Electronic Supplementary Material (ESI) for Polymer Chemistry.

Metallopolymers from Direct Polymerization of Functionalized Cobalt Chalcogenide Clusters and Thiophene Comonomers

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Supplementary Information

Estimation of Degree of Polymerization

For a copolymer with three monomers, degree of polymerization (DP) is defined as:

$$DP = \frac{MW_{polymer}}{n_1 MW_1 + n_2 MW_2 + n_3 MW_3}$$

Where *n* is the mole fraction of a given monomer unit in the polymer and *MW* is that monomer unit's molecular mass in the copolymer. In order to get an estimate of DP for **PCLTHTa-c**, we will assume the copolymers have molecular weights of about 40,000 g/mol as suggested by GPC data. In addition, we will define monomer 1 as thiophene (Th), monomer 2 as $Co_6Se_8(P(Ph)_2(C_4H_2S))_6$ (CL), and monomer 3 as 3-hexylthiophene (HT). Therefore, the ideal equation for **PCLTHTa-c** becomes:

$$DP = \frac{40{,}000\ g/mol}{n_{Th} MW_{Th} + n_{CL} MW_{CL} + n_{HT} MW_{HT}}$$

However, we know from the analysis of methanol wash during polymer workup that some cluster is not incorporated into the copolymers. Therefore, the equation for DP should be adjusted accordingly:

$$DP = \frac{40{,}000\ g/mol}{n_{Th} MW_{Th} + p \cdot n_{CL} MW_{CL} + n_{HT} MW_{HT}}$$

Where p is the percent of cluster incorporated into the copolymer. Finally, we know from the mechanism of the polymerization that a Th comonomer must be present for every CL and HT comonomer:

$$n_{Th} = p \cdot n_{CL} + n_{HT}$$

Therefore, this final substitution can be made:

$$DP = \frac{40{,}000\ g/mol}{(p \cdot n_{CL} + n_{HT})MW_{Th} + p \cdot n_{CL}MW_{CL} + n_{HT}MW_{HT}}$$

It should be noted that this equation assumes all HT is incorporated into the copolymer. While this is likely not true, it is assumed for the purpose of getting an estimate of DP. As an example, we know **PCLTHTa** is synthesized using a mole ratio of 0.125:0.5:0.375 cluster:thiophene:3-hexylthiophene. We also know the MW_{Th} is 82.1 g/mol, the MW_{CL} is 2588.9 g/mol, the MW_{HT} = 166.3 g/mol, and that 97.5% of the cluster is incorporated into the copolymer. Therefore:

$$DP = \frac{40{,}000\ g/mol}{(0.975 \cdot 0.125 + 0.375)82.1\ g/mol + 0.975 \cdot 0.125 \cdot 2588.9\ g/mol + 0.375 \cdot 166.3\ g/mol}$$

And after simplification:

$$DP = 95.7$$

Supplemental Figures

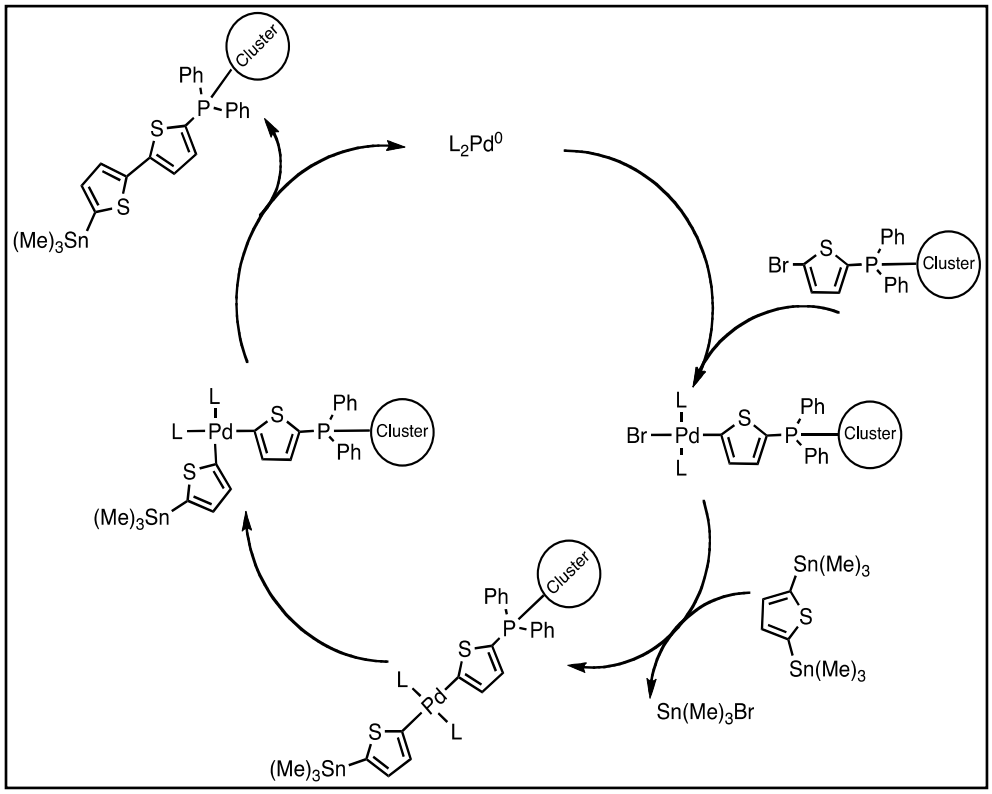

Figure S-1: Schematic mechanism of cluster polymerization.

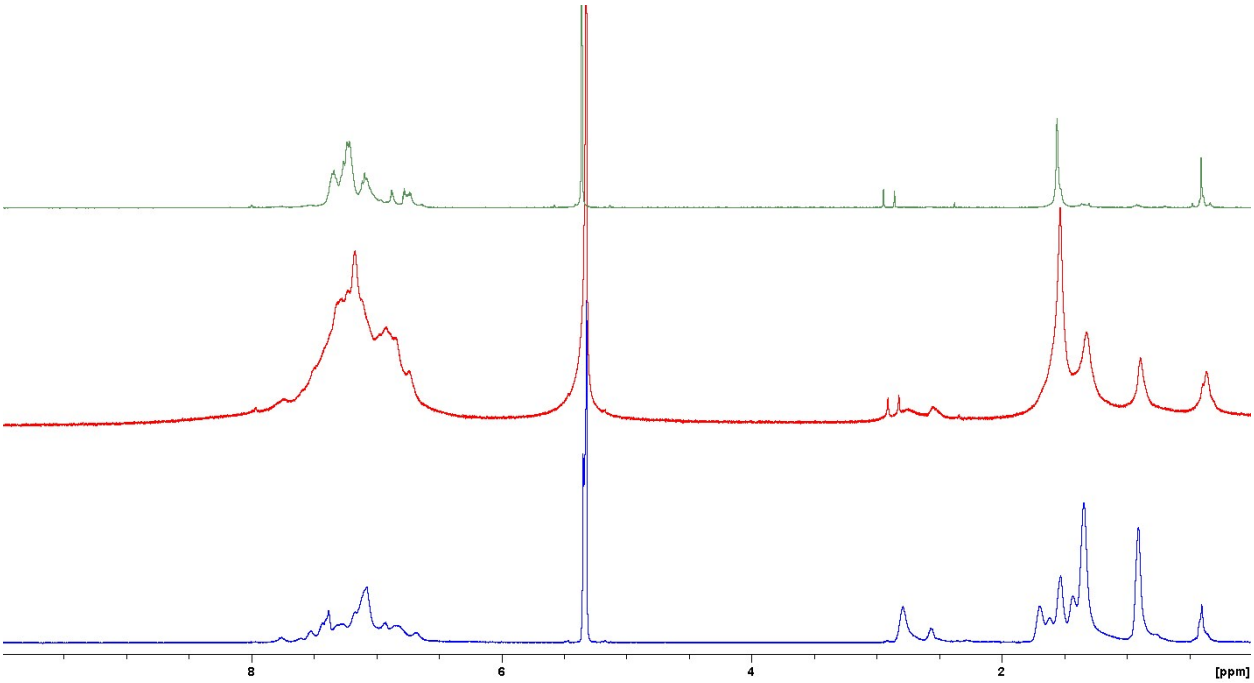

Figure S-2: ^{1}H NMR of **PCLTHTa-c** (green, red, and blue, respectively).

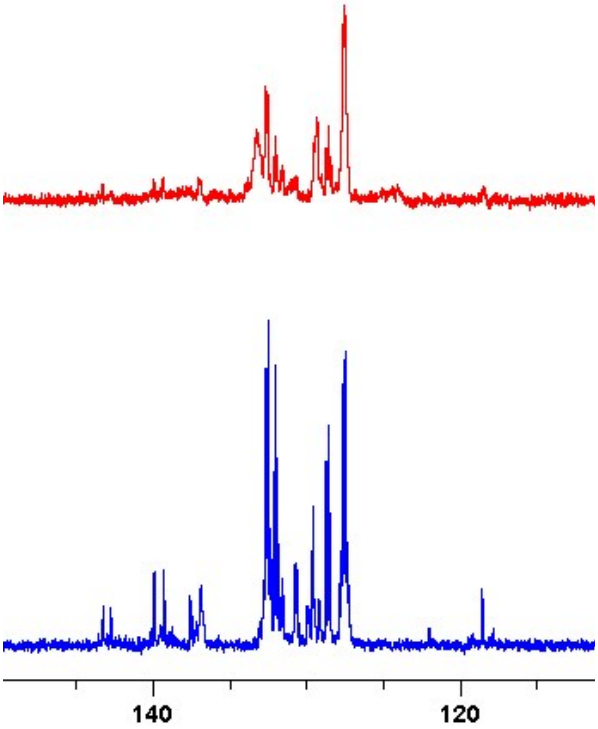

Figure S-3: ^{13}C NMR spectra of **1** (blue) and **PCLTHTa** (red).

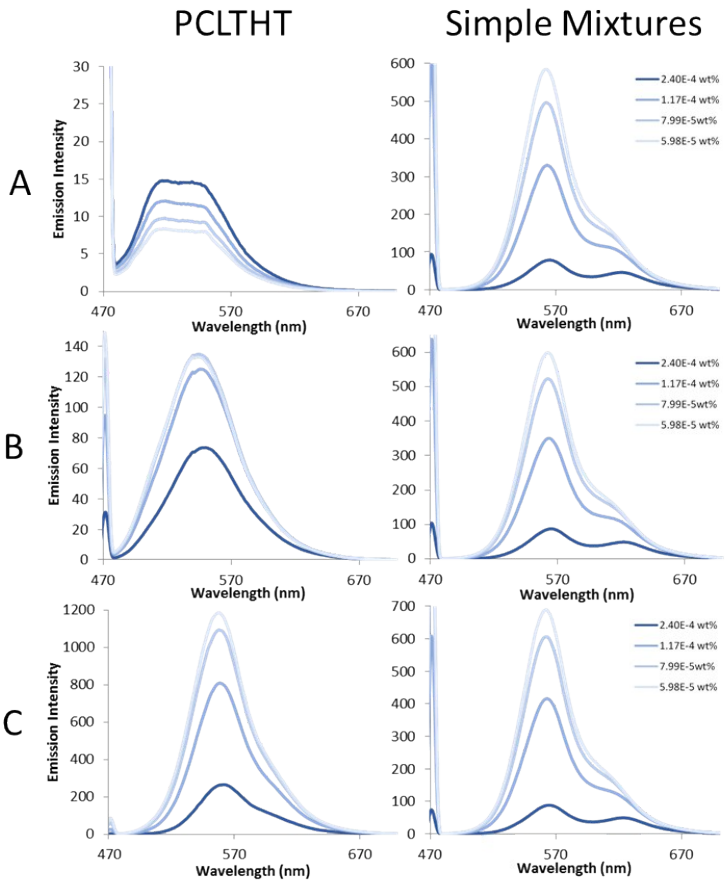

Figure S-4. Emission spectral overlay of increasing dilution of **PCLTHTa-c** (left) and representative simple mixtures (right). System **A** is shown on top, system **B** in the middle, and system **C** on the bottom. All spectra are taken in benzene at the weight percents shown in the legends on the right.

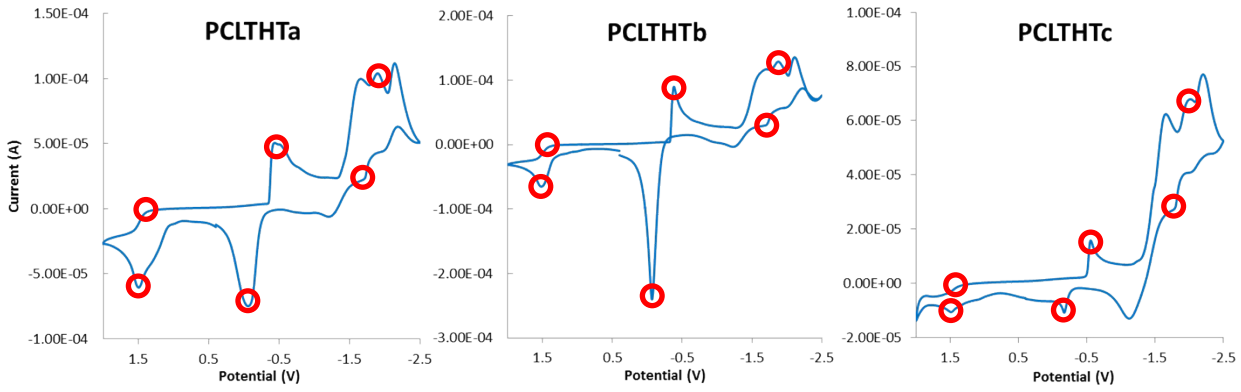

Figure S-5. Cyclic voltamograms of **PCLTHTa-c** thin films drop cast from 1 mg/mL solutions in DCM. All samples were run in 0.1M $TBAPF_6$ supporting electrolyte solution in acetonitrile using a $Ag^+/AgNO_3$ reference electrode. Peaks circled in red are have been assigned to the copolymers, while all other peaks seen have been attributed to the solvent by comparison to a background measurement.

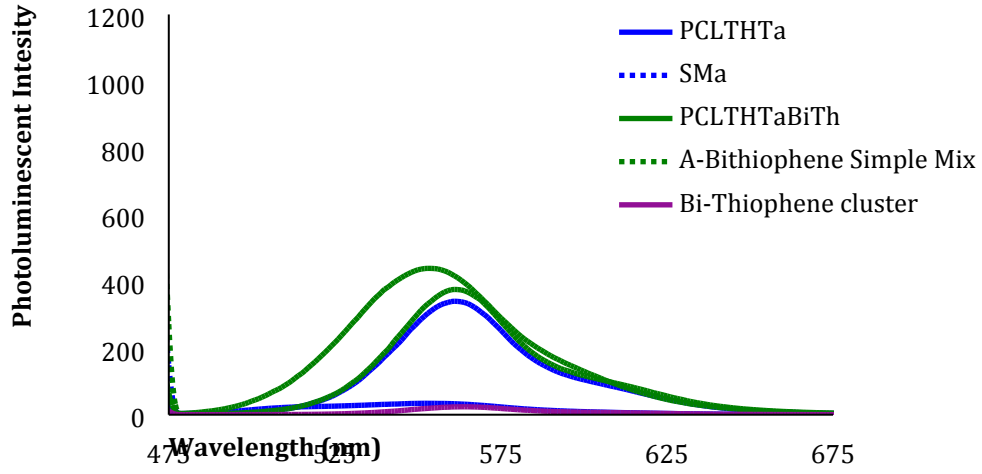

Figure S-6: Emission spectra of **PCLTHTa** (blue), **SMa** (blue dotted), **PCLTHTaBiTh** (green), **SMa** with cluster **4** (green dotted), and cluster **4** (purple).

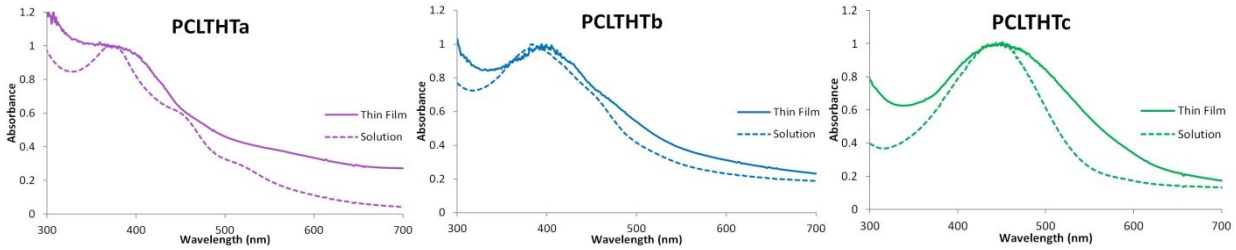

Figure S-7. PCLTHTa-c thin film absorbance spectra compared to their respective solution absorbance spectra.

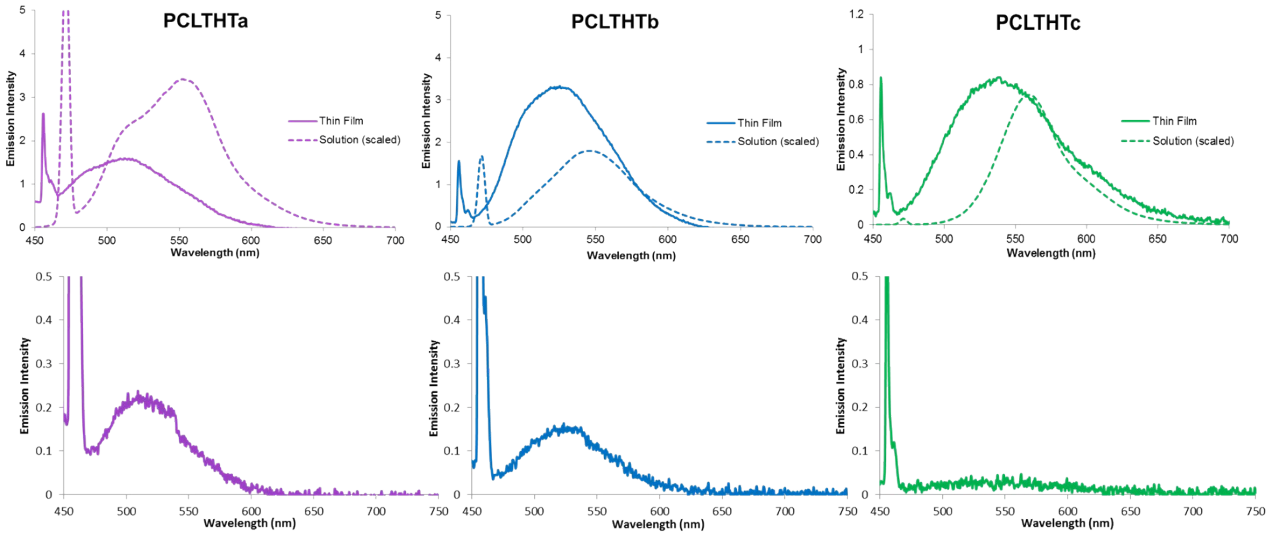

Figure S-8. (Top-A) **PCLTHTa-c** thin film emission spectra compared to their solution spectra. Note: solution spectra are arbitrarily scaled to fit in the figures. (Bottom-B) **PCLTHTa-c** thin films cast from 0.5 mg/mL solutions of each polymer to compare charge transfer of **PCLTHTa-c** in the solid state.