#### SUPPLEMENTARY INFORMATION

# Single-Electron Currents in Designer Single-Cluster Devices

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### 1. Experimental

General considerations. All synthetic procedures were conducted under an inert N<sub>2</sub> 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 hexaflurophosphate, trimethylsilane diazomethane solution, and tetrabutylammonium hexafluorophosphate were purchased from Sigma Aldrich and used as received. The starting materials  $trans-Co_6Se_8(PEt_3)_4(PEt_2(p-C_6H_4SMe))_2,$  $trans-Co_6Se_8(PEt_3)_4(CO)_2$ , cis-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(CO)<sub>2</sub>, and PEt<sub>2</sub>(p-C<sub>6</sub>H<sub>4</sub>SMe) were prepared according to previously published procedures.<sup>1-2</sup> The material  $[Co_6Se_8(PEt_2(p-C_6H_4SMe))_6][BF_4]$  (L6) was prepared according to a previously published procedure.<sup>3</sup><sup>1</sup>H 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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>][PF<sub>6</sub>] (trans-L2). To a flask loaded with a stir bar was added 30 mg *trans*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub> (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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>][PF<sub>6</sub>] (trans-L2) 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.

<sup>1</sup>H NMR: (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -0.64$  (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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>. To a flask loaded with a stir bar was added 50 mg of *cis*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(CO)<sub>2</sub> (0.033 mmol, 1.0 eq) and 17.5 mg of PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe) (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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub> as a black powder (50 mg, 80%).

<sup>1</sup>H NMR: (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>][PF<sub>6</sub>] (cis-L2). To a flask loaded with a stir bar was added 30 mg *cis*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub> (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*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>][PF<sub>6</sub>] (cis-L2) 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.

<sup>1</sup>H NMR: (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = -1.35$  (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<sub>12</sub>Se<sub>16</sub>(PEt<sub>3</sub>)<sub>8</sub>(PEt<sub>2</sub>(p-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>][PF<sub>6</sub>] (dimer-L2). To a flask loaded with a stir bar was added 60 mg trans- $Co_6Se_8(PEt_3)_4(CO)_2$  (0.040 mmol, 1.0 eq) and 12.6 mg  $PEt_2(p-C_6H_4SMe)$  (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  $trans-Co_6Se_8(PEt_3)_4(CO)(PEt_2(p-C_6H_4SMe))$  and byproduct *trans*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub> in a 1:1 mixture as determined by <sup>1</sup>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<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(C(H)SiMe<sub>3</sub>)(PEt<sub>2</sub>(p-C<sub>6</sub>H<sub>4</sub>SMe)) along with the byproduct *trans*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(PEt<sub>2</sub>(p-C<sub>6</sub>H<sub>4</sub>SMe))<sub>2</sub>, which remains from the initial reaction, in a 1:1 mixture as determined by <sup>1</sup>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- $Co_{12}Se_{16}(PEt_3)_8(PEt_2(p-C_6H_4SMe))_2$  along with the byproduct trans- $Co_6Se_8(PEt_3)_4(PEt_2(p-C_6H_4SMe))_2$  $C_6H_4SM_e)_2$  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<sub>12</sub>Se<sub>16</sub>(PEt<sub>3</sub>)<sub>8</sub>(PEt<sub>2</sub>(p- $C_6H_4SM_{e})_2$  [PF<sub>6</sub>] (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.<sup>4</sup>

<sup>1</sup>H NMR for intermediate *trans*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(CO)(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe)): (400 MHz, C<sub>6</sub>D<sub>6</sub>, 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.

<sup>1</sup>H NMR for intermediate *trans*-Co<sub>6</sub>Se<sub>8</sub>(PEt<sub>3</sub>)<sub>4</sub>(C(H)SiMe<sub>3</sub>)(PEt<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>SMe)): (400 MHz, C<sub>6</sub>D<sub>6</sub>, 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 K $\alpha$  radiation. Data collection, integration, scaling (ABSPACK) and absorption correction (face-indexed Gaussian integration)<sup>5</sup> were performed in CrysAlisPro.<sup>6</sup> Structure solution was performed using ShelXT.<sup>7</sup> Subsequent refinement was performed by full-matrix least-squares on F<sub>2</sub> in ShelXL.3.<sup>8</sup> PLATON<sup>9</sup> was used to model disordered solvent in the structure of **dimer-L2** by the SQUEEZE<sup>10</sup> algorithm. A solvent mask was applied in Olex2<sup>11</sup> to model disordered solvent in **cis-L2**. Olex2 was used for viewing and to prepare CIF files. Thermal ellipsoid plots were prepared in CrystalMaker.<sup>12</sup> 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<sup>13-15</sup> but is included here for completeness. For the two-level Marcus model, there are a total of 8 hopping rates that must be considered,

Red
 Ox

 L
 R
 L
 R

 level 1
 
$$k_{1,L}^+$$
 $k_{1,R}^ k_{1,L}^ k_{1,R}^-$ 

 level 2
  $k_{2,L}^+$ 
 $k_{2,R}^+$ 
 $k_{2,L}^ k_{2,R}^-$ 

The master equation at steady-state is,

$$\frac{d}{dt} \begin{pmatrix} P(2) \\ P(1) \\ P(0) \end{pmatrix} = \begin{pmatrix} -(k_{2,L}^- + k_{2,R}^-) & (k_{2,L}^+ + k_{2,R}^+) & 0 \\ (k_{2,L}^- + k_{2,R}^-) & -(k_{2,L}^+ + k_{2,R}^+) - (k_{1,L}^- + k_{1,R}^-) & (k_{1,L}^+ + k_{1,R}^+) \\ 0 & (k_{1,L}^- + k_{1,R}^-) & -(k_{1,L}^+ + k_{1,R}^+) \end{pmatrix} \begin{pmatrix} P(2) \\ P(1) \\ P(0) \end{pmatrix} = 0$$

This system of equations can be solved to yield,

$$P(2) = (k_{2,L}^{+} + k_{2,R}^{+})(k_{1,L}^{+} + k_{1,R}^{+})/N$$
$$P(1) = (k_{2,L}^{-} + k_{2,R}^{-})(k_{1,L}^{+} + k_{1,R}^{+})/N$$
$$P(0) = (k_{2,L}^{-} + k_{2,R}^{-})(k_{1,L}^{-} + k_{1,R}^{-})/N$$

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 ( $\mu_R$ ). Biasing 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**]<sup>+</sup> is not favorable, current blockade is observed. At negative bias, when  $\mu_L$  is greater than the reduction potential of [**trans-L2**]<sup>+</sup> (E<sub>0/1+</sub>), 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**]<sup>+</sup> (E<sub>1+/2+</sub>), 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  $[Co_6Se_8(PEt_2(p-C_6H_4SMe))_6]^{n+}$  (blue)<sup>3</sup> and  $[Co_{12}Se_{16}(PMe_3)_{10}]^{n+}$  (red)<sup>4</sup>.

# 4. Additional Tables

Compound	trans-L2	cis-L2	dimer-L2
Formula	$C_{54}H_{110}Co_6F_6O_2P_7S_2Se_8$	$C_{46}H_{94}Co_6F_6P_7S_2Se_8$	$C_{74}H_{162}Co_{12}F_6OP_{11}S_2Se_{16}$
MW	2171.58	2027.38	3557.34
Space group	C2/c	P6 <sub>3</sub> 22	P-1
<i>a</i> (Å)	28.1746(4)	21.8220(8)	13.5505(2)
<b>b</b> (Å)	12.00577(15)	21.8220(8)	17.7338(5)
<i>c</i> (Å)	23.5749(3)	26.4747(8)	25.7572(6)
a (°)	90	90	74.953(2)
β (°)	108.0493(14)	90	86.191(2)
γ (°)	90	120	79.111(2)
V (Å <sup>3</sup> )	7581.95(18)	10918.2(9)	5868.7(2)
Z	4	6	2
$\rho_{calc}$ (g cm <sup>-3</sup> )	1.902	1.850	2.013
T (K)	100	100	100
λ (Å)	1.54184	1.54184	1.54184
$2\theta_{min}, 2\theta_{max}$	7, 146	7, 141	7, 146
Nref	42908	69745	82392
$R(int), R(\sigma)$	.0460, .0316	.0972, .0481	.0964, .1006
$\mu(\mathrm{mm}^{-1})$	16.8	17.5	20.7
Size (mm)	.27 x .05 x .04	.14 x .08 x .05	.50 x .05 x .05
T <sub>max</sub> / T <sub>min</sub>	4.96	2.65	1.82
Data	7511	6938	23251
Restraints	280	7	804
Parameters	522	308	1265
R <sub>1</sub> (obs)	0.0441	0.0676	0.0722
wR <sub>2</sub> (all)	0.1192	0.1914	0.1968
S	1.071	1.051	1.016
Peak, hole (e <sup>-</sup> Å <sup>-3</sup> )	1.26, -1.12	.561,594	2.44, -1.81
CCDC	1996815	2014690	1996814

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

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