

Synthesis and Investigation of Cobalt Chalcogenide Clusters with Thienyl Phosphine Ligands as New Acceptor Materials for P3HT

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Supplementary Information

Experimental

General Remarks. All manipulations were performed under inert atmosphere using standard glovebox and Schenk techniques, unless otherwise noted. Chlorodiethylphosphine (90%), chlorodiphenylphosphine (99%), 2,5-dibromothiophene (95%), and *n*-butyllithium (2.5 M in hexanes) were used as received from *Sigma-Aldrich*. All solvents were obtained from an Innovative Technology Solvent Purification System and were degassed before use. Nuclear magnetic resonance (¹H NMR and ³¹P NMR) spectra were obtained using a Bruker Advance DPX-400 or 300 NMR spectrometer; chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale) and 85% H₃PO₄ respectively. Gas chromatography mass spectrometry (GC-MS) analyses were performed with an Agilent Technologies 6890N Network GC system with a 5973 Network Mass Selective Detector. UV-Visible spectra were taken in toluene and recorded using an HP 8453 Diode Array. Cyclic Voltammetry was performed on a CH Instruments CHI700D Electrochemical Analyzer. Powder X-Ray diffraction data was collected on a PANalytical X'Pert PRO MPD theta-theta Diffractometer.

Preparation of 2-bromo-5-diethylphosphinothiophene (1): 2,5-Dibromothiophene (0.449 mL, 3.98 mmol) was cooled to -78 °C in anhydrous diethyl ether (50 mL). *n*-Butyllithium (1.59 mL, 3.98 mmol) was then added and the mixture was allowed to warm to room temperature and stir for 2 hours. The resulting lithio-thiophene was then cooled back to -78 °C and chlorodiethylphosphine (0.485 mL, 3.98 mmol) was added. The solution was allowed to warm to room temperature overnight. H₂O (50 mL) was

added to solubilize all precipitated materials. The isolated organic layer was then washed with H₂O (3x 20mL) and dried on sodium sulfate. The resulting pale orange/brown oil was purified on silica gel using petroleum ether as an effluent to afford slightly yellow oil, 0.842 g, 84.2% yield.

NMR ¹H (CDCl₃) (Br-Th=C₄H₂BrS): 0.99, 1.01, 1.04, 1.04, 1.07, 1.09 (d of t, 6H, *J*_{H-H}=7.65 Hz, *J*_{P-H}=16 Hz, (Br-Th)P(CH₂CH₃)₂), 1.65, 1.68, 1.70, 1.73(q, 4H, *J*_{H-H}=7.6 Hz, (Br-Th)P(CH₂CH₃)₂), 6.99, 7.00 (d of d, 1H, , *J*_{H-H}=3.6 Hz, *J*_{P-H}=0.8 Hz (Br-Th)P(CH₂CH₃)₂), 7.06, 7.07, 7.08, 7.09 (d of d, 1H, , *J*_{H-H}=6.3 Hz, *J*_{P-H}=2.7 Hz (Br-Th)P(CH₂CH₃)₂); NMR ³¹P (CDCl₃): -22.0 ((Br-Th)P(CH₂CH₃)₂). GC-MS (CDCl₃) m/z: 250, 252. calc. mass: 250. λ_{Abs} = 293 nm, λ_{Em} = 366 nm, 527 nm.

Preparation of 2-bromo-5-diphenylphosphinothiophene (2): 2,5-Dibromothiophene (0.324 mL, 2.88 mmol) was cooled to -78 °C in anhydrous diethyl ether (50 mL). n-Butyllithium (1.15 mL, 2.88 mmol) was then added and the mixture was allowed to warm to room temperature and stir for 2 hours. The resulting lithio-thiophene was then cooled back to -78 °C and chlorodiphenylphosphine (1.15 mL, 2.88 mmol) was added. The solution was allowed to warm to room temperature overnight. H₂O (50 mL) was added to solubilize all precipitated materials. The isolated organic layer was then washed with H₂O (3x 20mL) and dried on sodium sulfate. The resulting pale orange/brown oil was purified on silica gel using petroleum ether as an effluent to afford a white crystalline solid, 0.78.9 g, 78.9% yield.

NMR ¹H (CDCl₃) (Br-Th=C₄H₂BrS, Ph=C₆H₅): 7.05, 7.05, 7.06, 7.06 (d of d, 1H, , *J*_{H-H}=3.7 Hz, *J*_{P-H}=1.24 Hz (Br-Th)P(CH₂CH₃)₂), 7.09, 7.10, 7.11, 7.11 (d of d, 1H, *J*_{H-H}=6.2 Hz, *J*_{P-H}=3.7 Hz (Br-Th)P(Ph)₂), 7.36 (m, 10H, (Br-Th)P(Ph)₂); NMR ³¹P (CDCl₃): -17.9 ((Br-Th)P(C₆H₅)₂). GC-MS (CDCl₃) m/z: 346, 348. calc. mass: 347. λ_{Abs} = 295 nm, λ_{Em} = 361 nm, 516 nm. Experimental Mp (79.5 – 81.6 °C)

Electrochemistry

Solutions of **3** and **4** in dimethylformamide (DMF) containing 0.1M of the supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆) in a single cell and potentiostat assembly were used for cyclic voltammetry measurements. The measurements were carried out with a glassy carbon working,

a platinum counter electrode, an Ag^+/AgCl reference electrode, and ferrocene/ferrocenium as in internal standard. The potentials were measured against a Ag^+/AgCl reference electrode and each measurement was calibrated using Fc/Fc^+ redox system. HOMO energy levels were calculated as detailed in the text. The voltammograms from **3** and **4** (Figure S-1 and S-2) can be seen below.

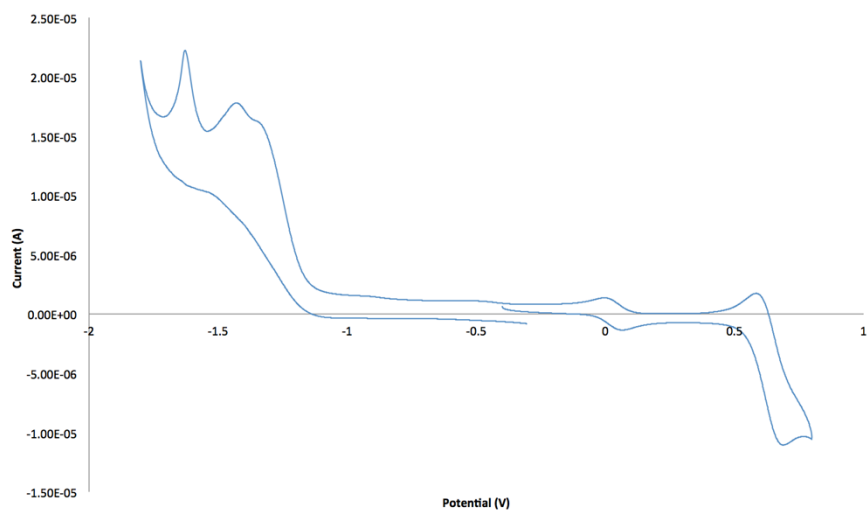


Figure S1: CV trace of $\text{Co}_6\text{Se}_8(\text{P}(\text{Et})_2(\text{C}_4\text{H}_2\text{SBr})_6)$ in the presence of the ferrocene/ferrocenium internal standard .

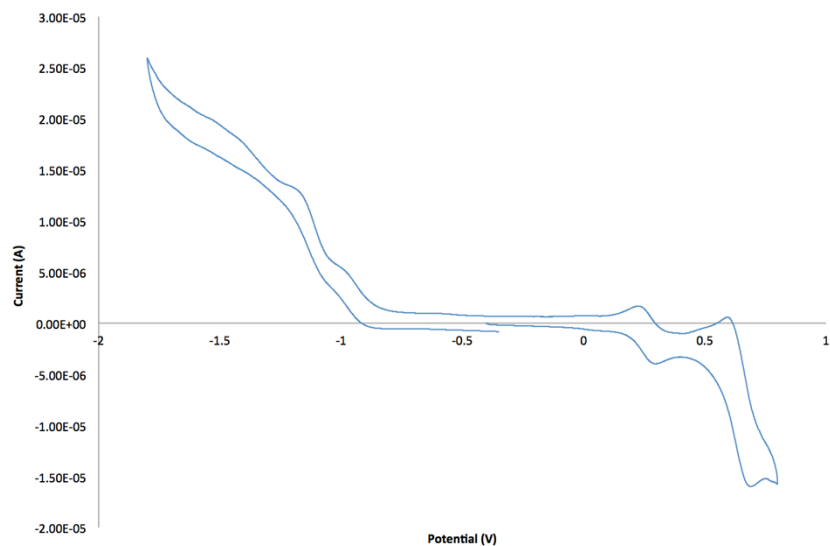


Figure S2: CV trace of $\text{Co}_6\text{Se}_8(\text{P}(\text{Ph})_2(\text{C}_4\text{H}_2\text{SBr})_6)$ in the presence of the ferrocene/ferrocenium internal standard .

UV-Visible and Fluorescence Data

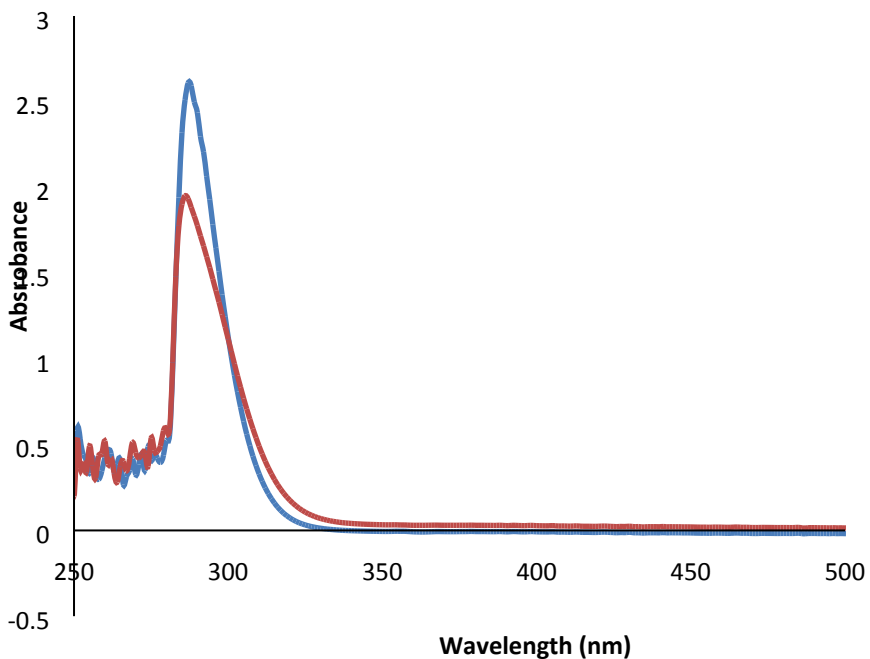


Figure S3. UV-Visible spectra of 1 (blue) and 2 (red) in toluene.

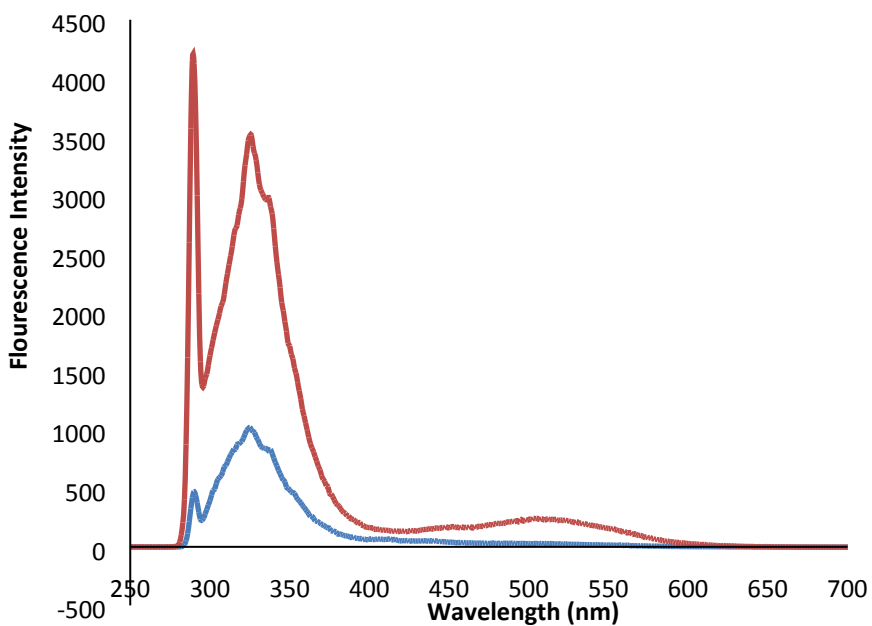


Figure S4. Emission spectrum spectra of 1 (blue) and 2 (red) in toluene excited at 287 nm.

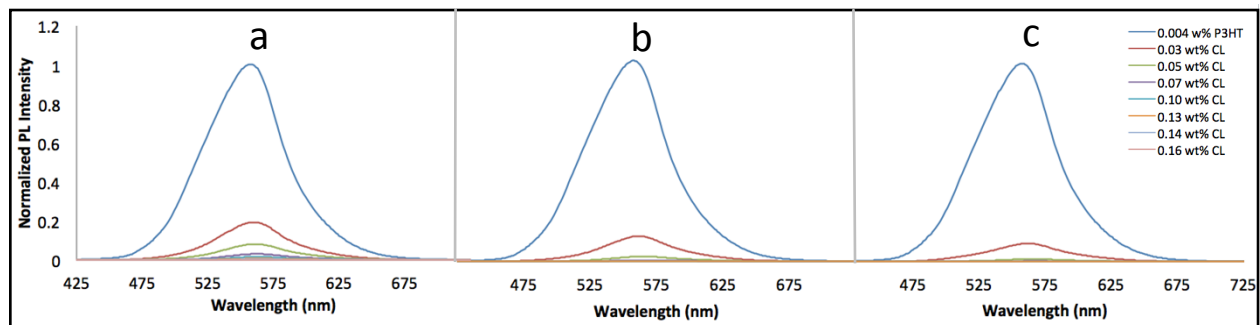


Figure S5. Photoluminescence spectra of P3HT with addition of clusters 5 (a), 3 (b), and 4 (c).

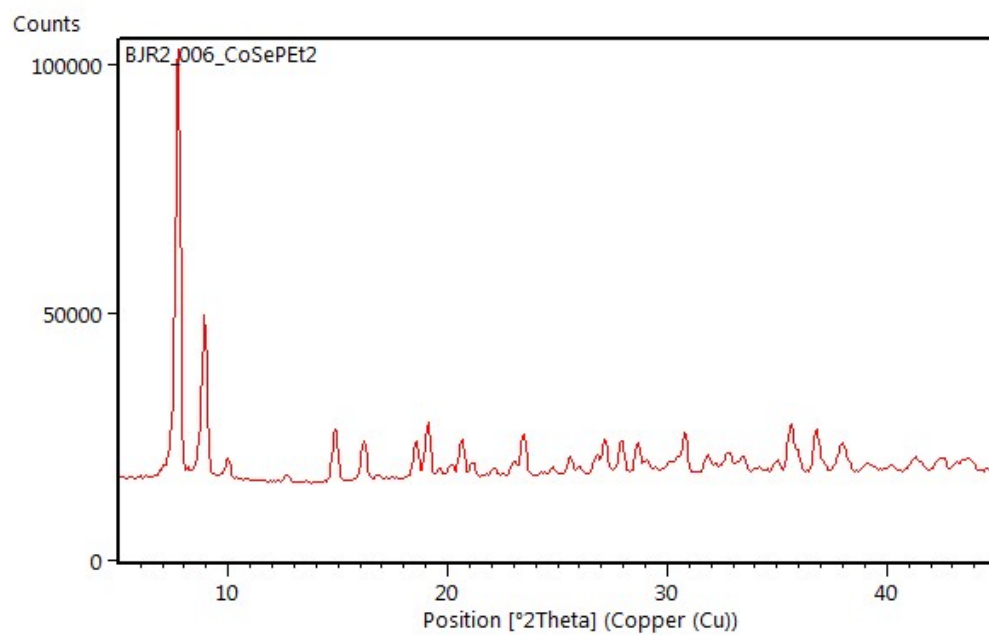


Figure S6. PXRD of 3.

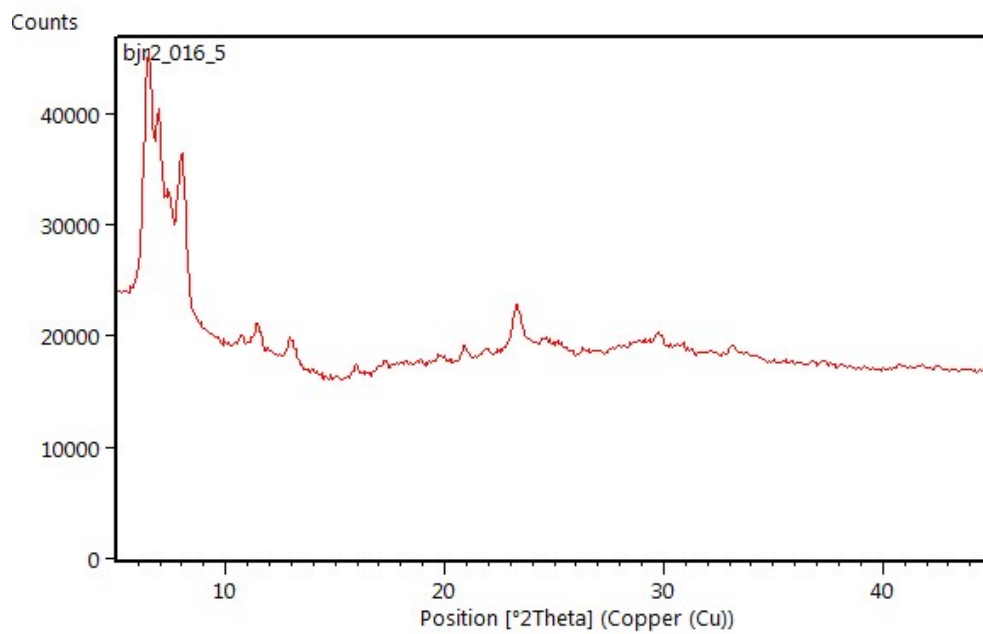


Figure S7. PXRD of 4.