# Redox-Switchable Allosteric Effects in Molecular Clusters

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S1 General Information

No unexpected or unusually high safety hazards were encountered during the experimental work reported in here.

The syntheses were conducted under a dinitrogen atmosphere using standard Schlenk or glovebox techniques (LC Technology Solutions glovebox equipped with a freezer set to −35 °C). The glassware was dried at 160 °C for a minimum of 12 h and cooled in an evacuated antechamber prior to use in the glovebox.

Solvents were purchased from Fischer Scientific and degassed, dried and purified using solvent purification columns housed in a stainless-steel cabinet and dispensed by a stainless-steel Schlenk line manufactured by JC Meyer Solvent Systems. Tetrahydrofuran (THF), diethyl ether, acetonitrile, and methylene chloride (DCM) are passed through two packed columns of neutral alumina. In the cases of n-pentane and toluene, one of the columns is packed with alumina and the other with Q5 reactant, a copper(II) oxide oxygen scavenger. All solvents were passed through an in-line, 2 µm filter, then stored over activated 3Å molecular sieves in the glovebox for a minimum of 72 h before use. 3Å molecular sieves were purchased from Sigma Aldrich and activated under vacuum at 300 °C for 48 h.

Deuterated solvents (CDCl₃, C₆D₆, CD₂Cl₂, CD₃CN) were purchased from Sigma Aldrich and stored over activated 3Å molecular sieves in the glovebox for a minimum of 72 h prior to use. Li₆(py)₆Co₆Se₃L₆ was prepared via reported literature methods.¹ ZnCl₂ (99.99%-Zn, PURATREM) was purchased from Strem Chemicals, Inc. and used as received without further purification. 1,10-phenanthroline (99%, anhydrous) was purchased from Sigma Aldrich and used without further purification. Ferrocenium hexafluorophosphate was purchased from Sigma Aldrich and recrystallized from diethyl ether prior to use. Tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2'',3'',j]phenazine was prepared using reported literature methods.² Tetra(n-butyl)ammonium hexafluorophosphate (98%) was purchased from Sigma Aldrich; prior to use it was recrystallized from ethanol three times, and brought to constant mass under reduced pressure at 110 °C for 24 h. [Ru(bpy)₃(phenedione)][PF₆]; was prepared using reported literature methods.³

Samples were prepared for elemental analysis by first crushing crystalline material into a powder, bringing it to constant mass under reduced pressure (ca. 12 h). Co, Se, P elemental analysis was conducted using a Perkin-Elmer Nexion 200B inductively-coupled plasma mass spectrometer (ICP-MS). Prior to ICP-MS analysis, samples were digested in neat nitric acid (Fisher Scientific, ICP-MS grade) at 50 °C.

UV-vis-nIR absorption spectra were acquired using a Varian Cary 5000 UV-Vis-nIR spectrometer using nIR quartz cuvettes (Spectrocell Inc., 10 mm path length, 220–3500 nm spectral window). Emission spectra were acquired using a Horiba FluoroMax-4, using fluorometer optical borosilicate VIS cuvettes (Spectrocell Inc., 10 mm path length, 340-2000 nm spectral window).

NMR spectra were acquired at 25 °C on Bruker 300, 500, or 700 MHz spectrometers. ¹H and ¹³C NMR spectra were referenced to residual deuterated solvent peaks. ³¹P and ¹⁹F NMR spectra were externally referenced to phosphoric acid and CCl₃F, respectively.

Cyclic voltammetry was conducted using a Gamry Interface 1010B potentiostat. A three-electrode cell setup was used with a glassy carbon disk working electrode, a platinum wire counter electrode, and a silver-wire pseudo-reference electrode. A three-electrode cell was also used for solid-state electrochemical measurements; in this instance, the analyte was dropcasted onto a carbon fiber paper electrode (1x1 cm, Spectracarb 2050A-1550) from a suspension of toluene. All potentials were referenced to the Fe₃+/Fe₂⁺ redox couple by adding a small amount of ferrocene (Fc) after each measurement. All electrochemical measurements were conducted under a dinitrogen atmosphere, at 25 °C.
S2  Synthetic Details and Characterization of Products

S2.1  Synthesis and isolation of \(\text{Zn}_3(\text{py})_2\text{Co}_6\text{Se}_8\text{L}_6 \) (\(\text{Zn}_3(\text{py})_2\))

A 100 mL Schlenk flask equipped with a 1-inch magnetic stir bar was loaded with Li(\text{py})_6\text{Co}_6\text{Se}_8\text{L}_6 (1.269 g, 0.391 mmol, 1.0 equiv) and toluene (60 mL), and the resulting mixture was partially frozen using the glovebox cold-well. Upon thawing, ZnCl\(_2\) (0.176 g, 1.29 mmol, 3.3 equiv) dissolved in THF (6 mL) was added dropwise over the course of 2 minutes to the stirring mixture. The reaction flask was then degassed, sealed, and removed from the glovebox. The dark-red reaction mixture was then stirred at 60 °C for 20 h. Volatiles were removed under reduced pressure. The residue was first triturated with diethyl ether (3 x 5 mL), extracted in DCM (50 mL) and then passed through a plug of Celite on a fritted-glass funnel. The filtrate was placed under reduced pressure yielding a dark colored, black looking solid, which was slurried in acetonitrile (100 mL) for 1 h, and then recollected on a fine-porosity fritted-glass filter. The isolated solids were washed with a second portion of acetonitrile (30 mL) to yield \(\text{Zn}_3(\text{py})_2\) as an analytically pure, black, microcrystalline solid (0.811 g, 0.263 mmol, 67%).

\(^1\text{H NMR}\) (C\(_6\)D\(_6\), 300 MHz): \(\delta = 8.38\) (br, 4 H, \text{py-N(CH}_2\text{CH)}), 7.11 (m, 24 H, PPh\(_2\) \text{ArH}), 7.08 (m, 18 H, PPh\(_2\) \text{ArH}), 6.98 (m, 6 H, PPh\(_2\) \text{ArH}), 6.76 (br, 4 H, \text{py-N(CH}_2\text{CH)}), 7.61 (d, 12 H, \text{J = 8.0 Hz, tolyl o-ArH}), 6.51 (d, 12 H, \text{J = 8.0 Hz, tolyl m-ArH}), 1.80 (s, 18 H, 4-tolyl-CH\(_3\) ppm).

\(^{13}\text{C NMR}\) (C\(_6\)D\(_6\), 125 MHz): \(\delta = 147.0\) (d, 15.0 Hz, i-tolyl), 142.0 (d, \(\text{J = 40 Hz, i-PPh}_2\)), 139.6 (d, \(\text{J = 40 Hz, i-PPh}_2\)), 132.6 (d, \(\text{J = 10.0 Hz, PPh CH}\)), 132.1 (d, \(\text{J = 10.0 Hz, PPh CH}\)), 129.2 (s, PPh \text{p-CH}), 128.9 (s, \text{tolyl m-(CH)}), 128.7 (s, PPh \text{p-CH}), 128.5 (s, \text{tolyl CH}_3), 127.6 (d, \(\text{J = 10.0 Hz, PPh CH}\)), 127.3 (d, \(\text{J = 10.0 Hz, PPh CH}\)), 122.9 (d, \(\text{J = 10.0 Hz, tolyl o-(CH)}_2\)), 20.4 (s, 4-tolyl-CH\(_3\)) ppm. \(^{31}\text{P NMR}\) (C\(_6\)D\(_6\), 283 MHz): \(\delta = +86.9\) (\(\nu_{1/2} = 333\) Hz) ppm. \textbf{UV-vis}: Figure S10. \textbf{Elemental analysis} found (calc.) for \(\text{Zn}_3(\text{py})_2\) (Formula: C\(_{124}\)H\(_{112}\)Co\(_6\)N\(_8\)P\(_6\)Se\(_8\)Zn\(_3\)): Co 11.66 (11.47), Se 20.74 (20.50), P 5.86 (6.03).

![Image](image-url)

Figure S1. \(^1\text{H NMR}\) (C\(_6\)D\(_6\), 25 °C, 700 MHz) spectrum of \(\text{Zn}_3(\text{py})_2\).
Isolation of Zn$_3$ from Zn$_3$(py)$_2$

Removal of the coordinated pyridine ligands in Zn$_3$(py)$_2$ was accomplished by extensive trituration with diethyl ether. Zn$_3$(py)$_2$ was first slurried in diethyl ether under vigorous stirring for 3-8 hours, then placed under reduced pressure while being heated at 80 °C for 3-12 hours. This process was repeated three times to ensure the coordinated pyridine was completely removed from the nanocluster.

$^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$: 7.74 (m, 24 H, PPh$_2$ArH), 7.21 (s, 18 H, PPh$_2$ArH), 7.13 (m, 12 H, PPh$_2$ArH), 6.63 (d, 12 H, $J = 8.1$ Hz, tolyl o-ArH), 6.51 (d, 12 H, $J = 8.1$ Hz, tolyl m-ArH), 1.81 (s, 18 H, 4-tolyl-CH$_3$) ppm.

S2.2 Isolation of Zn$_3$ from Zn$_3$(py)$_2$

Removal of the coordinated pyridine ligands in Zn$_3$(py)$_2$ was accomplished by extensive trituration with diethyl ether. Zn$_3$(py)$_2$ was first slurried in diethyl ether under vigorous stirring for 3-8 hours, then placed under reduced pressure while being heated at 80 °C for 3-12 hours. This process was repeated three times to ensure the coordinated pyridine was completely removed from the nanocluster.

$^1$H NMR (C$_6$D$_6$, 300 MHz) $\delta$: 7.74 (m, 24 H, PPh$_2$ArH), 7.21 (s, 18 H, PPh$_2$ArH), 7.13 (m, 12 H, PPh$_2$ArH), 6.63 (d, 12 H, $J = 8.1$ Hz, tolyl o-ArH), 6.51 (d, 12 H, $J = 8.1$ Hz, tolyl m-ArH), 1.81 (s, 18 H, 4-tolyl-CH$_3$) ppm.

S2.3 Synthesis and isolation of Zn$_3$(phen)$_2$Co$_6$Se$_4$L$_6$ (Zn$_3$(phen)$_2$)

Zn$_3$(py)$_2$ (500 mg, 0.162 mmol, 1.0 equiv) was charged into a 20 mL scintillation vial and dissolved in DCM (10 mL). 1,10-Phenanthroline (93 mg, 0.513 mmol, 3.15 equiv) was dissolved separately in DCM (2 mL) and added to the Zn$_3$(py)$_2$ solution with stirring. The reaction was stirred at room temperature for 30 minutes. The reaction mixture was concentrated under reduced pressure to half of its original volume, layered with n-pentane (~15 mL), and placed in the glovebox freezer overnight. The dark, black looking precipitate was isolated via vacuum filtration through a fine porosity glass fritted funnel and identified as Zn$_3$(phen)$_2$ (437 mg, 0.133 mmol, 82% yield). The product showed very poor solubility in C$_6$D$_6$ and CD$_3$CN, however it was very soluble in CD$_2$Cl$_2$. Upon dissolution in pyridine-$d_5$ the phenanthroline ligands dissociate from the cluster. $^1$H NMR spectrum reveals the formation of Zn$_3$(py)$_2$ cluster and uncoordinated 1,10-phenanthroline (Figure S5).

$^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300 MHz) $\delta$: 8.73 (s, br, 4 H, v$_{1/2}$ = 23.0 Hz, phen-NCHCH), 8.10 (s, br, 4 H, v$_{1/2}$ = 18.1 Hz, phen-NCHCH), 7.64 (s, 6 H.), 7.32 (s, br), 7.23 (s, br), 7.18 (s, br), 7.04 (s, br), 5.86 (s, br, 24 H, v$_{1/2}$ = 110.1 Hz, 4-tolyl-ArH), 1.74 (s, br, 18 H, v$_{1/2}$ = 46.3 Hz, 4-tolyl-CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, 25 °C, 125 MHz) $\delta$: 150.06, 136.90, 133.39, 132.87, 128.40, 128.01, 127.61, 126.93, 126.38, 123.92, 20.25 ppm. $^{31}$P NMR (CD$_2$Cl$_2$, 25 °C, 283 MHz): $\delta$ +101.25 (v$_{1/2}$ = 710.3
Hz), +83.15 (ν\(\frac{1}{2}\) = 1044.4 Hz) ppm. **Elemental analysis** found (calc.) for Zn\(_3\)(phen)\(_2\) (Formula: C\(_{138}\)H\(_{118}\)Co\(_6\)N\(_{10}\)P\(_6\)Se\(_8\)Zn\(_3\)):

Co 10.89 (10.77), Se 19.58 (19.24), P 5.50 (5.66).

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**Figure S3.** \(^1\)H NMR (CD\(_2\)Cl\(_2\), 25 °C, 300 MHz) spectrum of Zn\(_3\)(phen)\(_2\).

**Figure S4.** \(^{31}\)P NMR (CD\(_2\)Cl\(_2\), 25 °C, 121 MHz) spectrum of Zn\(_3\)(phen)\(_2\).
Figure S5. $^1$H NMR (pyr-$d_5$, 25 °C, 300 MHz) spectrum of $\text{Zn}_3(\text{phen})_2$ after dissolution in pyridine-$d_5$ reveals formation of free 1,10-phenanthroline and $\text{Zn}_3(\text{py})_x$.

Figure S6. $^1$H NMR (CD$_2$Cl$_2$, 25 °C, 300 MHz) spectrum of a mixture of $\text{Zn}_3(\text{phen})_2$ with increasing amounts of pyridine.
A 20 mL scintillation vial equipped with a magnetic stir bar was charged with \(\text{Zn}_3(\text{py})_2\) (217 mg, 0.071 mmol, 1.0 equiv) and DCM (8 mL) and cooled in the glovebox freezer (–35 °C) for 15 minutes. A solution of ferrocenium hexafluorophosphate (23 mg, 0.071 mmol, 1.0 equiv) in DCM (2 mL) was added dropwise to the cold stirring solution of \(\text{Zn}_3(\text{py})_2\). The reaction was allowed to stir for 15 minutes at room temperature and a solution of 1,10-phenanthroline (40 mg, 0.223 mmol, 3.15 equiv) in DCM (1 mL) was added dropwise. After two hours the reaction mixture was concentrated to half of its volume in vacuo, layered with \(n\)-pentane, and placed in the glovebox freezer (–35 °C) for 1 hour. The precipitate was collected on a medium porosity glass fritted funnel to yield a dark, black looking solid, identified as \([\text{Zn}_3(\text{phen})_3]\)[PF$_6$] (202 mg, 0.057 mmol, 80% yield). Single crystals suitable for X-ray diffraction studies were grown via the vapor diffusion of diethyl ether into a saturated solution of the product in acetonitrile at room temperature over the course of 2 days.

**1H NMR** (CD$_2$Cl$_2$, 300 MHz) \(\delta\): 8.76 (s, 6 H, phen-ArH), 8.10 (d, 6 H, \(J = 8.1\) Hz, phen-ArH), 7.70 (t, 6 H, \(J = 7.1\) Hz, PPh$_2$ p-ArH), 7.67 (s, 6 H, phen-ArH), 7.61 (t, 6 H, \(J = 7.1\) Hz, PPh$_2$ p-ArH), 7.39 (d, 12 H, PPh$_2$ o-ArH), 7.30 (s, 12 H, PPh$_2$ o-ArH), 7.02 (m, 6 H, phen-ArH), 6.84 (t, 12 H, \(J = 6.2\) Hz, PPh$_2$ m-ArH), 6.46 (t, 12 H, \(J = 6.2\) Hz, PPh$_2$ m-ArH), 5.78 (d, 12 H, \(J = 5.6\) Hz, tolyl ArH), 5.57 (d, 12 H, \(J = 7.4\) Hz, tolyl ArH), 1.37 (s, 18 H, 4-tolyl-CH$_3$) ppm. **13C NMR** (CD$_2$Cl$_2$, 125 MHz) \(\delta\) 145.48 (s, CH), 142.71 (s, C), 142.57 (s, C), 141.61 (s, C), 137.15 (s, CH), 134.36 (s, CH), 132.22 (s, C), 128.45 (s, CH), 127.27 (s, CH), 126.92 (s, CH), 125.42 (s, CH), 125.42 (s, CH), 124.04 (s, CH), 20.63 (s, CH$_3$) ppm. **31P NMR** (CD$_2$Cl$_2$, 121 MHz): \(\delta\) –143.92 (m, \(J_{FP} = 715\) Hz), –521.23 (\(v_{1/2} = 2283\) Hz) ppm. **19F NMR** (CD$_2$Cl$_2$, 471 MHz) \(\delta\) –73.85 (d, \(J_{FP} = 711\) Hz) ppm. **UV-vis**: Figure S10. **Elemental analysis** found (calc.) for \([\text{Zn}_3(\text{phen})_3]\)[PF$_6$] (Formula: C$_{150}$H$_{126}$Co$_8$F$_8$N$_{12}$P$_6$Se$_8$Zn$_3$): Co 9.82 (9.80), Se 17.79 (17.51), P 5.67 (6.01).
Figure S8. $^1\text{H}$ NMR (CD$_2$Cl$_2$, 25 °C, 300 MHz) spectrum of [Zn$_3$(phen)$_3$][PF$_6$].

Figure S9. $^{13}\text{C}$ NMR (CD$_2$Cl$_2$, 25 °C, 125 MHz) spectrum of [Zn$_3$(phen)$_3$][PF$_6$].
S2.5 Synthesis and isolation of Zn₃(bipy)Co₆Se₈L₆ (1-bipy)

Zn₃(py)₂ (50 mg, 0.016 mmol, 1.0 equiv) was dissolved in toluene (5 mL) with gentle heating and stirring over the course of 30 minutes. The solution was filtered through a plug of Celite into a 20 mL scintillation vial charged with 4,4ʹ-bipyridine (4 mg, 0.022 mmol, 1.8 equiv). The Celite plug was washed with additional toluene (2 mL). The reaction was allowed to sit undisturbed at 60 °C. Dark prismatic crystals suitable for single crystal X-ray diffraction formed on the sides of the vial. After 2 days, the mother liquor was decanted, and the crystals were soaked in toluene (3 x 5 mL; 15 minutes each cycle), decanting the supernatant after each treatment. The volatiles were removed in vacuo to yield 1-bipy (25 mg, 0.0082 mmol, 51% yield). The material is insoluble in toluene and DCM but dissolves in pyridine-d⁵, reforming free monomer Zn₃(py)₂ and 4,4ʹ-bipyridine. **Elemental analysis** found (calc.) for 1-bipy (Formula: C₁₂₅H₁₁ₐCo₆N₈P₆Se₈Zn₃): Co 11.25 (11.47), Se 20.76 (20.50), P 6.32 (6.03).

S2.6 Formation and single crystal growth of Zn₃(tpphz)Co₆Se₈L₆ (1-tpphz)

Tetrapyrido[3,2-a:2',3'-c:3''-h:2'':3'''-j]phenazine (4 mg, 0.011 mmol, 1.0 equiv) was suspended in DCM (8 mL) and added to a solution of Zn₃(py)₂ (33 mg, 0.011 mmol, 1.0 equiv) in DCM (2 mL). The reaction was allowed to stand at room temperature in the glovebox without stirring. After one week, a crystalline solid was collected on a fine porosity sintered glass filter. The material was washed with toluene (~15 mL) and then DCM (~30 mL) until the filtrate ran clear. The solids were brought to constant mass in vacuo to yield 1-tpphz as a dark crimson red solid (24 mg, 0.007 mmol, 65% yield). The material is insoluble in toluene and DCM but can be digested in pyridine-d₅ reforming free monomer Zn₃(py)₂. **Elemental analysis** found (calc.) for 1-tpphz (Formula: C₁₃₈H₁₁₁aCo₆N₁₂P₆Se₈Zn₃): Co 10.75 (11.47), Se 20.40 (20.50), P 6.01 (5.62). Incomplete digestion of 1-tpphz in concentrated nitric acid at 80 °C for 18 hours precluded accurate ICP-MS analysis.

Figure S10. UV-Vis-nIR absorption spectrum of Zn₃ and [Zn₃(phen)]₃[PF₆] in THF.
Synthesis and Isolation of $\text{[Zn}_3\text{(bpy)}_2\text{]}\cdot\text{Co}_6\text{Se}_8\text{L}_6\text{]}\cdot\text{[PF}_6\text{]}\$ (2-bipy)

$\text{Zn}_{3}\text{(py)}_2$ (100 mg, 0.032 mmol, 1.0 equiv) and FcPF$_6$ (11 mg, 0.032 mmol, 1.0 equiv) were dissolved separately in DCM (7 mL and 3 mL, respectively). The FcPF$_6$ solution was added dropwise to the stirring solution of $\text{Zn}_3\text{(py)}_2$ and the reaction was allowed to stir at room temperature for 10 minutes. The reaction mixture was filtered through a plug of Celite into a 20 mL scintillation vial charged with 4,4'-bipyridine (11 mg, 0.068 mmol, 2.1 equiv). The Celite plug was washed with additional DCM (2 mL). The reaction was allowed to sit undisturbed at room temperature. Dark prismatic crystals suitable for single crystal X-ray diffraction formed on the sides of the vial. After 2 days, the mother liquor was decanted, and the crystals were soaked in DCM (3 x 5 mL; 15 minutes each cycle), decanting the supernatant after each treatment. The volatiles were removed in vacuo to yield 2-bipy (45 mg, 0.014 mmol, 44% yield). The material is insoluble in toluene and DCM, however it dissolves in pyridine-$d_5$ forming free oxidized monomer, $\text{[Zn}_3\text{(py)}_3\text{]}\cdot\text{[PF}_6\text{]}\$ and 4,4'-bipyridine. **Elemental analysis** found (calc.) for 2-bpy (Formula: C$_{129}$H$_{114}$Co$_6$F$_6$N$_9$P$_7$Se$_8$Zn$_3$): Co 10.50 (10.46), Se 18.89 (18.69), P 6.39 (6.42).

**Characterization of $\text{[Zn}_3\text{(py)}_2\text{]}\cdot\text{[PF}_6\text{]}$**

$^1\text{H NMR}$ (pyridine-$d_5$, 500 MHz) δ: 8.86 (m, 6 H), 8.22 (m, 12 H), 8.10 (m, 6 H), 7.91 (m, 6 H), 7.76 (s, 12 H), 7.61 (m, 6 H), 6.99 (s, 12 H), 6.85 (s, 12 H), 6.79 (d, 12 H, $J = 8.0$ Hz), 6.49 (d, 12 H, $J = 7.0$ Hz), 1.66 (s, 18 H) ppm. $^{13}\text{C NMR}$ (pyridine-$d_5$, 125 MHz) δ 151.64 (s), 145.76 (s), 134.12 (s), 131.25 (s), 130.20 (s), 128.93 (s), 128.73 (s), 127.72 (s), 126.05 (s), 124.77 (s), 122.15 (s), 21.32 (s) ppm. $^{31}\text{P NMR}$ (pyridine-$d_5$, 121 MHz): δ −142.30 (sept, $J_{PF} = 712$ Hz) ppm. The aminophosphine $^{31}$P feature was not observed. $^{19}\text{F NMR}$ (pyridine-$d_5$, 470 MHz) δ −71.26 (d, $J_{PF} = 710$ Hz) ppm.

**S2.8 Reaction of $\text{Zn}_3\text{(py)}_2$ with [Ru(bipy’)$_2$(phenidione)][PF$_6$]$_2$**: synthesis of 3

A solution of [Ru(bipy’)$_2$(phenidione)][PF$_6$]$_2$ (11 mg, 0.012 mmol, 1.0 equiv) in acetonitrile (1 mL) was added dropwise to a stirring solution of $\text{Zn}_3\text{(py)}_2$ (34 mg, 0.012, 1.0 equiv) in toluene (2 mL). The reaction was stirred at room temperature for 10 minutes and then concentrated under reduced pressure. The residue was triturated with diethyl ether (2 x 4 mL) and then washed with n-pentane (~10 mL) and diethyl ether (~10 mL). The product was completely solubilized in acetonitrile and passed through a plug Celite. Notably, the starting $\text{Zn}_3\text{(py)}_2$ is completely insoluble in acetonitrile. The volatiles were removed in vacuo to yield...
a dark, black looking, solid (45 mg, 0.011 mmol, 92% yield) $^1$H NMR (CD$_3$CN, 500 MHz) 8.47, 7.99, 7.83, 7.77, 7.66, 7.56, 7.52, 7.40, 7.33, 6.94, 6.88, 6.87, 6.81, 6.72, 6.59, 6.34, 6.27, 6.21, 1.74 (s, 12 H), 1.68 (s, 6 H) ppm. $^{31}$P NMR (CD$_3$CN, 202 Hz) –144 (sept, $J_{FP} = 707$ Hz), –415 ($\nu_{1/2} = 1445$ Hz) ppm. ATR-FTIR (film): $\nu_{SQ} = 1464$ cm$^{-1}$. Elemental analysis found (calc.) for 3 (Formula: C$_{156}$H$_{134}$Co$_6$F$_{12}$N$_{14}$O$_2$P$_8$Ru$_8$Se$_8$Zn$_3$): Co 8.56 (8.85), Se 16.16 (15.81), P 6.56 (6.20).

Figure S12. $^1$H NMR (CD$_3$CN, 25 °C, 500 MHz) spectrum of 3.

Figure S13. $^{31}$P NMR (CD$_3$CN, 25 °C, 202 MHz) spectrum of 3.
Figure S14. IR spectra of $\text{Zn}_3(\text{py})_2$, $[\text{Ru}(\text{bipy'})_2(\text{phendione})][\text{PF}_6]_2$, and 3.

Figure S15. Absorption and emission spectra of $\text{Zn}_3(\text{py})_2$, 3 and $[\text{Ru}(\text{bipy'})_2(\text{phendione})][\text{PF}_6]_2$ in MeCN.
S3  Electrochemistry

Table S1. Half-wave potentials ($E_{1/2}$) and peak-to-peak separation potentials ($\Delta E_p$) of Co$_6$Se$_8$L$_6^H$ and Zn$_3$(py)$_2$ recorded in 0.1 M TBAPF$_6$ DCM or THF solutions and 1-tpphz drop casted onto a carbon paper electrode in a solution of 0.1 M TBAPF$_6$ in MeCN. All samples measured at a scan rate of 200 mV/s. Values recorded in DCM and THF solutions are reported with and without parenthesis, respectively.

| redox couple ($n_{\text{red}}$/$n_{\text{ox}}$) | $E_{1/2}$ (V vs Fe$^{0+}/+$) | $\Delta E_p$ (mV) |
|-----------------------------------------------|-------------------------------|------------------|
|                                              |                               | Co$_6$Se$_8$L$_6^H$ | Zn$_3$(py)$_2$ | 1-tpphz          |
| +3/+4                                        | 1.01; 110                     | -                 | -              |
| +2/+3                                        | 0.57 (0.41); 110 (201)         | 0.49; 131         | -              |
| +1/+2                                        | 0.05 (–0.08); 131 (201)        | 0.12 (–0.05); 181 (180) | –0.02 (irr) |
| 0/+1                                         | –0.63 (–0.69); 110 (191)      | –0.37 (–0.67); 121 (190) | –0.65; 122 |
| –1/0                                         | –1.98 (–2.13); 151 (313)      | –1.59 (–1.77); 111 (170) | –1.14 (irr) |

Figure S16. Cyclic voltammograms of Co$_6$Se$_8$L$_6^H$ and Zn$_3$(py)$_2$ recorded in DCM (solid) and THF (dashed) solutions with TBAPF$_6$ (0.1 M) at 200 mV/s. Due to the instability of the 1-tpphz in THF and the limited electrochemical window of DCM, the solid state cyclic voltammogram of 1-tpphz was recorded in a MeCN solution with TBAPF$_6$ (0.1 M) at 200 mV/s.
Figure S17. Cyclic voltammograms of $\text{Zn}_3(\text{py})_2$ recorded between 50 and 500 mV s$^{-1}$ in THF (0.1 M TBAPF$_6$) and referenced to ferrocene/ferrocenium (left) and plot of current density ($j_p$) versus the square root of scan rate ($v^{1/2}$) with linear fits used to model the data with the Randels-Sevcik equation (right).

Figure S18. Cyclic voltammograms of $\text{Zn}_3(\text{py})_2$ in THF (0.1 M TBAPF$_6$) and the 1-bipy nanowire digested in pyridine and recorded in MeCN (0.1 M TBAPF$_6$).
S4 X-ray Diffraction Studies

Single crystals suitable for X-ray analysis were coated in deoxygenated paratone oil and mounted on a 20 µm CryoLoop™ (Hampton Research, 18 mm mount, 0.2 to 0.3 mm loop diameter). Data was collected at –173 °C on a Bruker APEX II single crystal X-ray diffractometer, with a Mo source. Data was integrated and scaled using SAINT, SADABS within the APEX2 software package by Bruker. Solution by direct methods (SHELXT5 or SIR976,7) produced a complete heavy atom phasing model consistent with the proposed structure. Structures were completed by difference Fourier synthesis with SHELXL.8–10 Scattering factors are from Waasmair and Kirfel.11 Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances in the range 0.95–1.00 Å. Isotropic thermal parameters Ueq were fixed such that they were 1.2Ueq of their parent atom Ueq for CHs and 1.5Ueq of their parent atom Ueq in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

S4.1 Zn₃(THF)₂

Thin, dark-red prismatic crystals suitable for X-ray analysis were grown via vapor diffusion of diethyl ether into a saturated solution of Zn₃(py)₂ in THF at room temperature over the course of 5 days. The asymmetric unit contains a full cluster with two of the three zinc atoms bound by THF, and an unbound, disordered THF molecule that was modeled over two positions.

Figure S19. Microscope image of Zn₃(THF)₂ Crystals.

Figure S20. Molecular structure of Zn₃(THF)₂ with thermal ellipsoids shown at a 50% probability level.
S4.2  \( \text{Zn}_3(\text{phen})_2 \)

Dark-red prismatic crystals suitable for X-ray diffraction studies were grown over the course of two days via vapor diffusion of diethyl ether into a saturated solution of \( \text{Zn}_3(\text{phen})_2 \) in THF at room temperature. The asymmetric unit contains two clusters of opposite helical chirality. The phenyl and tolyl groups of three aminophosphines are disordered over two positions.

Figure S21. Microscope image of \( \text{Zn}_3(\text{phen})_2 \) crystals.

Figure S22. Molecular structure of \( \text{Zn}_3(\text{phen})_2 \) with thermal ellipsoids shown at a 50% probability level.

S4.3  \[ \text{Zn}_3(\text{phen})_3][\text{PF}_6] \]

Dark-red prismatic crystals were grown via vapor diffusion of diethyl ether into a saturation solution \( [\text{Zn}_3(\text{phen})_3][\text{PF}_6] \) in acetonitrile at room temperature over the course of two days. The asymmetric unit contains one cluster with a disordered \( \text{PF}_6^- \) anion, and two acetonitrile molecules and one diethyl ether molecule.
Dark red prismatic crystals were grown from the reaction mixture at 60 °C over the course of two days. The data was of slightly reduced quality due to possible growth defects, and with some solvent toluene disorder present, a few restraints were required (ISOR on all carbon, nitrogen and DELU on carbon, nitrogen and connecting phosphorous, AFIX 66 on toluene rings, flat and EADP on disordered toluene) and 450 bad reflections were omitted (0.34%).

![Figure S23. Molecular structure of \([\text{Zn}_3(\text{phen})_3][\text{PF}_6]\) with thermal ellipsoids shown at a 50% probability level.](image)

**S4.4 1-bipy**

Dark red prismatic crystals were grown from the reaction mixture at room temperature over the course of one week. The unit cell contained disordered DCM solvent molecules which were removed with SQUEEZE.

![Figure S24. Molecular structure of 1-bipy with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms, disorder, and co-crystallized solvent molecules are omitted for clarity.](image)

**S4.5 1-tpphz**

Dark red prismatic crystals were grown from the reaction mixture at room temperature over the course of one week. The unit cell contained disordered DCM solvent molecules which were removed with SQUEEZE. 12–14
S4.6  2-bipy

Data was collected at -173° C on a Nonius Kappa CCD FR590 single crystal X-ray diffractometer, Mo-radiation. Small, dark red, prismatic crystals were grown from the reaction mixture at room temp over the course of 2 days. The contribution of about 18 disordered DCM solvent molecules per asymmetric unit to the diffraction pattern was removed with SQUEEZE (1563eV in voids). Two PF₆⁻ anions were found, where one of which appeared disordered. The structure required several constraints and restraints. All phenyls were optimized with AFIX 66 … AFIX 0 loops. All complex motives aminophosphines were related with the SAME command. All pyridine halves of 4,4'-bipyridines were coupled with SAME. Pyridine moieties required FLAT restraints. Overall, an ISOR for carbons, nitrogen, and fluorine to prevent non-positive definite displacement matrices, and a DELU command including carbons, nitrogen and phosphorous were needed connecting the isotropic displacements along bonds. Some hydrogen atoms came slightly too close to each other which required their distances to be maintained with DFIX (since the data quality did not allow for a more detailed disorder model of phenyls and toluene) and 200 bad reflections were removed. While the small crystal size, the large unit cell (14771(12) Å³), and solvent disorder resulted in weak higher angle scattering, the structure is publishable, and the connectivity (and stoichiometry) is reliable.

Figure S25. Structure of one 1-tpphz unit with thermal ellipsoids shown at a 50% probability level.

Figure S26. Structure of one Zn₃(bipy)₁.₅ unit with thermal ellipsoids shown at a 50% probability level.
### S4.7 X-ray Structure Tables

Table S2. Crystallographic data for Zn3(THF)2, Zn3(phen)2 and [Zn3(phen)3][PF6]-Et2O-2 MeCN

| Compound | Zn₃(THF)₂·2 THF | Zn₃(phen)₂ | [Zn₃(phen)₃][PF₆]-Et₂O-2 MeCN |
|----------|-----------------|------------|--------------------------------|
| **CCDC number** | 2102887 | 2102892 | 2102890 |
| **Empirical formula** | C₂₅₆H₂₆₀Co₁₂N₁₂O₇P₁₂Se₁₆Zn₆ | C₁₃₈H₁₁₈Co₁₉P₆Se₆Zn₃ | C₁₃₈H₁₄₂Co₁₉F₆N₁₄OP₇Se₈Zn₃ |
| **Formula weight** | 6351.12 | 3283.61 | 3765.01 |
| **Temperature (°K)** | 100(2) | 100(2) | 100(2) |
| **Wavelength (Å)** | 0.71073 | 0.71073 | 0.71073 |
| **Crystal system** | Monoclinic | Triclinic | Triclinic |
| **Space group** | P 2₁/c | P -1 | P -1 |
| **a (Å)** | 23.165(4) | 16.5919(16) | 15.2771(8) |
| **b (Å)** | 19.118(3) | 18.8643(17) | 25.6348(14) |
| **c (Å)** | 28.120(4) | 24.195(2) | 26.4908(13) |
| **α (°)** | 90 | 92.481(6) | 117.056(3) |
| **β (°)** | 92.232(9) | 96.376(6) | 102.934(3) |
| **γ (°)** | 90 | 102.106(6) | 95.533(3) |
| **Volume (Å³)** | 12444(3) | 7560.0(12) | 8766.7(8) |
| **Z** | 2 | 2 | 2 |
| **ρ calc (g cm⁻³)** | 1.695 | 1.442 | 1.426 |
| **Absorption coefficient (mm⁻¹)** | 3.818 | 3.144 | 2.736 |
| **F(000)** | 6328 | 3260 | 3758 |
| **Crystal size (mm³)** | 0.080 x 0.070 x 0.040 | 0.230 x 0.100 x 0.020 | 0.170 x 0.100 x 0.100 |
| **Theta range for data collection (°)** | 1.381 to 25.123 | 1.334 to 25.350 | 1.405 to 28.507 |
| **Index ranges** | -27≤h≤27, -22≤k≤22, -33≤l≤33 | -19≤h≤19, -22≤k≤22, -30≤l≤30 | -20≤h≤20, -34≤k≤34, -35≤l≤35 |
| **Reflections collected** | 43602 | 131590 | 87063 |
| **Independent reflections** | 22177 [R(int) = 0.1891] | 27423 [R(int) = 0.2127] | 43852 [R(int) = 0.0463] |
| **Completeness to theta = 25.000°** | 99.8% | 99.3% | 99.8% |
| **Data / restraints / parameters** | 22177 / 1255 / 1470 | 27473 / 544 / 1619 | 43852 / 159 / 1890 |
| **Goodness-of-fit on F²** | 1.012 | 1.009 | 1.021 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.1138, wR2 = 0.2526 | R1 = 0.0918, wR2 = 0.2106 | R1 = 0.0380, wR2 = 0.0782 |
| **R indices (all data)** | R1 = 0.2375, wR2 = 0.3103 | R1 = 0.2344, wR2 = 0.2894 | R1 = 0.0731, wR2 = 0.0881 |
| **Largest diff. peak and hole (e⁻Å⁻³)** | 1.856 and -1.603 | 1.379 and -1.170 | 0.945 and -0.860 |
| Compound | 1-bipy - 4 toluene | 2-bipy | 1-tpphz |
|----------|-------------------|--------|---------|
| CCDC number | 2102891 | 2102888 | 2102899 |
| Empirical formula | \( \text{C}_{311}\text{H}_{292}\text{Co}_{12}\text{N}_{16}\text{P}_{12}\text{Se}_{16}\text{Zn}_{6} \) | \( \text{C}_{258}\text{H}_{228}\text{Co}_{12}\text{F}_{12}\text{N}_{18}\text{P}_{14}\text{Se}_{16}\text{Zn}_{6} \) | \( \text{C}_{138}\text{H}_{114}\text{Co}_{12}\text{OP}_{6}\text{Se}_{8}\text{Zn}_{3} \) |
| Formula weight | 6987.97 | 6604.89 | 3307.60 |
| Temperature (°K) | 100(2) | 100(2) | 100(2) |
| Wavelength | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | \( \text{P} 2_1/n \) | \( \text{P} -1 \) | \( \text{P} -1 \) |
| a (Å) | 26.093(3) | 18.943(9) | 19.1661(16) |
| b (Å) | 18.874(3) | 28.237(13) | 20.5691(16) |
| c (Å) | 30.338(4) | 31.465(14) | 21.9034(18) |
| \( \alpha \) (°) | 90 | 112.489(11) | 69.547(4) |
| \( \beta \) (°) | 106.615(4) | 97.563(12) | 65.685(4) |
| \( \gamma \) (°) | 90 | 102.224(12) | 86.539(4) |
| Volume (Å\(^3\)) | 14317(3) | 14771(12) | 7337.6(11) |
| \( Z \) | 2 | 2 | 2 |
| \( \rho_{\text{calc}} \) (g cm\(^{-3}\)) | 1.621 | 1.485 | 1.497 |
| Absorption coefficient (mm\(^{-1}\)) | 3.325 | 3.234 | 3.240 |
| F(000) | 6996 | 6536 | 3280 |
| Crystal size (mm\(^3\)) | 0.220 x 0.130 x 0.050 | 0.100 x 0.050 x 0.040 | 0.140 x 0.070 x 0.070 |
| Theta range for data collection (°) | 1.286 to 28.565 | 0.828 to 25.027 | 1.502 to 25.027 |
| Index ranges | \(-34 \leq h \leq 34, -25 \leq k \leq 25, -40 \leq l \leq 40 \) | \(-22 \leq h \leq 22, -32 \leq k \leq 32, -35 \leq l \leq 35 \) | \(-22 \leq h \leq 22, -24 \leq k \leq 24, -26 \leq l \leq 26 \) |
| Refractions collected | 133057 | 51575 | 50410 |
| Independent reflections | 35562 [R(int) = 0.1236] | 51575 [R(int) = 0.2341] | 25882 [R(int) = 0.1757] |
| Completeness to theta = 25.000° | 98.2% | 99.8% | 99.8% |
| Data / restraints / parameters | 35562 / 1576 / 1686 | 51575 / 6364 / 2614 | 25882 / 97 / 1575 |
| Goodness-of-fit on F\(^2\) | 1.144 | 1.012 | 0.929 |
| Final R indices [I>2\(\sigma(I)\)] | R1 = 0.1082, wR2 = 0.2726 | R1 = 0.1495, wR2 = 0.2958 | R1 = 0.0781, wR2 = 0.1631 |
| R indices (all data) | R1 = 0.1508, wR2 = 0.2939 | R1 = 0.3551, wR2 = 0.4257 | R1 = 0.2194, wR2 = 0.2219 |
| Largest diff. peak and hole (e Å\(^{-3}\)) | 2.533 and -1.776 | 2.131 and -1.378 | 1.258 and -1.033 |
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