>S<sub>4</sub>H: C 67.42; H 6.87 found C 67.51; H 6.85.

**5,5'''-dibromo-3,3'''-bis(hexyl)-2,2':5',2'':5'',2'''-quaterthiophene (11).**<sup>6</sup> A solution of **10** (2.00 g, 4.01 mmol) in anhydrous dimethylformamide (30mL) is stirred at 0 °C and N-bromosuccinimide (1.50 mg, 8.42 mmol) is added portion wise to the reaction mixture in the absence of light. After stirring for five hours while warming up to room temperature, a precipitate crashes out of the solution. Filtration and washing with methanol yields the title compound (2.32 g, 3.53 mmol) as a yellow powder, which is then recrystallized from a hexanes/ethanol mixture to afford yellow crystals (2.05 g, 3.12 mmol, 78%) Mp 67-68 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.11 (d, J = 3.8 Hz, 1H), 6.96 (d, J = 3.8 Hz, 1H), 6.90 (s, 1H), 2.71 (t, J = 7.7 Hz, 2H), 1.61 (m, 2H), 1.33 (m, 6H), 0.89 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 140.76, 137.25, 134.30,

132.92, 131.91, 127.19, 124.22, 110.88, 31.82, 30.71, 29.43, 29.31, 22.79, 14.30. HRMS (ESI-TOF):  $m/z$  calcd for  $C_{28}H_{32}Br_2S_4H$  ( $MH^+$ ) 656.9782 found 656.9806. Anal. calcd for  $C_{28}H_{32}Br_2S_4$ : C 51.22; H 4.91 found C 51.07; H 5.02.

**5-bromo-3,3'',5''''-trihexyl-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (12).** In a dry Schlenk flask, compound **11** (3.35 g, 5.1 mmol),  $Pd_2dba_3$  (114 mg, 0.11 mmol, chloroform adduct) and  $P(o\text{-}t\text{-}yl)_3$  (70 mg, 0.23 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. 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.25 g, 7.65 mmol) was dissolved in degassed toluene (50 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (11.5 mL, 11.5 mmol) was then added to the reaction flask, and the mixture was vigorously stirred under argon at 90°C for twelve hours. After the mixture had cooled down, it was poured in water and washed several times with water and finally with brine, then dried over magnesium sulfate. The solvents were then evaporated to afford a dark red oil. Column chromatography on silica gel using pure hexanes as eluent ( $R_f$  = 0.45) yielded the title compound **12** as an orange oil (1.17 g, 1.6 mmol, 31 %). *Note: With an  $R_f$  of 0.3 in pure hexanes, the decoupled sexithiophene by-product was isolated as an orange solid (0.98 g, 1.18 mmol, 23 %).*  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.12 (d,  $J$  = 3.8 Hz, 1H), 7.11 (d,  $J$  = 3.8 Hz, 1H), 7.02 (d,  $J$  = 3.8 Hz, 1H), 6.97 (d,  $J$  = 3.6, 1H), 6.96 (d,  $J$  = 3.8, 1H), 6.94 (s, 1H), 6.90 (s, 1H), 6.68 (d,  $J$  = 3.6, 1H), 2.80 (t,  $J$  = 7.8, 2H), 2.75 (t,  $J$  = 7.6, 2H), 2.72 (t,  $J$  = 7.8, 2H), 1.68 (m, 4H), 1.62 (m, 2H), 1.39 (m, 6H), 1.33 (m, 12H), 0.90 (m, 9H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  145.82, 140.68, 140.66, 137.56, 136.45, 136.11, 135.66, 134.65, 134.00, 132.90, 132.02, 128.75, 127.18,

126.38, 126.12, 125.04, 124.28, 123.97, 123.57, 110.77, 31.88, 31.83, 31.79, 31.77, 30.72, 30.65, 30.43, 29.74, 29.45, 29.44, 29.32, 28.97, 22.83, 22.81, 22.80, 14.32, 14.30. HRMS (APCI):  $m/z$  calcd for  $C_{38}H_{47}BrS_5H$  ( $MH^+$ ) 745.1510 found 745.1539. Anal. calcd for  $C_{38}H_{47}BrS_5$ : C 61.34; H 6.37 found C 61.27; H 6.39.

**Diethyl thiophen-2-ylphosphonate (13).**<sup>7</sup> 2-bromothiophene (10 g, 62.5 mmol) and anhydrous nickel chloride (387 mg, 3.1 mmol) were added in a dry flask equipped with a stir bar, an addition funnel and a short path distillation apparatus under a flow of argon. The mixture was heated to 145°C while stirring, at which point triethylphosphite was added dropwise from the addition funnel into the reaction mixture. The mixture alternates from deep blue to brown at each drop of triethylphosphite, with a concomitant evolution of ethylbromide which is distilled off. The reaction is left to stir at 145°C for 3 hours until the phosphite addition was complete and no more ethylbromide evolution was observed. The mixture is then allowed to cool back to room temperature, and the crude is distilled under reduced pressure (1 mtorr). After some of the starting material is collected off at 30°C under reduced pressure, the title compound is collected at 85°C as a pale yellow oil. (7.58 g, 34.4 mmol, 55 %).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.70-7.62 (m, 2H), 7.16 (quartet,  $J$  = 3.3 Hz, 1H), 4.20-4.00 m, 4H), 1.31 (t,  $J$  = 7.1 Hz, 6H).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  136.98, 136.81, 133.63, 133.53, 128.35, 128.10, 62.88, 62.81, 16.46, 16.37.  $^{31}P$  NMR ( $CDCl_3$ , against  $H_3PO_4$ ): 13.07.

**Diethyl (5-(trimethylstannyl)thiophen-2-yl)phosphonate (14).** Thienylphosphonate **13** was diluted with anhydrous tetrahydrofuran (40 mL) in a dry flask equipped with stir bar under argon

flow, and cooled down to  $-78^{\circ}\text{C}$ . Lithium diisopropylamine was prepared in a separate flask by adding *n*-butyllithium (4.5 mmol, 1.4 M in hexanes) to a diisopropylamine (0.71 mL, 5 mmol) solution in anhydrous THF (7mL) cooled to  $-78^{\circ}\text{C}$  and stirring at  $-78^{\circ}\text{C}$  for 30 minutes. The LDA solution was then added slowly to the cooled thienylphosphonate reaction mixture over the course of five minutes, and left to stir at such temperature for 3 hours, after which trimethyltin chloride (solid) was added to the reaction flask in one portion. The mixture was left stirring while slowly warming up to room temperature over 3 hours. The solvent was then evaporated, and the crude was redissolved in 3 mL of dichloromethane to which the addition of 20 mL of hexanes results in white precipitates. The salts were filtered off, and the clear yellow solution was evaporated to afford the title compound as a clear oil in 85-90 % purity (by  $^1\text{H}$ NMR), which was used without further purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.74 (dd,  $J = 4.2, 3.3$  Hz, 1H), 7.23 (t,  $J = 2.7$ , 1H), 4.20–4.00 (m, 4H), 1.33 (t,  $J = 7.1$ , 6H), 0.40 (s, 9H).

**4,7-bis(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (15).**<sup>8</sup> In a dry Schlenk flask, 4,7-dibromobenzo[c][1,2,5]thiadiazole (3.0 g, 10.3 mmol),  $\text{Pd}_2\text{dba}_3$  (283 mg, 0.23 mmol, chloroform adduct) and  $\text{P}(o\text{-tyl})_3$  (338 mg, 1.11 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. 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.3 g, 24.8 mmol) was dissolved in degassed toluene (40 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (36 mL, 36 mmol) was then added to the reaction flask, and the mixture was vigorously stirred under argon at  $90^{\circ}\text{C}$  for twelve hours. After it cooled back to room temperature, the mixture was poured in 300 mL of cold methanol

(0°C). The orange precipitates that formed were filtered and redissolved in 100 mL of hexanes and passed through a short plug of silica gel using pure hexanes. After evaporation of the solvent, the title compound was obtained as a bright orange solid (4.58 g, 9.77 mmol, 92 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.98 (d, J = 1.3 Hz, 1H), 7.83 (s, 1H), 7.04 (s, 1H), 2.70 (t, J = 7.9 Hz, 2H), 1.71 (quintet, J = 7.7 Hz, 2 H), 1.35 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.81, 144.55, 139.20, 129.25, 126.20, 125.71, 121.72, 31.93, 30.87, 30.69, 29.28, 22.86, 14.34.

**4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (16).**<sup>8</sup> Compound **15** (4.58 g, 9.77 mmol) was dissolved in chloroform (150 mL) and cooled to 0°C while protecting the solution from light exposure. N-bromosuccinimide (3.97 g, 22.3 mmol) was then added to the mixture in one portion, followed by two drops of acetic acid. The mixture was allowed to stir while warming up to room temperature for 12 hours. The mixture was then poured in water and washed once with water. The solvent was evaporated and the crude was purified by column chromatography on silica gel using pure hexanes as eluent. Evaporating the collected fractions afforded the title compound as a thick red oil which eventually crystallized to a bright red solid (5.97 g, 9.53 mmol, 97 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.74 (s, 1H), 7.69 (s, 1H), 2.63 (t, J = 7.4 Hz, 2H), 1.67 (quintet, J = 3.9 Hz, 2H), 1.36 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 152.38, 143.26, 138.69, 128.29, 125.45, 124.98, 111.81, 31.87, 29.97, 29.90, 29.19, 22.85, 14.33.

**4-(5-bromo-4-hexylthiophen-2-yl)-7-(3,5'-dihexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (17).** In a dry Schlenk flask, compound **16** (5.97 g, 9.53 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (250 mg, 0.20 mmol, chloroform adduct) and P(*o*-tyl)<sub>3</sub> (275 mg, 0.90 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. 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.26 g, 7.69 mmol) was dissolved in degassed toluene (100 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (11.5 mL, 11.5 mmol) was then added to the reaction flask, and the mixture was vigorously stirred under argon at 90°C for twelve hours. The mixture was allowed to cool down to room temperature, diluted with 100 mL of hexanes and poured in water. The organic phase was washed with water twice, dried over magnesium sulfate and evaporated. The red oil was then purified by column chromatography using pure hexanes as eluent ( $R_f = 0.5$ ) to afford the title compound as a red thick oil (1.75 mg, 2.45 mmol, 26 %). *Note: With an  $R_f$  of 0.75 in pure hexanes, the starting material 16 was recovered (3.16 g, 5.04 mmol).*  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H), 7.72 (s, 1H), 7.70, 7.66 (ABq,  $J_{AB} = 7.7$  Hz, 2H), 7.02 (d,  $J = 3.6$  Hz, 1H), 6.75 (d,  $J = 3.6$  Hz, 1H), 2.84 (t,  $J = 8.1$  Hz, 2H), 2.81 (t,  $J = 9.2$  Hz, 2H), 2.63 (t,  $J = 7.5$  Hz, 2H), 1.72 (m, 6H), 1.45-1.30 (m, 12 H), 0.92 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  152.52, 152.44, 146.72, 143.14, 140.01, 138.88, 136.29, 133.58, 133.39, 130.97, 127.93, 125.94, 125.88, 125.05, 125.00, 124.87, 124.69, 111.51, 31.92, 31.87, 31.79, 30.80, 30.39, 29.97, 29.90, 29.72, 29.55, 29.21, 29.05, 22.89, 22.86, 22.81, 14.34, 14.32. HRMS (APCI):  $m/z$  calcd for  $\text{C}_{36}\text{H}_{45}\text{BrN}_2\text{S}_4\text{H}$  ( $\text{MH}^+$ ) 713.1649 found 713.1665. Anal. calcd for  $\text{C}_{36}\text{H}_{45}\text{BrN}_2\text{S}_4$ : C, 60.56; H, 6.35; N 3.92 found C, 60.68; H, 6.23; N 3.72.

**T6-E (18).** In a dry Schlenk flask, compound **12** (1.82 g, 2.45 mmol),  $\text{Pd}_2\text{dba}_3$  (40 mg, 0.04 mmol, chloroform adduct) and  $\text{P}(o\text{-tyl})_3$  (30 mg, 0.1 mmol) were loaded together and kept under

vacuum during 30 minutes while being subjected to three vacuum/argon purge cycles, and finally refilled with argon. Compound **14** (3 mmol) was dissolved in degassed anhydrous toluene (30 mL) and transferred to the reaction flask through a septum using a syringe. The mixture was heated to 90°C and stirred for 12 hours. After cooling back to room temperature, the mixture was diluted with ethyl acetate and washed with water and brine. After drying over magnesium sulfate, the solvent was evaporated and the crude was purified by column chromatography using 9:1 dichloromethane : ethyl acetate ( $R_f = 0.2$ ) as eluent. This afforded the title compound as thick red oil which eventually solidifies to a red-orange solid over time (650 mg, 0.74 mmol, 30 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.55 (dd,  $J = 4.2, 3.8$  Hz, 1H), 7.18 (t,  $J = 3.5$  Hz, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 7.10 (s, 1H), 7.06 (d,  $J = 3.8$  Hz, 1H), 7.03 (d,  $J = 3.8$  Hz, 1H), 6.97 (d,  $J = 3.5$  Hz, 1H), 6.93 (s, 1H), 6.68 (d,  $J = 3.6$  Hz, 1H), 4.20–4.00 (m, 4H), 2.79 (t,  $J = 7.6$  Hz, 2H), 2.77 (t,  $J = 7.9$  Hz, 2H), 2.75 (t, 7.8 Hz, 2H), 1.68 (m, 6H), 1.40 (m, 6H), 1.36 (t,  $J = 7.1$  Hz, 6H), 1.33 (m, 12H), 0.90 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  145.75, 140.70, 140.58, 136.95, 136.66, 136.02, 135.46, 135.18, 135.03, 134.68, 129.72, 128.86, 126.77, 126.46, 126.34, 126.11, 125.03, 124.09, 124.05, 123.53, 31.90, 31.80, 31.77, 30.65, 30.63, 30.43, 29.79, 29.76, 29.49, 29.48, 28.99, 22.85, 22.80, 14.34, 14.31.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , against  $\text{H}_3\text{PO}_4$ ):  $\delta$  11.80. HRMS (APCI):  $m/z$  calcd for  $\text{C}_{46}\text{H}_{59}\text{O}_3\text{PS}_6\text{H}$  ( $\text{MH}^+$ ) 883.2599 found 883.2526. Anal. calcd for  $\text{C}_{46}\text{H}_{59}\text{O}_3\text{PS}_6$ : C, 62.55; H, 6.73 found C 62.93; H 7.04.

**T6-A (19).** Compound **18** (300 mg, 0.34 mmol) was added in a dry flask equipped with a stir bar and under argon flow, then dissolved in anhydrous dichloromethane (10 mL). To the orange solution was added trimethylsilylbromide (0.45 mL, 3.4 mmol) dropwise at room temperature, over the course of five minutes. The mixture was stirred at room temperature for 5 hours, after

which methanol (10 mL) was added to the flask and allowed to stir for an additional 3 hours at room temperature. The precipitates that formed were filtered to give an orange solid. Only one spot with  $R_f = 0$  was observed by TLC on silica gel plates eluting with a 1:1 mixture of dichloromethane : ethyl acetate, suggesting complete conversion. The solids were dissolved in a minimum of dichloromethane and reprecipitated in methanol then filtered, and repeating this twice afforded the title compound as an orange solid (240 mg, 0.29 mmol, 85%).  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  7.40-7.36 (br, 5H), 7.23 (br, 1H), 7.18 (br, 1H), 7.15 (br, 1H), 7.14 (br, 1H), 6.82 (br, 1H), 2.59-2.57 (br, 6H), 1.63 (br, 6H), 1.40-1.20 (br, 18H), 0.87 (br, 9H).  $^{31}\text{P}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , against  $\text{H}_3\text{PO}_4$ ):  $\delta$  5.91. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{42}\text{H}_{51}\text{O}_3\text{PS}_6\text{-H}$  (M-H $^-$ ) 825.1827 found 825.1812. Anal. calcd for  $\text{C}_{42}\text{H}_{51}\text{O}_3\text{PS}_6$ : C, 60.98; H, 6.21 found C 60.15; H 6.41.

**T4BTD-E (20).** In a dry Schlenk flask, compound **17** (1.75 g, 2.45 mmol),  $\text{Pd}_2(\text{dba})_3$  (60 mg, 0.05 mmol, chloroform adduct) and  $\text{P}(o\text{-tyl})_3$  (70 mg, 0.23 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. Compound **14** (9 mmol) was dissolved in degassed toluene (30 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. The mixture was then heated to 90°C and stirred for 12 hours. After cooling down to room temperature, the mixture was diluted with chloroform (100 mL) and washed once with water. The solvent was evaporated to a dark red oil. The crude was purified by column chromatography using 7:3 hexanes : ethyl acetate as eluent, followed by a second column using 9:1 dichloromethane : acetone as eluent, to afford the title compound as a dark red thick oil (1.34 g, 1.57 mmol, 64 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.90 (s, 1H), 7.88 (s, 1H), 7.69, 7.65 (ABq,  $J_{\text{AB}} = 7.7$  Hz, 2H), 7.62 (dd,  $J = 4.2, 3.7$  Hz, 1H), 7.24 (d,  $J = 3.6$  Hz, 1H), 7.01



(d,  $J = 3.6$  Hz, 1H), 6.73 (d,  $J = 3.6$  Hz, 1H), 4.21 (m, 4H), 2.85-2.75 (m, 6H), 1.71 (m, 6H), 1.50-1.30 (m, 24H), 0.90 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  152.46, 152.44, 146.64, 144.65, 144.54, 141.85, 139.91, 138.33, 137.26, 137.12, 136.18, 133.529, 133.418, 130.958, 130.837, 130.807, 130.438, 128.353, 126.542, 126.319, 125.975, 125.79, 125.56, 125.50, 124.82, 124.67, 124.64, 62.94, 62.87, 31.86, 31.84, 31.75, 31.73, 30.73, 30.60, 30.33, 29.82, 29.68, 29.51, 29.46, 29.00, 22.84, 22.81, 22.76, 16.54, 16.45, 14.30, 14.27.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , against  $\text{H}_3\text{PO}_4$ ):  $\delta$  12.00. HRMS (APCI):  $m/z$  calcd for  $\text{C}_{44}\text{H}_{57}\text{N}_2\text{O}_3\text{PS}_5\text{H}$  ( $\text{MH}^+$ ): 853.2783 found 853.2790. Anal. calcd for  $\text{C}_{44}\text{H}_{57}\text{N}_2\text{O}_3\text{PS}_5$ : C, 61.94; H, 6.73; N, 3.28 found: C, 61.60, N, 7.10, H, 3.16.

**T4BTD-A (21).** In a dry round-bottom flask equipped with a stir bar, **T4BTD-PE** (300 mg, 0.35 mmol) was added and dissolved in 10 mL of anhydrous dichloromethane. The mixture was stirred under a flow of argon, and trimethylsilylbromide (0.46 mL, 0.35 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 without drying, and kept under vacuum to afford the title compound as a dark purple solid (265 mg, 0.33 mmol, 94 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.70-7.55 (br, 3H), 7.15-7.00 (br, 3H), 6.90 (br, 1H), 6.68 (br, 1H), 2.80 (br, 2H), 2.75-2.55 (br, 4H), 1.80-1.50 (m, 6H), 1.50-1.35 (m, 18H), 1.00-0.85 (m, 9H).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , against  $\text{H}_3\text{PO}_4$ ):  $\delta$  12.44. Anal. calcd for  $\text{C}_{40}\text{H}_{49}\text{N}_2\text{O}_3\text{PS}_5$ : C, 60.27; H, 6.20; N, 3.51 found .60.17, 6.22, 3.31.

### CdSe Nanocrystals Synthesis

CdSe nanocrystals were synthesized according to the reported procedures with some modifications.<sup>9,10</sup> CdO (76 mg), oleic acid (OA, 90%, 3 mL), and trioctylphosphine oxide (TOPO, 99%, 3 g) were mixed and heated to 280 °C under N<sub>2</sub> flow. Then the selenium/trioctylphosphine (Se, 78 mg; and TOP, 1 mL) mixture was injected at 280 °C, and the reaction had been kept at the temperature of 270 – 290 °C for 5 min to produce ~6 nm CdSe particles. The reaction was terminated by toluene. The CdSe nanocrystals were precipitated by adding methanol and collected using centrifugation. The purification procedure were repeated twice and then dispersed in pure chloroform for further study or characterization.

### 3. Supporting Figures

#### 3.1. Electrochemistry.

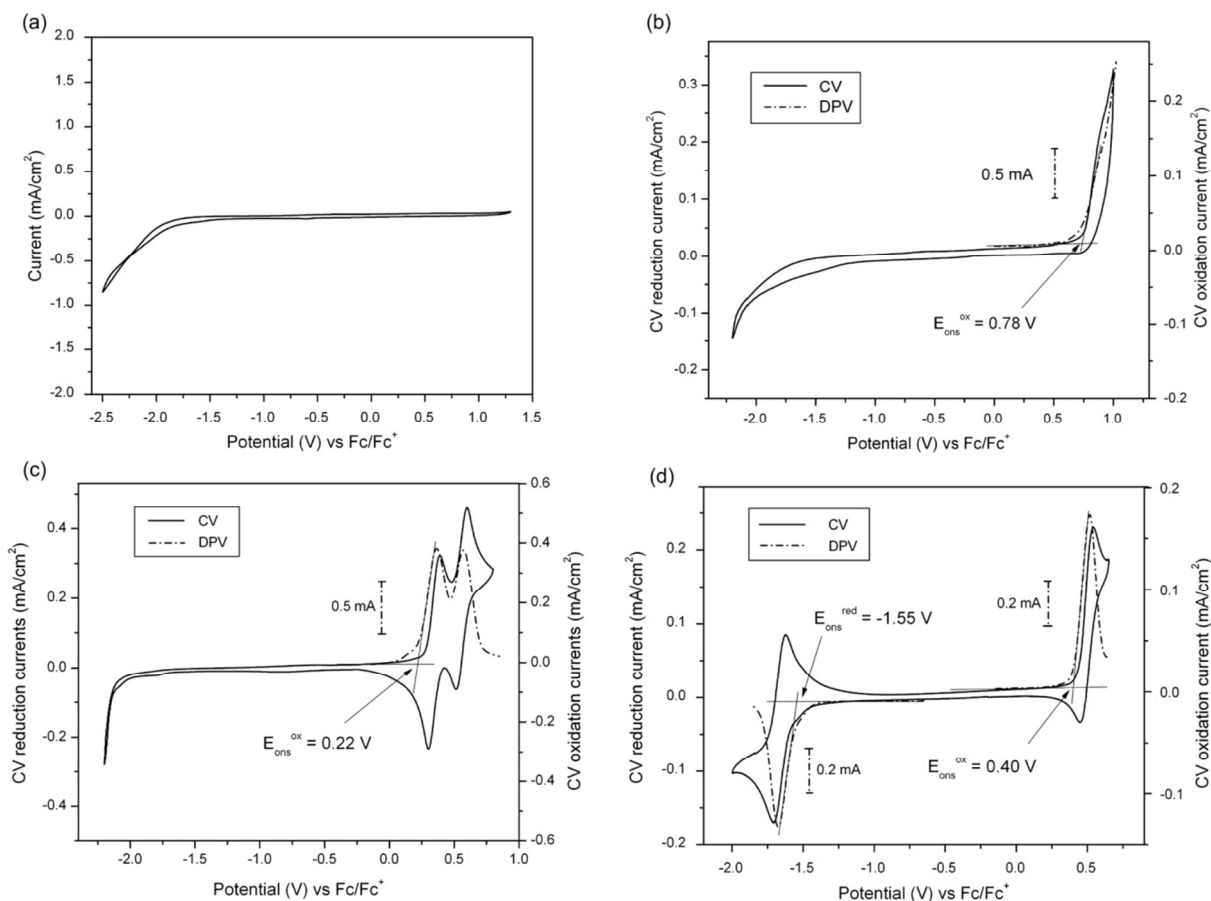


Figure S1. Background CV of (a) the pure 0.1 M TBAPF<sub>6</sub>/DCM electrolyte, at 50 mV/s scan rate. CV (solid line) and DPV (dashed line) of (b) **OPE-A**, (c) **T6-A** and (d) **T4BTD-A** in 0.1 M TBAPF<sub>6</sub> in dichloromethane, at 50 mV/s scan rate.

### 3.2. Photoluminescence Quenching Measurements.

The concentration of the CdSe NCs stock solution was determined to be  $27\mu\text{M}$  by a reported method,<sup>11</sup> and diluted to  $20\mu\text{M}$  for experiment A or to  $1\mu\text{M}$  for experiment B.

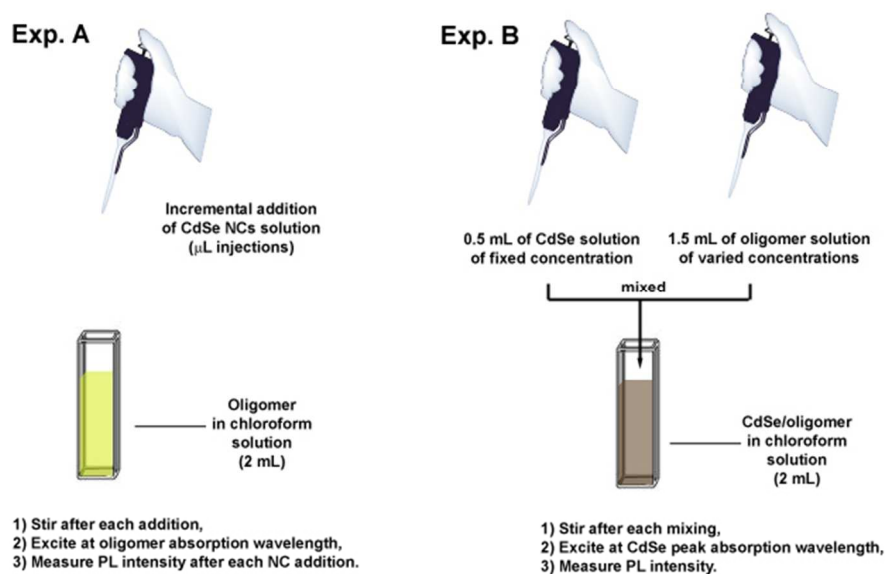


Figure S2. Pictorial description of the photoluminescence quenching experiments.

Experiment A (Figure S2) describes the PL quenching experiment of oligomer emission by addition of incremental amounts NC solution. To a solution of 2mL oligomer in  $\text{CHCl}_3$  ( $5\mu\text{M}$ ) in a 1cm quartz FL cuvette, CdSe NCs in  $\text{CHCl}_3$  with known concentration ( $20\mu\text{M}$ ) were added so that the ratio of oligomer to CdSe was controlled. More than 90% of photoluminescence of the oligomers were quenched when 100 nM of CdSe NCs were added (Oligomer: CdSe 50:1).

Experiment B describes the reverse experiment, where the evolution of the emission of the NCs in solution is monitored at various ratios of CdSe NC:oligomer. As depicted in Figure S2 (right), this was achieved by mixing 0.5 mL of a  $1\mu\text{M}$  CdSe solution with 1.5 mL of oligomer solution of the following concentrations:  $16.7\mu\text{M}$  (for 50:1 oligomer:CdSe);  $33.4\mu\text{M}$  (for 100:1 oligomer:CdSe) and  $66.8\mu\text{M}$  (for 200:1 oligomer:CdSe). The solutions were stirred and irradiated with light at the CdSe peak absorption wavelength (which does not overlap with the

absorption of **T6-A**). The resulting emission was recorded and plotted against that of other oligomer:CdSe ratio mixtures.

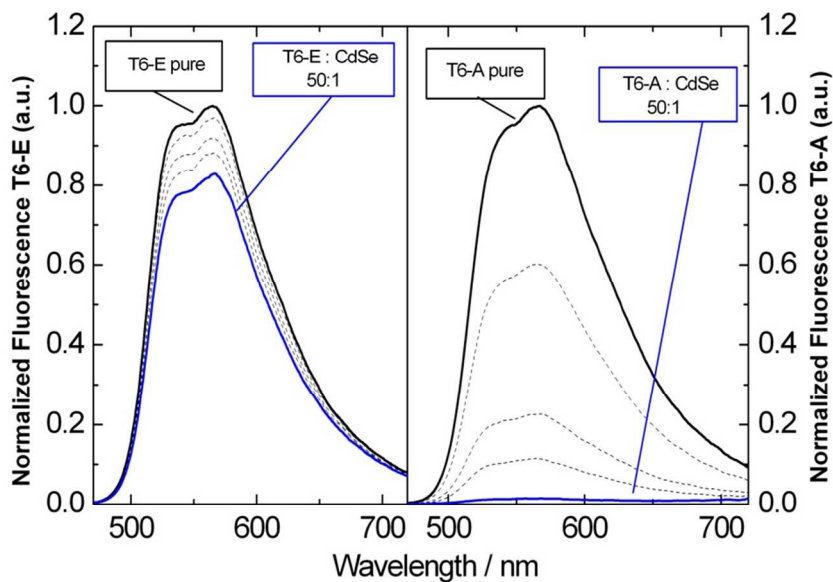


Figure S3. Evolution of the fluorescence in chloroform of **T6-E** (left) and **T6-A** (right) upon addition of CdSe NCs into the solution (Experiment A).

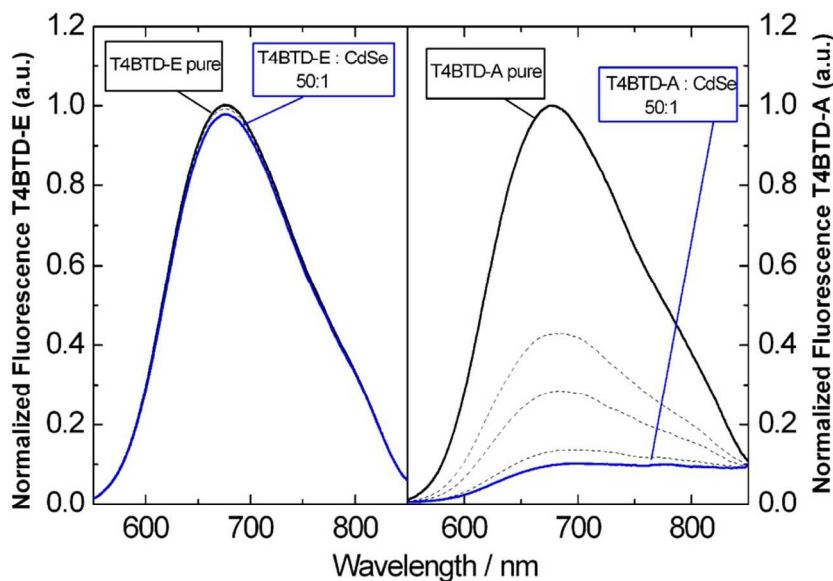


Figure S4. Evolution of the fluorescence in chloroform of **T4BTD-E** (left) and **T4BTD-A** (right) upon addition of CdSe NCs into the solution (Experiment A).

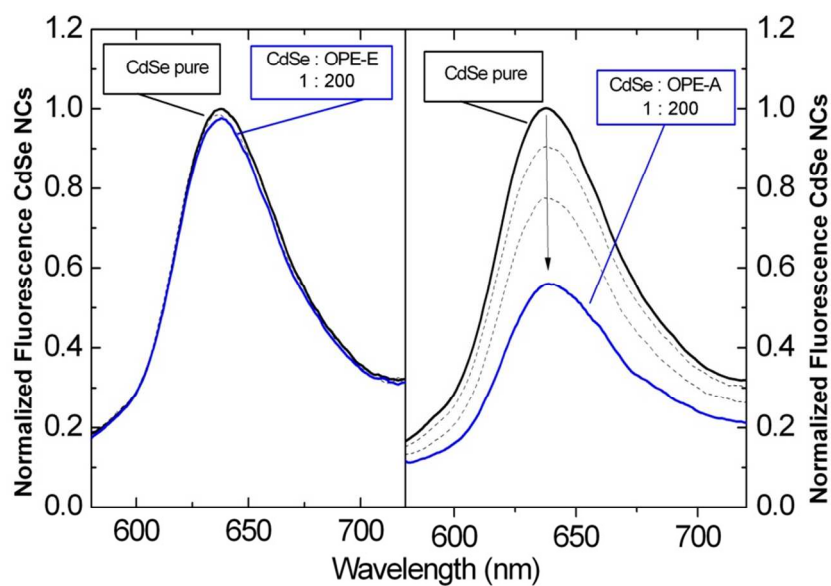


Figure S5. Evolution of the fluorescence in chloroform of CdSe NCs upon mixing with **OPE-E** (left) and **OPE-A** (right) at various CdSe:**OPE** ratios (Experiment B).

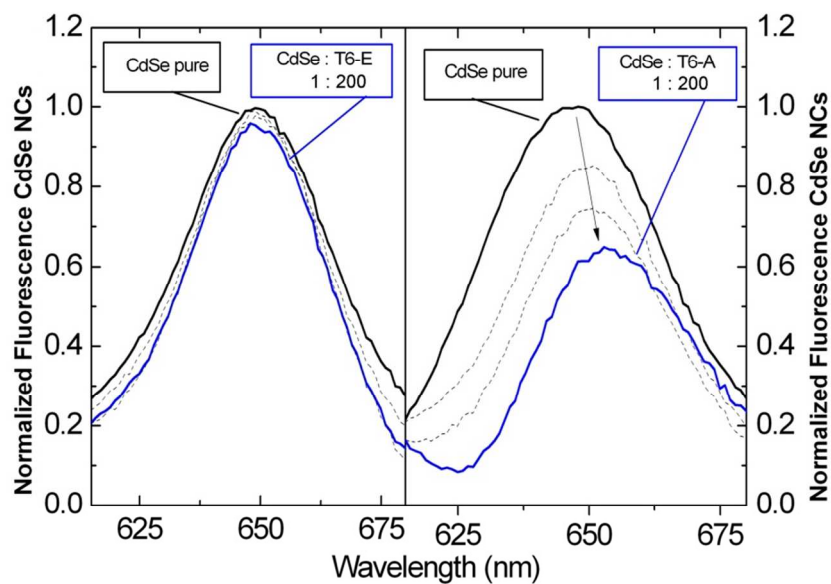


Figure S6. Evolution of the fluorescence in chloroform of CdSe NCs upon mixing with **T6-E** (left) and **T6-A** (right) at various CdSe:**T6** ratios (Experiment B).

### 3.3. Thermogravimetric Analysis

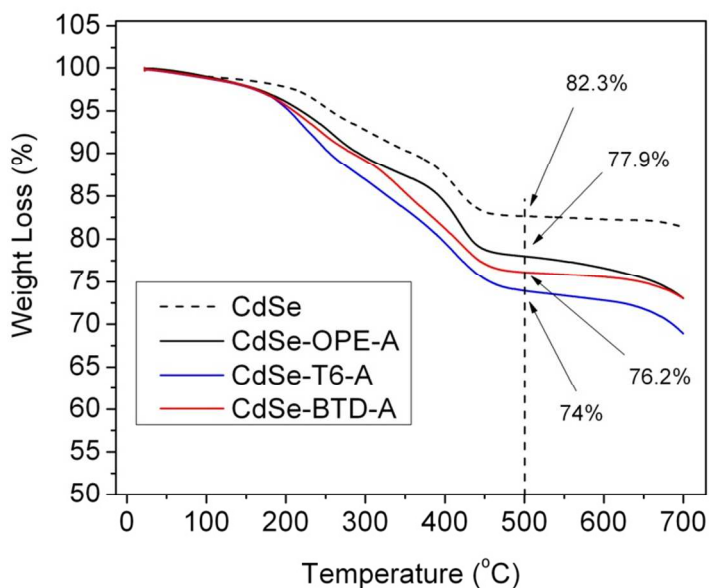


Figure S7. TGA thermograms of the pristine CdSe NCs (dashed line) and the three hybrids, under nitrogen flow, 10°C/min heating rate.

### 3.4. Spectral Analysis of Hybrid Composition.

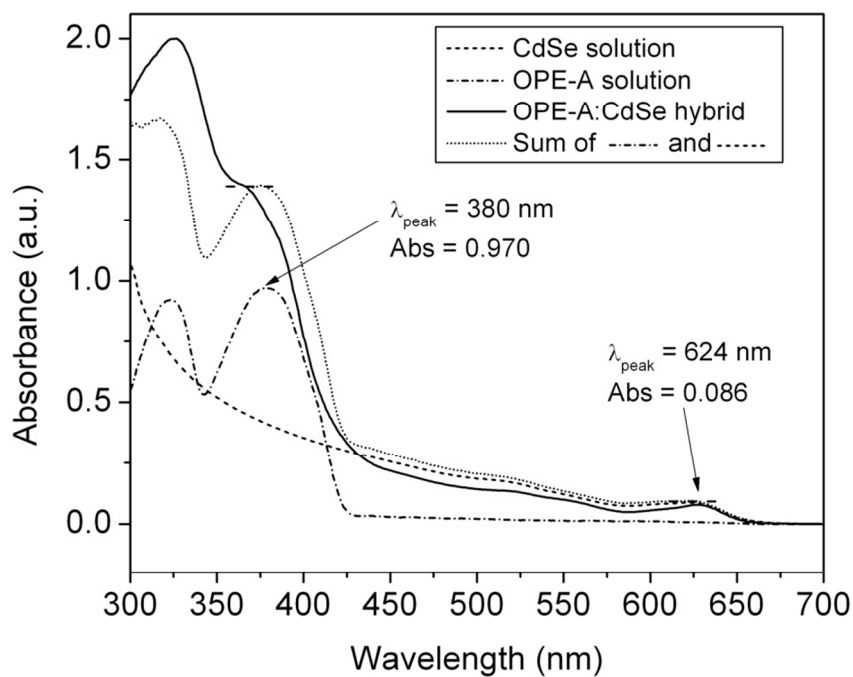


Figure S8. Absorption profiles of the **OPE-A/CdSe** hybrid (solid line), the free **T6-A** (dash-dot line), the free CdSe (dashed line) and the sum of the latter two (dotted line).

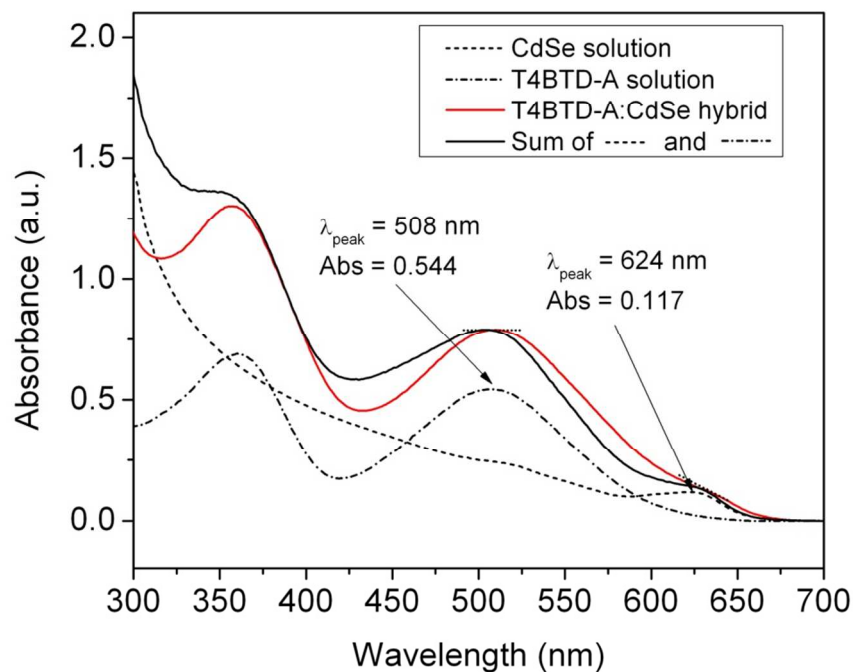


Figure S9. Absorption profiles of the **T4BTD-A/CdSe** hybrid (solid red line), the free **T4BTD-A** (dash-dot line), the free CdSe (dashed line) and the sum of the latter two (solid black line).

### 3.5. Transmission Electron Microscope Images.

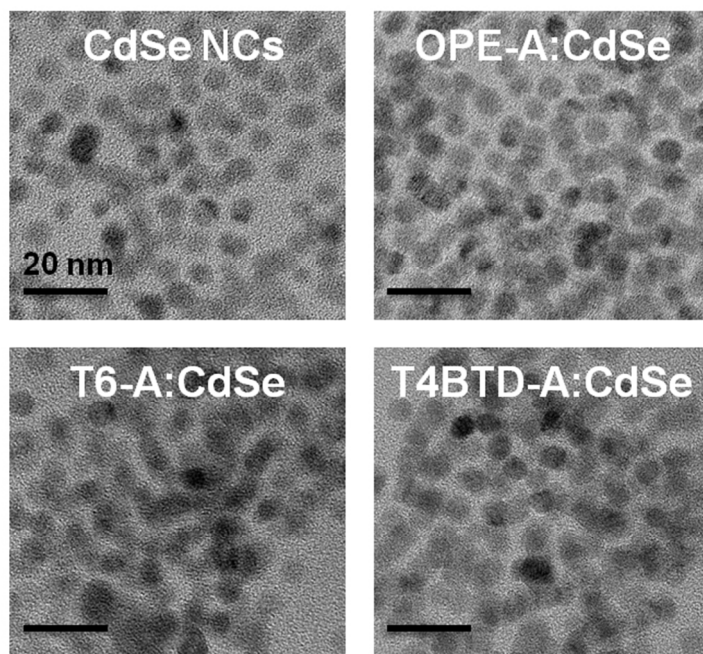


Figure S10. TEM images of the CdSe NCs used in this study (top left), along with that of the prepared **OPE** (top right), **T6** (bottom left) and **T4BTD** (bottom right) hybrids.



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