Supplementary Information

Solvent-Dependent Conductance Decay Constants in Single Cluster Junctions

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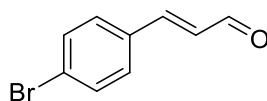
[†] These authors contributed equally to this work.

I. Synthetic Details

General Information: Chlorodiethylphosphine was purchased from Acros Organics. Selenium powder and dicobalt octacarbonyl were obtained from STREM Chemicals. Potassium *tert*-butoxide, 4-bromobenzaldehyde, and all other reagents and solvents were purchased from Sigma Aldrich. Dry and deoxygenated solvents were prepared by elution through a dual column solvent system (MBraun SPS). Unless otherwise noted, all reactions were carried out under nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox.
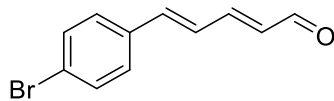
Compound **4**

(1,3-Dioxolan-2-ylmethyl)triphenylphosphonium bromide (11.60 g, 27.0 mmol) was dissolved in 120 mL of THF. To the solution, lithium methoxide (1.51 g, 39.7 mmol) suspended in 15 mL of THF was added and rinsed with 5 mL of THF and 5 mL of methanol. A reflux condenser was attached and the suspension was heated to reflux for 30 min. 4-Bromobenzaldehyde (2.00 g, 10.8 mmol) dissolved in 25 mL of THF was added dropwise to the refluxing suspension and was further heated to reflux for ~12 h. The mixture was cooled to RT. In air, 100 mL of 10 % HCl solution was added and stirred for 1 h. The mixture was poured into 225 mL of dichloromethane. The organic phase was extracted and the aqueous phase was washed with dichloromethane (3 x 30 mL). The combined organic phase was washed with saturated aqueous NaHCO$_3$ solution and brine, dried with MgSO$_4$, and evaporated to dryness. The crude product was purified by column chromatography. Yield: 1.85 g (81 %).

The structure of compound **4** was confirmed by ^{1}H NMR as published in literature.[1]
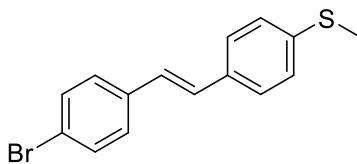
Compound **5**

This preparation was analogous to that of compound **4**, using 27.1 mmol of (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide, 29.0 mmol of lithium methoxide, and 10.8 mmol of compound **4**. Yield: 2.24 g (87 %).

¹H NMR (400 MHz, [d₂-dichloromethane], 298 K): δ = 6.23-6.29 (1H, m), 6.95-7.07 (2H, m), 7.24-7.30 (1H, m), 7.38-7.42 (2H, m), 7.52-7.55 (1H, m), 9.61 (1H, d).
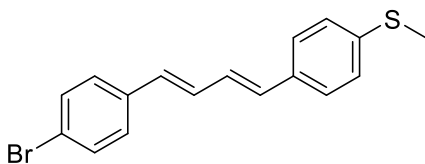

Compound **6**

4-Bromobenzaldehyde (0.89 g, 4.8 mmol) was dissolved in 40 mL of THF and cooled to 0 °C. Dimethyl-4-thiomethylbenzyl phosphonate[2] (1.18 g, 4.8 mmol) was added and the solution was stirred for 30 min. A solution of potassium *tert*-butoxide (0.62 g, 5.5 mmol) in 10 mL of THF was added dropwise to the cold solution. The reaction was stirred and warmed gradually to RT over ~12 h. In air, 50 mL of water was added and the mixture was poured into 50 mL of dichloromethane. The organic phase was extracted and the aqueous phase was washed with dichloromethane (2 x 10 mL). The combined organic phase was washed with water then brine, dried with MgSO₄ and evaporated to dryness. The white solid was recrystallized at -30 °C from a mixture of toluene and *n*-hexanes. Yield: 1.35 g (92 %).

¹H NMR (300 MHz, [d₂-dichloromethane], 298 K): δ = 2.50 (3H, s), 7.00 (2H, m), 7.21-7.25 (2H, m), 7.32-7.48 (6H, m).
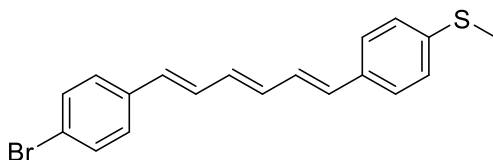
Compound **7**

This preparation was analogous to that of compound **6**, using 4.1 mmol of aldehyde **4**, 4.1 mmol of dimethyl-4-thiomethylbenzyl phosphonate, and 4.5 mmol of potassium *tert*-butoxide. The white solid was recrystallized at -30 °C from dichloromethane and washed with *n*-hexanes. Yield: 803 mg (60 %).

^{1}H NMR (300 MHz, [d$_2$-dichloromethane], 298 K): δ = 2.51 (3H, s), 6.61 (2H, m), 6.91 (2H, m), 7.21-7.47 (8H, m).
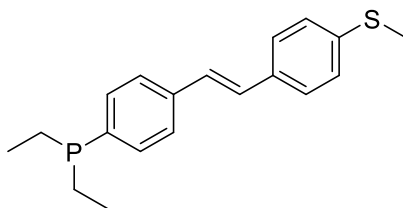

Compound **8**

This preparation was analogous to that of compound **6**, using 1.1 mmol of compound **5**, 1.1 mmol of dimethyl-4-thiomethylbenzyl phosphonate, and 1.2 mmol of potassium *tert*-butoxide. The yellow solid was recrystallized at -30 °C from dichloromethane and washed with *n*-hexanes. Yield: 270 mg (67%).

^{1}H NMR (400 MHz, [d$_2$-dichloromethane], 298 K): δ = 2.49 (3H, s), 6.48-6.61 (4H, m), 6.84-6.94 (2H, m), 7.19-7.46 (8H, m).
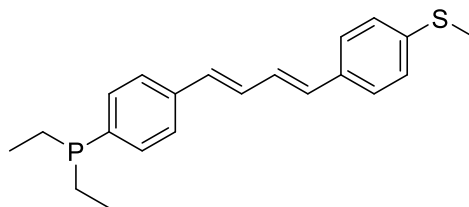
Conducting ligand **L1**

Compound **6** (1.16 g, 3.8 mmol) was dissolved in 50 mL of THF and cooled to -78 °C. *n*-Butyllithium (1.6 M in hexanes, 2.6 mL, 4.2 mmol) was added dropwise and the reaction was stirred for 45 min. Chlorodiethylphosphine (0.57 g, 4.6 mmol) in 10 mL of THF was added dropwise to the solution and the reaction was warmed gradually to RT over ~12 h. The solvent was removed *in vacuo* and 20 mL of toluene was added to the crude product. The mixture was filtered through a fine frit and the solvent was once again removed *in vacuo*. The white solid was recrystallized at -30 °C from a mixture of toluene and *n*-hexanes. Yield: 1.00 g (84 %).

¹H NMR (400 MHz, [d₂-dichloromethane], 298 K): δ = 1.02 (6H, m), 1.70 (4H, m), 2.50 (3H, s), 7.10 (2H, m), 7.25 (2H, m), 7.45-7.51 (6H, m).

³¹P NMR (162 MHz, [d₂-dichloromethane], 298 K): δ = -15.
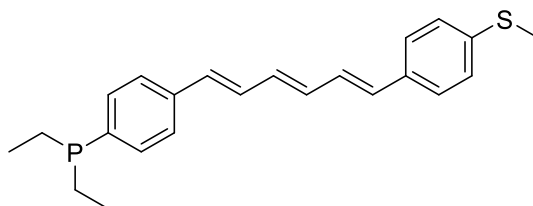

Conducting ligand **L2**

This preparation was analogous to that of conducting ligand **L1**, using 1.2 mmol of compound **7**, 1.3 mmol of *n*-butyllithium, and 1.4 mmol of chlorodiethylphosphine. The yellow solid was recrystallized at -30 °C from THF and washed with *n*-hexanes. Yield: 178 mg (40 %).

¹H NMR (300 MHz, [d₂-dichloromethane], 298 K): δ = 0.98 (6H, m), 1.67 (4H, m), 2.47 (3H, s), 6.65 (2H, m), 6.96 (2H, m), 7.19 (2H, m), 7.35-7.42 (6H, m).

³¹P NMR (162 MHz, [d₂-dichloromethane], 298 K): δ = -15.
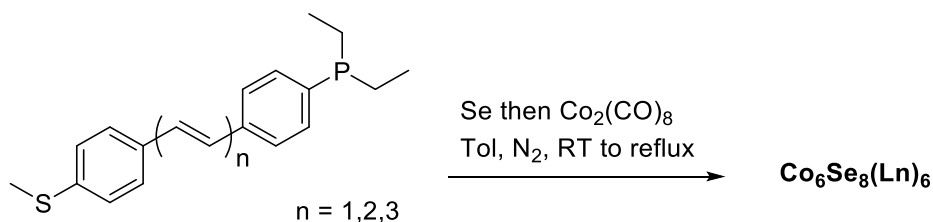

Conducting ligand **L3**

A solution of tetramethylethylenediamine (0.1 mL, 0.67 mmol) and *n*-butyllithium (1.7 M in THF, 0.4 mL, 0.67 mmol) in 10 mL of THF was stirred at -78 °C for 30 min. The solution was cannula transferred to compound **8** (200 mg, 0.56 mmol) dissolved in 40 mL of THF at -78 °C and stirred for 1.5 h. Chlorodiethylphosphine (210 mg, 1.68 mmol) in 3 mL of THF was added dropwise, and the mixture was warmed gradually to RT over ~12 h. The solvent was removed *in vacuo* and 5 mL of THF was added to the crude product. The mixture was filtered through a fine frit and recrystallized at -30 °C from THF. Yield: 92 mg (44 %).

¹H NMR (400 MHz, [d₂-dichloromethane], 298 K): δ = 1.04 (6H, m), 1.71 (4H, m), 2.51 (3H, s), 6.52-6.62 (4H, m), 6.84-6.96 (2H, m), 7.21-7.47 (8H, m).

³¹P NMR (162 MHz, [d₂-dichloromethane], 298 K): δ = -16.

General synthesis of $Co_6Se_8(\mathbf{Ln})_6$ clusters **1-3**:

$Co_6Se_8(\mathbf{L1})_6$ (**1**)

Conducting ligand **L1** (223 mg, 0.71 mmol) was dissolved in 40 mL of toluene. Selenium powder (56 mg, 0.71 mmol) was added and the suspension was stirred until the solid dissolved. Dicobalt octacarbonyl (56 mg, 0.16 mmol), dissolved in 5 mL of toluene, was added to the solution and the reaction was heated to reflux for ~12 h. The hot mixture was filtered through a fine frit. The dark brown solution was cooled to RT and concentrated *in vacuo*, and the product was precipitated with diethyl ether. Yield: 102 mg (65 %). The crystal structure of **1** has been published in a recent report[3], and crystallographic data is available from the Cambridge Crystallographic Data Centre (deposition number 894790).

^{1}H NMR (400 MHz, [d$_8$-tetrahydrofuran], 298 K): δ = 0.89 (36H, m), 2.06 (24H, m), 2.48 (18H, s), 7.13 (12H, s), 7.20 (12H, m), 7.32-7.43 (36H, m).

^{31}P NMR (162 MHz, [d$_8$-tetrahydrofuran], 298 K): δ = 58 (broad peak).

$Co_6Se_8(\mathbf{L2})_6$ (**2**)

This preparation was analogous to that of **1**, using 0.88 mmol of conducting ligand **L2**, 0.88 mmol of selenium powder, and 0.40 mmol of dicobalt octacarbonyl. Yield: 137 mg (66 %).

^{1}H NMR (400 MHz, [d$_8$-tetrahydrofuran], 298 K): δ = 0.90 (36H, m), 2.04 (24H, m), 2.47 (18H, s), 7.04-7.33 (72H, m).

We were not able to measure the ^{31}P NMR spectrum of compound **2** because of its low solubility.

Co$_6$Se$_8$(**L3**)$_6$ (**3**)

This preparation was analogous to that of **1**, using 0.24 mmol of conducting ligand **L3**, 0.24 mmol of selenium powder, and 0.06 mmol of dicobalt octacarbonyl. The dark brown product precipitated upon cooling the hot filtrate to RT. Yield: 8 mg (14 %).

^{1}H NMR (400 MHz, [d$_8$-tetrahydrofuran], 298 K): δ = 0.89 (36H, m), 2.07 (24H, m), 2.46 (18H, s), 6.50-7.38 (84H, m).

We were not able to measure the ^{31}P NMR spectrum of compound **3** due to its low solubility.

II. Instrumentation Details

All ^{1}H and ^{31}P NMR were recorded on a Bruker DRX300 (300 MHz) or Bruker DRX400 (400 MHz) spectrometer. Absorption spectra were taken on a Shimadzu UV-1800 spectrophotometer.

III. Additional Conductance Data

2D Conductance versus Displacement Histograms

Below are 2D conductance versus displacement histograms for ligands **L1-L3** and clusters **1-3** in 1-bromonaphthalene. Both 1D and 2D conductance histograms for **L1** and **L2** are constructed from 5000 individual conductance traces, while those of **L3** are constructed from 6000 traces; all data was collected at an applied voltage of 500mV. Histograms for **1** were constructed from 4000 traces, for **2** were constructed from 3000 traces and for **3** were constructed from 2000 traces. In solution, the clusters tend to decompose over time, so we were unable to obtain as much data as we collected for the ligands. Cluster traces were collected at an applied voltage of 375mV and solution concentration of 5-10 μM.
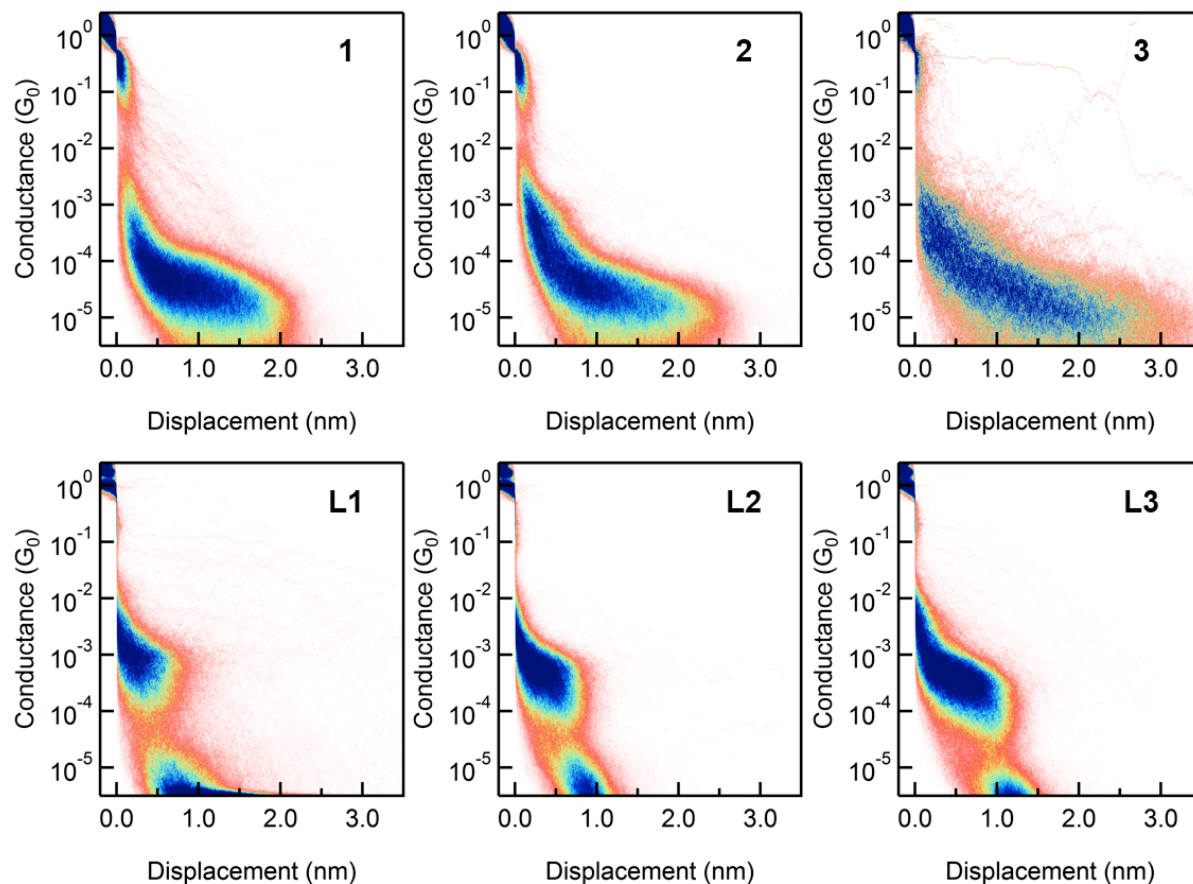
Figure S1. Two-dimensional (2D) conductance versus displacement histograms for **1-3** and **L1-L3** collected in 1-bromonaphthalene. Histograms were created by aligning individual conductance traces at 0.5 G_0 and then overlaying all traces to generate the 2D image. Molecular plateau lengths for the clusters are roughly twice as long as their ligand only counterparts.

We have also carried out conductance measurements on **1-3** and **L1-L3** in 1,2,4-trichlorobenzene (TCB). 2D conductance versus displacement histograms for ligands **L1-L3** and clusters **1-3** in 1-TCB are shown in Figure S2. Conductance histograms are constructed from 3000 traces for **1**, 1000 traces for **2**, 4000 traces for **3**, and 10000 traces for **L1-L3**.
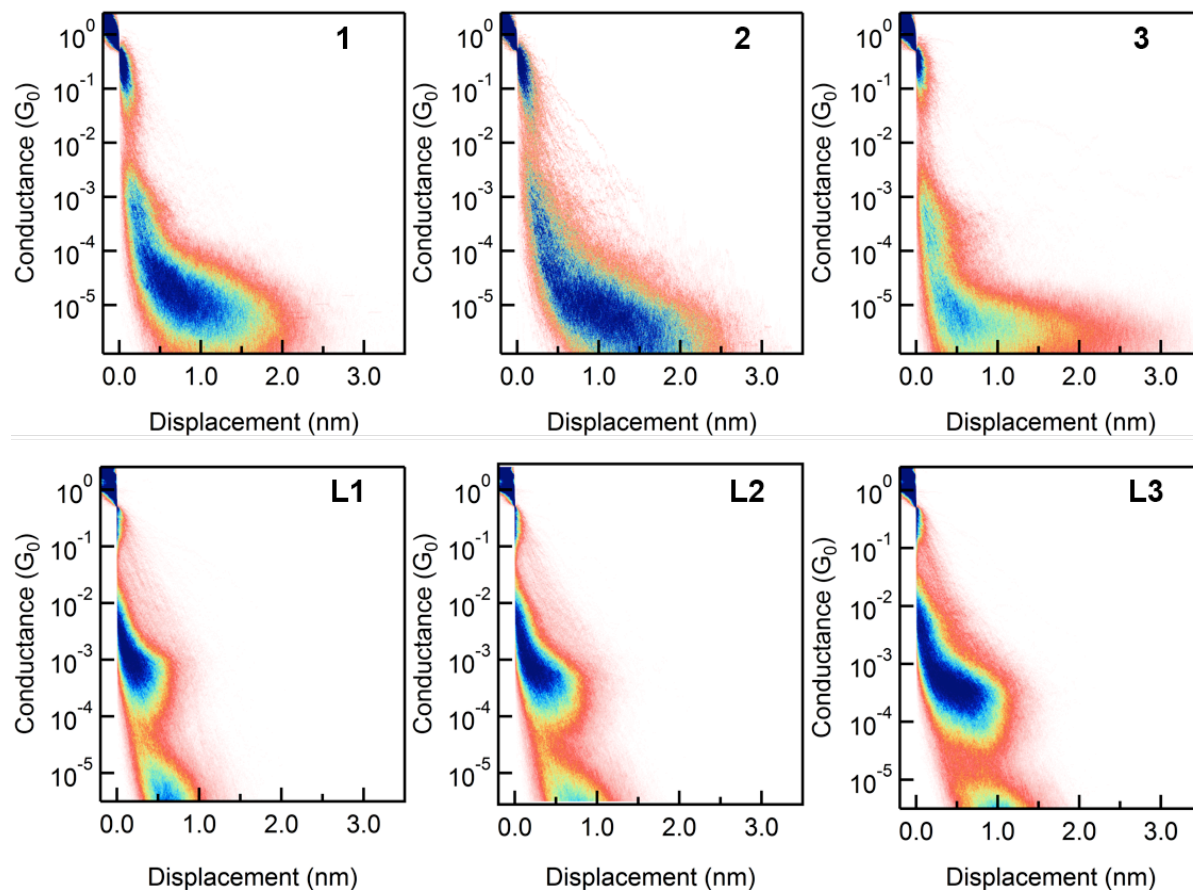
Figure S2. Two-dimensional (2D) conductance versus displacement histograms for **1-3** and **L1-L3** collected in 1,2,4-trichlorobenzene. Histograms were created by aligning individual conductance traces at 0.5 G_0 and then overlaying all traces to generate the 2D image. Molecular plateau lengths for the clusters are roughly twice as long as their ligand only counterparts.

We measured the conductance of **1** under an inert atmosphere of Ar gas to examine whether the presence of oxygen or water in the cluster solution impacts the measurement (Figure S3). We observe no change in the conductance of **1**.
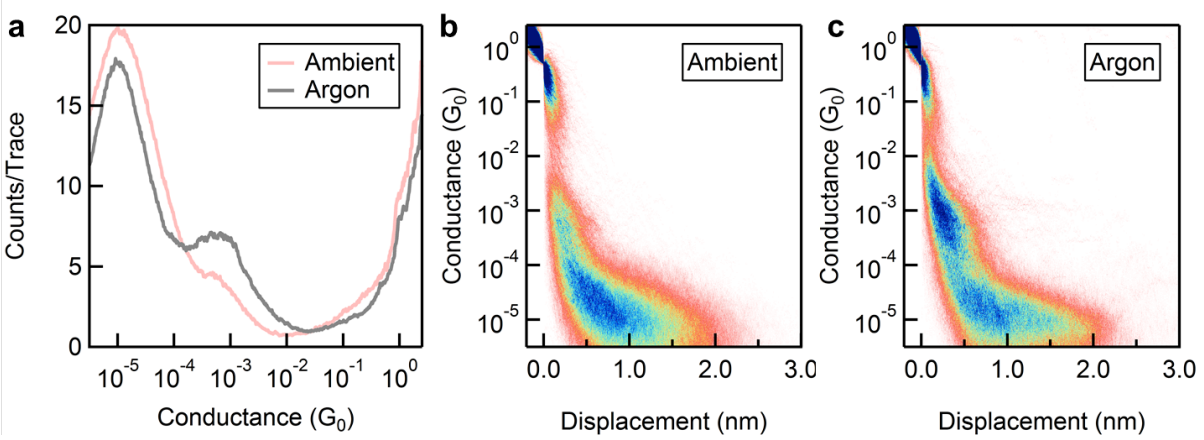
Figure S3. (a) Logarithmically-binned conductance histograms, and (b) and (c) two-dimensional (2D) conductance versus displacement histograms for **1** collected in 1,2,4-trichlorobenzene under under ambient conditions and under an inert atmosphere of Ar. The peak at ~10^{-3} G_0 comes from uncoordinated **L1**. Histograms were created by aligning individual conductance traces at 0.5 G_0 and then overlaying all traces to generate the 2D image.

IV. Tight Binding

We use a tight binding model to determine a Hamiltonian matrix and then use a non-equilibrium Green's Function formalism in order to qualitatively model transmission through the molecular junctions. As described in the main text, we use an n-site model to represent the molecule, and couple only nearest neighbor sites. For the ligands, the model consists of 1, 2 and 3 sites (for **L1-L3**) of energy ε, with nearest neighbors coupled by δ. The cluster model consists of two n-length ligands with an additional site in between the ligands. This site has an energy E_0 and is coupled to its nearest neighbors by τ. In all cases, the molecule is coupled to the leads by an imaginary, energy independent, self-energy term $-i\Gamma/2$. In order to compute molecular transmission functions, we turn to the non-equilibrium Green's Function formalism. The retarded Green's function for the molecular junction is defined as $G(E) = [EI-H]^{-1}$, and transmission is then given as $T(E)= \text{Tr}(\Gamma_L G \Gamma_R G)$, which is computed numerically. Here, Γ_L and Γ_R are coupling

matrices coupling the molecule to the left and right leads, respectively. Values for Γ, ε, and δ are chosen such that the ligand conductance values are similar to the experimental values.

When adding the cluster site, we explore a parameter space of -1.5 to -0.1 eV for τ and -3.0 to -1.6 eV for E_0 to see the impact that these values have on the decay constant for the two systems. This is demonstrated in Figure 4d, where it is clear that it is not possible to obtain significantly different conductance decay constant (β) values using this model. As mentioned in the text, we also show in Figure S3 that it is possible to obtain higher conductances for a given cluster as compared to its corresponding ligand.
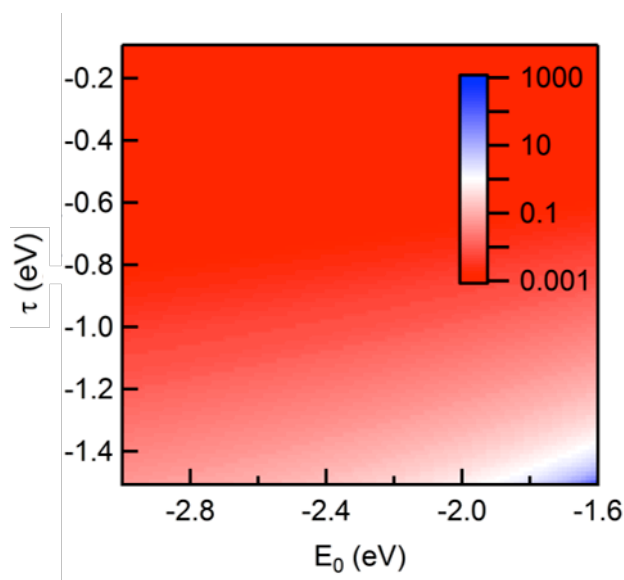

Figure S4. Two-dimensional plot showing the conductance ratio of **1** to **L1** (G_1/G_{L1}) as obtained from our tight binding model. We kept Γ, ε, and δ constant while varying E_0 and τ. We find that, given certain parameters, we can wind up with a system in which the cluster is more conducting than its corresponding ligand.

V. UV-Vis Absorption Spectroscopy

General Information: All spectra were taken in a quartz cuvette sealed under nitrogen in the glovebox following a recording of the background spectrum. UV-Vis spectrum of cluster **1** is provided in a previously published report.[3]
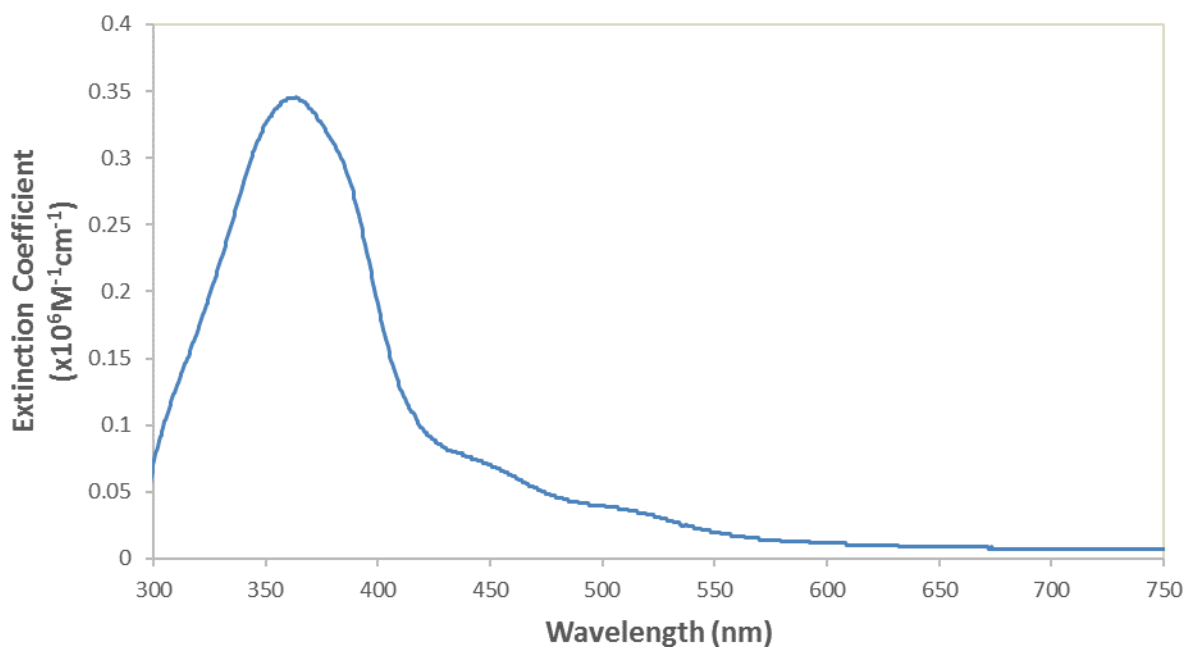

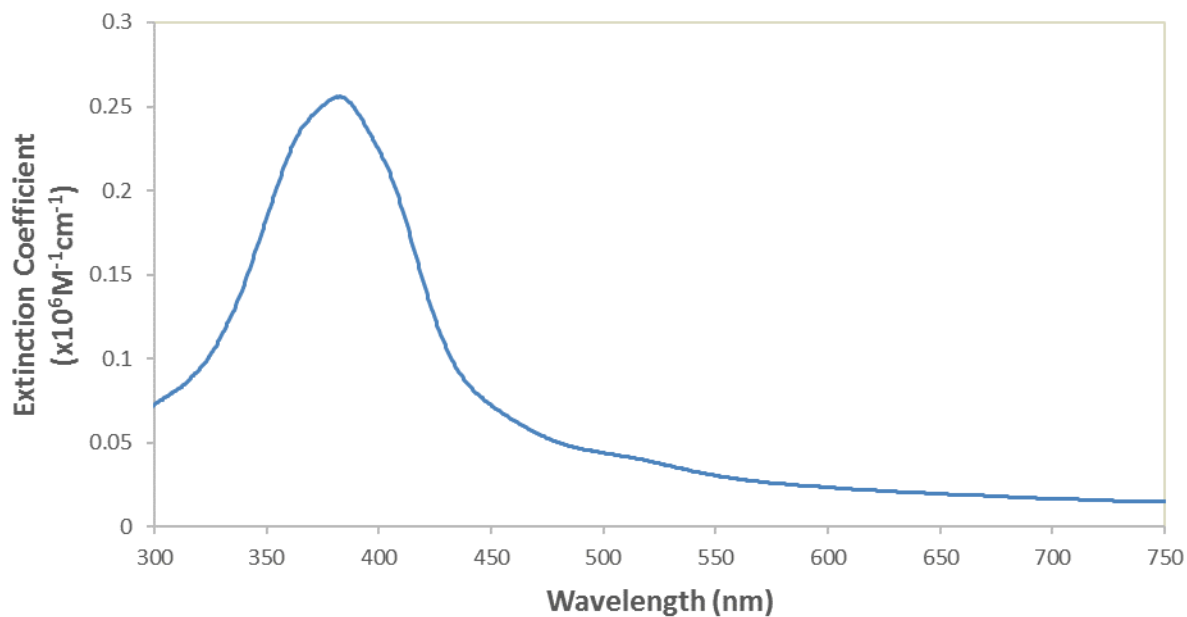**Figure S5**. UV-Vis spectrum of cluster **2** was taken in dry and degassed THF (0.7 μM).

Figure S6. UV-Vis spectra of cluster **3** was taken in dry and degassed THF (4.5 μM).

VII. References

1. J. S. Meisner, D. F. Sedbrook, M. Krikorian, J. Chen, A. Sattler, M. E. Carnes, C. B. Murray, M. Steigerwald and C. Nuckolls, *Chem. Sci.*, 2012, **3**, 1007-1014.

2. C. H. Xue and F. T. Luo, *J. Org. Chem.*, 2003, **68**, 4417-4421.

3. X. Roy, C. L. Schenck, S. Ahn, R. A. Lalancette, L. Venkataraman, C. Nuckolls and M. L. Steigerwald, *Angew. Chem. Int. Ed.*, 2012, **51**, 12473-12476.