SUPPLEMENTARY INFORMATION

Single-Electron Currents in Designer Single-Cluster Devices

Suman Gunasekaran¹#, Douglas A. Reed¹#, Daniel W. Paley¹, Amymarie K. Bartholomew¹, Latha Venkataraman¹,²*, Michael L. Steigerwald¹*, Xavier Roy¹*, Colin Nuckolls¹*

¹Department of Chemistry, Columbia University, New York, NY 10027
²Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027

Table of Contents:

1. Experimental
2. Hopping Transport Model
3. Additional Figures
4. Additional Tables
5. References
1. Experimental

General considerations. All synthetic procedures were conducted under an inert N₂ atmosphere in a glovebox or using standard Schlenk techniques. Solvents were purchased from Sigma-Aldrich and dried with an alumina column or 3 Å molecular sieves prior to use. Ferrocenium hexafluorophosphate, trimethylsilane diazomethane solution, and tetrabutylammonium hexafluorophosphate were purchased from Sigma Aldrich and used as received. The starting materials trans-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂, trans-Co₆Se₈(PEt₃)₄(CO)₂, cis-Co₆Se₈(PEt₃)₄(CO)₂, and PEt₂(p-C₆H₄SMe) were prepared according to previously published procedures. The material [Co₆Se₈(PEt₂(p-C₆H₄SMe))₆][BF₄] (L.6) was prepared according to a previously published procedure. ¹H nuclear magnetic resonance (NMR) measurements were carried out on Bruker DRX400 (400 MHz) spectrometers. The blue light source was a Kessil PR160-456nm lamp.

Synthesis of [trans-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂][PF₆] (trans-L.2). To a flask loaded with a stir bar was added 30 mg trans-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂ (0.016 mmol, 1.0 eq) and 5.3 mg ferrocenium hexafluorophosphate (0.016 mmol, 1.0 eq) dissolved in 5 mL of tetrahydrofuran. The solution was stirred at room temperature for 3 hours. The solvent was removed in vacuo, and the resulting powder was dissolved in a minimal amount of toluene, layered with ether, and let stand at −35 °C for 3 days to afford [trans-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂][PF₆] (trans-L.2) as a black powder (22 mg, 68%). Dark needle-like crystals suitable for X-ray diffraction were grown from vapor diffusion of pentanes into a concentrated tetrahydrofuran solution.

¹H NMR: (400 MHz, C₆D₆, 298 K): δ = −0.64 (24H, br), 0.12 (12H, br), 0.29 (36H, br), 2.01 (8H, br), 2.27 (6H, br m), 6.95 (4H, d), 7.49 (4H, d) ppm.

Synthesis of cis-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂. To a flask loaded with a stir bar was added 50 mg cis-Co₆Se₈(PEt₃)₄(CO)₂ (0.033 mmol, 1.0 eq) and 17.5 mg of PEt₂(p-C₆H₄SMe) (0.083 mmol, 2.5 eq) dissolved in 5 mL of tetrahydrofuran. The solution was stirred under blue light at room temperature for 3 hours. The solvent was removed in vacuo, and the resulting powder was triturated with acetonitrile (3 x 5 mL) to afford the product cis-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂ as a black powder (50 mg, 80%).

¹H NMR: (400 MHz, C₆D₆, 298 K): δ = 1.08 (48H, m), 1.88 (24H, m), 2.00 (8H, m), 2.36 (6H, br m), 7.12 (4H, d), 7.48 (4H, d) ppm.

Synthesis of [cis-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂][PF₆] (cis-L.2). To a flask loaded with a stir bar was added 30 mg cis-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂ (0.016 mmol, 1.0 eq) and 5.3 mg ferrocenium hexafluorophosphate (0.016 mmol, 1.0 eq) dissolved in 5 mL of tetrahydrofuran. The solution was stirred at room temperature for 3 hours. The solvent was removed in vacuo, and the resulting powder was dissolved in a minimal amount of toluene, layered with ether, and let stand at −35 °C for 3 days to afford [cis-Co₆Se₈(PEt₃)₄(PEt₂(p-C₆H₄SMe))₂][PF₆] (cis-L.2) as a black powder (15 mg, 46%). Dark hexagonal plate-like crystals suitable for X-ray diffraction were grown from vapor diffusion of pentanes into a concentrated tetrahydrofuran solution.

¹H NMR: (400 MHz, C₆D₆, 298 K): δ = −1.35 (8H, br), −0.70 (12H, br), −0.44 (12H, br), 0.00 (12H, br), 0.31 (36H, br), 2.20 (6H, br m), 7.02 (4H, d), 7.55 (4H, d) ppm.
Synthesis of [trans-Co$_{12}$Se$_{16}$(PEt)$_8$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$][PF$_6$] (dimer-L2). To a flask loaded with a stir bar was added 60 mg trans-Co$_6$Se$_8$(PEt)$_3$(CO)$_2$ (0.040 mmol, 1.0 eq) and 12.6 mg PEt$_2$(p-C$_6$H$_4$SMe) (0.059 mmol, 1.5 eq) dissolved in 6 mL of tetrahydrofuran. The solution was stirred under blue light at room temperature for 3 hours. The solvent was removed in vacuo to produce a mixture of the desired product trans-Co$_6$Se$_8$(PEt)$_3$(CO)(PEt$_2$(p-C$_6$H$_4$SMe)) and byproduct trans-Co$_6$Se$_8$(PEt)$_3$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$ in a 1:1 mixture as determined by $^1$H NMR spectroscopy. The crude mixture was then added to a flask loaded with a stir bar, and 6 mL of tetrahydrofuran was added. The solution was cooled to $-40$ °C, and 30 µL of trimethylsilane diazomethane solution (2.0 M in hexanes, 0.060 mmol, 1.5 eq) was added dropwise. The solution was stirred under blue light at 0 °C for 3 hours. The solvent was removed in vacuo to produce a mixture of the desired product trans-Co$_6$Se$_8$(PEt)$_3$(C(H)SiMe$_3$)(PEt$_2$(p-C$_6$H$_4$SMe)) along with the byproduct trans-Co$_6$Se$_8$(PEt)$_3$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$, which remains from the initial reaction, in a 1:1 mixture as determined by $^1$H NMR spectroscopy. The crude mixture was dissolved in 2 mL of pyridine and let sit at room temperature overnight. The solvent was removed in vacuo, and the resultant mixture was dissolved in 2 mL of benzene and stirred at room temperature overnight. The solvent was removed in vacuo to produce a crude mixture of the desired product trans-Co$_{12}$Se$_{16}$(PEt)$_8$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$ along with the byproduct trans-Co$_6$Se$_8$(PEt)$_3$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$ that remains from the initial reaction to produce a total of 50 mg of powder, which is assumed to be 33% of desired product and 66% byproduct (by molarity). The crude mixture was then added to a flask loaded with a stir bar, and a solution of 3.5 mg of ferrocenium hexafluorophosphate (0.011 mmol, 0.27 eq) dissolved in 6 mL of tetrahydrofuran was added. The solution was stirred at room temperature overnight. The solvent was removed in vacuo, and the product was extracted from the crude mixture with acetonitrile (3 x 5 mL). The solvent was removed in vacuo, and the resulting powder was dissolved in a minimal amount of toluene, layered with ether, and let stand at $-35$ °C for three days to produce [trans-Co$_{12}$Se$_{16}$(PEt)$_8$(PEt$_2$(p-C$_6$H$_4$SMe))$_2$][PF$_6$] (dimer-L2) as a black powder (20 mg, 25%). Dark needle-like crystals suitable for X-ray diffraction were grown from vapor diffusion of pentanes into a concentrated tetrahydrofuran solution. Similar to previously reported Co$_{12}$Se$_{16}$$L$$_{10}$ clusters, the monocationic dimer-L2 is NMR silent.$^6$

$^1$H NMR for intermediate trans-Co$_6$Se$_8$(PEt)$_3$(CO)(PEt$_2$(p-C$_6$H$_4$SMe)): (400 MHz, C$_6$D$_6$, 298 K): $\delta = 0.96$ (36H, m), 1.07 (4H, m), 1.74 (24H, m), 1.97 (6H, m), 2.44 (3H, br m), 7.10 (2H, d), 7.60 (2H, d) ppm.

$^1$H NMR for intermediate trans-Co$_6$Se$_8$(PEt)$_3$(C(H)SiMe$_3$)(PEt$_2$(p-C$_6$H$_4$SMe)): (400 MHz, C$_6$D$_6$, 298 K): $\delta = 0.10$ (3H, s), 0.84 (4H, m), 1.08 (36H, m), 1.85 (6H, m), 1.88 (24H, m), 2.41 (3H, br m), 6.75 (1H, s), 7.58 (2H, d), 8.53 (2H, d) ppm.

Single crystal X-ray diffraction. Data for all compounds was collected on an Agilent SuperNova diffractometer using mirror-monochromated Cu Kα radiation. Data collection, integration, scaling (ABSPACK) and absorption correction (face-indexed Gaussian integration)$^5$ were performed in CrysAlisPro.$^6$ Structure solution was performed using ShelXT.$^7$ Subsequent refinement was performed by full-matrix least-squares on F$_2$ in ShelXL.$^3$ $^3$ PLATON$^9$ was used to model disordered solvent in the structure of dimer-L2 by the SQUEEZEl$^{10}$ algorithm. A solvent mask was applied in Olex2$^{11}$ to model disordered solvent in cis-L2. Olex2 was used for viewing and to prepare CIF files. Thermal ellipsoid plots were prepared in CrystalMaker.$^{12}$ Thermal ellipsoids are rendered at the 50% probability level.
**Ex situ cyclic voltammetry.** Cyclic voltammetry was collected using a BioLogic VSP-300 potentiostat in an N$_2$ filled glovebox. The measurement was collected in a 0.1 M solution of tetrabutylammonium hexafluorophosphate supporting electrolyte in tetrahydrofuran, using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode, with a scan speed of 50 mV/s. All measurements were then referenced to the ferrocene/ferrocenium redox couple.
2. Hopping Transport Model

The derivation of the steady-state current for a two-level Marcus model as been presented previously\textsuperscript{13-15} but is included here for completeness. For the two-level Marcus model, there are a total of 8 hopping rates that must be considered,

\[
\begin{array}{cccc}
\text{Red} & \text{Ox} \\
L & R & L & R \\
\text{level 1} & k^+_{1,L} & k^+_{1,R} & k^-_{1,L} & k^-_{1,R} \\
\text{level 2} & k^+_{2,L} & k^+_{2,R} & k^-_{2,L} & k^-_{2,R} \\
\end{array}
\]

The master equation at steady-state is,

\[
\begin{pmatrix}
\frac{d}{dt} P(2) \\
\frac{d}{dt} P(1) \\
\frac{d}{dt} P(0)
\end{pmatrix} =
\begin{pmatrix}
-(k^-_{2,L} + k^-_{2,R}) & (k^+_{2,L} + k^+_{2,R}) & 0 \\
(k^-_{2,L} + k^-_{2,R}) & -(k^+_{2,L} + k^+_{2,R}) - (k^-_{1,L} + k^-_{1,R}) & (k^+_{1,L} + k^+_{1,R}) \\
0 & (k^-_{1,L} + k^-_{1,R}) & -(k^+_{1,L} + k^+_{1,R})
\end{pmatrix}
\begin{pmatrix}
P(2) \\
P(1) \\
P(0)
\end{pmatrix} = 0
\]

This system of equations can be solved to yield,

\[
P(2) = \frac{(k^+_{2,L} + k^+_{2,R})(k^+_{1,L} + k^+_{1,R})}{N}
\]

\[
P(1) = \frac{(k^-_{2,L} + k^-_{2,R})(k^+_{1,L} + k^+_{1,R})}{N}
\]

\[
P(0) = \frac{(k^+_{2,L} + k^+_{2,R})(k^-_{1,L} + k^-_{1,R})}{N}
\]

where \( N \) is the normalization so that \( P(0) + P(1) + P(2) = 1 \),

\[
N = (k^+_{2,L} + k^+_{2,R})(k^+_{1,L} + k^+_{1,R}) + (k^-_{2,L} + k^-_{2,R})(k^+_{1,L} + k^+_{1,R}) + (k^-_{2,L} + k^-_{2,R})(k^-_{1,L} + k^-_{1,R})
\]

The steady-state current can be obtained by considering the net hopping between the left electrode and the cluster,

\[
I(V) = e \left( k^-_{2,L} P(2) - k^+_{2,L} P(1) + k^-_{1,L} P(1) - k^+_{1,L} P(0) \right)
\]
3. Additional Figures:

**Figure S1.** Molecular structure of (a) trans-L2 and (b) cis-L2. For each crystal structure, there is one-half cluster in the asymmetric unit; the other half is generated by inversion. PF$_6$ anions, disordered solvent, hydrogen atoms, and the minor positions of disordered ligands are omitted for clarity. Black, carbon; blue, cobalt; green, selenium; magenta, phosphorus; yellow, sulfur.

**Figure S2.** *Ex situ* cyclic voltammograms of trans-L2 (blue), cis-L2 (red), and L6 (green) in a 0.1 M tetrabutylammonium hexafluorophosphate solution in tetrahydrofuran at a scan rate of 50 mV/s.
**Figure S3.** 2D conductance histograms of (a) trans-L2, (b) cis-L2, and (c) L6 measured at 500 mV in PC. All compounds display similar conductances and plateau lengths.

**Figure S4.** Example I-V measurement for trans-L2, showing tip displacement (top), source-drain bias (middle), and measured current (bottom) as a function of time. Successful I-V measurements were selected using an automated algorithm that required the conductance during the initial 25 ms “hold” to be within the width of the molecular conductance histogram.
Figure S5. Molecular structures of the two independent molecules of dimer-L2. Each independent position has one-half cluster in the asymmetric unit; the other half is generated by inversion. PF$_6$ anions, disordered solvent, hydrogen atoms, and the minor positions of disordered ligands are omitted for clarity. Black, carbon; blue, cobalt; green, selenium; magenta, phosphorus; yellow, sulfur.
Figure S6. Expanded view of the core of dimer-L2, with selected bond lengths highlighted.

Figure S7. (a) 1D conductance histograms for trans-L2 and dimer-L2 measured at 500 mV in PC. The conductance of dimer-L2 is higher than trans-L2. (b) 2D conductance histogram of dimer-L2 measured at 500 mV. The plateau length is larger than for trans-L2, consistent with the difference in molecule length.
**Figure S8.** Schematic of proposed electron transport mechanism for trans-L2. The molecular junction is depicted with trans-L2 (blue) connecting the coated tip (left) and substrate (right). Due to the coated tip, the redox levels (vertical dashed blue lines) are effectively pinned to the chemical potential of the substrate ($\mu_R$). Biassing the junction modulates the chemical potential of the tip ($\mu_L$) relative to the redox levels of the cluster. At low bias, where oxidation/reduction of [trans-L2]$^+$ is not favorable, current blockade is observed. At negative bias, when $\mu_L$ is greater than the reduction potential of [trans-L2]$^+$ ($E_{0/1^+}$), the tip can reduce the cluster and the substrate can subsequently oxidize the cluster. At positive bias, when $\mu_L$ is lower than the oxidation potential of [trans-L2]$^+$ ($E_{1^+/2^+}$), the tip can oxidize the cluster and the substrate can subsequently reduce the cluster.

**Figure S9.** Comparison of change in average Co–Co distance as a function of oxidation state for the model compounds [Co$_6$Se$_8$(PET$_2$(p-C$_6$H$_4$SMe))$_6$]$^{n^+}$ (blue)$^3$ and [Co$_{12}$Se$_{16}$(PMe$_3$)$_{10}$]$^{n^+}$ (red)$^4$. 

S10
4. Additional Tables

Table S1. Crystallographic information for **trans-L2**, **cis-L2**, and **dimer-L2**.

<table>
<thead>
<tr>
<th>Compound</th>
<th>trans-L2</th>
<th>cis-L2</th>
<th>dimer-L2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>( \text{C}<em>{54}\text{H}</em>{110}\text{Co}<em>{6}\text{F}</em>{6}\text{O}<em>{2}\text{P}</em>{7}\text{S}<em>{2}\text{Se}</em>{8} )</td>
<td>( \text{C}<em>{46}\text{H}</em>{94}\text{Co}<em>{6}\text{F}</em>{6}\text{P}<em>{7}\text{S}</em>{2}\text{Se}_{8} )</td>
<td>( \text{C}<em>{74}\text{H}</em>{162}\text{Co}<em>{12}\text{F}</em>{6}\text{OP}<em>{11}\text{S}</em>{2}\text{Se}_{16} )</td>
</tr>
<tr>
<td><strong>MW</strong></td>
<td>2171.58</td>
<td>2027.38</td>
<td>3557.34</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C2/c</td>
<td>P6(_{3})22</td>
<td>P-1</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>28.1746(4)</td>
<td>21.8220(8)</td>
<td>13.5505(2)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>12.00577(15)</td>
<td>21.8220(8)</td>
<td>17.7338(5)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>23.5749(3)</td>
<td>26.4747(8)</td>
<td>25.7572(6)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
<td>90</td>
<td>90</td>
<td>74.953(2)</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>108.0493(14)</td>
<td>90</td>
<td>86.191(2)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90</td>
<td>120</td>
<td>79.111(2)</td>
</tr>
<tr>
<td><strong>V (Å(^3))</strong></td>
<td>7581.95(18)</td>
<td>10918.2(9)</td>
<td>5868.7(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td><strong>( \rho_{\text{calc}} ) (g cm(^{-3}))</strong></td>
<td>1.902</td>
<td>1.850</td>
<td>2.013</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>( \lambda ) (Å)</strong></td>
<td>1.54184</td>
<td>1.54184</td>
<td>1.54184</td>
</tr>
<tr>
<td><strong>( 2\theta_{\text{min}}, 2\theta_{\text{max}} )</strong></td>
<td>7, 146</td>
<td>7, 141</td>
<td>7, 146</td>
</tr>
<tr>
<td><strong>N_ref</strong></td>
<td>42908</td>
<td>69745</td>
<td>82392</td>
</tr>
<tr>
<td><strong>R(int), R(σ)</strong></td>
<td>.0460, .0316</td>
<td>.0972, .0481</td>
<td>.0964, .1006</td>
</tr>
<tr>
<td><strong>μ (mm(^{-1}))</strong></td>
<td>16.8</td>
<td>17.5</td>
<td>20.7</td>
</tr>
<tr>
<td><strong>Size (mm)</strong></td>
<td>.27 x .05 x .04</td>
<td>.14 x .08 x .05</td>
<td>.50 x .05 x .05</td>
</tr>
<tr>
<td><strong>( \frac{T_{\text{max}}}{T_{\text{min}}} )</strong></td>
<td>4.96</td>
<td>2.65</td>
<td>1.82</td>
</tr>
<tr>
<td><strong>Data</strong></td>
<td>7511</td>
<td>6938</td>
<td>23251</td>
</tr>
<tr>
<td><strong>Restraints</strong></td>
<td>280</td>
<td>7</td>
<td>804</td>
</tr>
<tr>
<td><strong>Parameters</strong></td>
<td>522</td>
<td>308</td>
<td>1265</td>
</tr>
<tr>
<td><strong>( R_1(\text{obs}) )</strong></td>
<td>0.0441</td>
<td>0.0676</td>
<td>0.0722</td>
</tr>
<tr>
<td><strong>wR(_2)(all)</strong></td>
<td>0.1192</td>
<td>0.1914</td>
<td>0.1968</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>1.071</td>
<td>1.051</td>
<td>1.016</td>
</tr>
<tr>
<td><strong>Peak, hole ( (e^- Ā^{-3}) )</strong></td>
<td>1.26, -1.12</td>
<td>.561, -.594</td>
<td>2.44, -1.81</td>
</tr>
<tr>
<td><strong>CCDC</strong></td>
<td>1996815</td>
<td>2014690</td>
<td>1996814</td>
</tr>
</tbody>
</table>
5. References