

Supplementary Information

Shape Matching in Superaom Chemistry and Assembly

Jingjing Yang, Feifan Wang, Jake C. Russell, Taylor J. Hochuli, Xavier Roy, Michael L.

Steigerwald, Xiaoyang Zhu, Daniel W. Paley,* and Colin Nuckolls*

***Corresponding authors.** dwp2111@columbia.edu, cn37@columbia.edu

Table of Content

- I. Synthetic Details
- II. Optical Images
- III. Single Crystal X-ray Crystallography
- IV. Charge States Analysis
- V. Structural Analysis
- VI. Mid-IR Electronic Absorption Measurements
- VII. Electrical Conductance Measurements
- VIII. References

I. Synthetic Details

General Information

Triethylphosphine, selenium powders, dicobalt octacarbonyl, C₇₀, toluene, and 1-methylnaphthalene were obtained from commercial sources. Dry and deoxygenated solvents were prepared with a dual column solvent system (Glass Contour Solvent Systems). All reactions and sample preparations were carried out under nitrogen using standard schlenk techniques or in a nitrogen-filled glovebox. Co₁₂Se₁₆(PEt₃)₁₀ was synthesized based on published procedures accordingly.¹

Single crystals of [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₃ and [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₂. Co₁₂Se₁₆(PEt₃)₁₀ (3 mg, 0.00095 mmol) was dissolved in 1 mL toluene, C₇₀ (2.4 mg, 0.0029 mmol) was dissolved in 1 mL 1-methylnaphthalene. The toluene solution was layered on the 1-methylnaphthalene solution slowly in a 4 mL glass vial. The solutions were then allowed to stand still for three days to yield a mixture of black plate [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₃ and rod shape [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₂ single crystals. The mother liquor was decanted and the crystals were washed and kept in toluene before structural analysis.

Single crystals of [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]_{1.44}. Single crystals of [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₃ were taken out from toluene and dried *in vacuo* for 20 mins or naturally dried under N₂ atmosphere for three days before structural analysis.

Further structural transformation. Further evacuating [Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]_{1.44} *in vacuo* for a longer time (24 h) or soaking the crystals in pentane could result in continuous structural transformation as indicated by the emergence of new unit cell parameters (triclinic $P\bar{1}$ space group with lattice constants of $a = 15.68 \text{ \AA}$, $b = 19.75 \text{ \AA}$, $c = 23.03 \text{ \AA}$, $\alpha = 69.83^\circ$, $\beta = 75.78^\circ$, $\gamma = 82.41^\circ$ and triclinic $P\bar{1}$ space group with lattice constants of $a = 17.47 \text{ \AA}$, $b = 21.20 \text{ \AA}$, $c =$

21.94 Å, $\alpha = 73.07^\circ$, $\beta = 67.06^\circ$, $\gamma = 68.52^\circ$, respectively), yet their X-ray diffraction patterns became too weak/smeared-out to provide structure solutions. As such, these two crystals are not further analyzed. However, these results suggest that toluene molecules could be removed gradually, and imply that there could be numerous potential transient structures.

II. Optical Images

Optical image of crystals was taken on a Nikon Eclipse LV150N optical microscope.

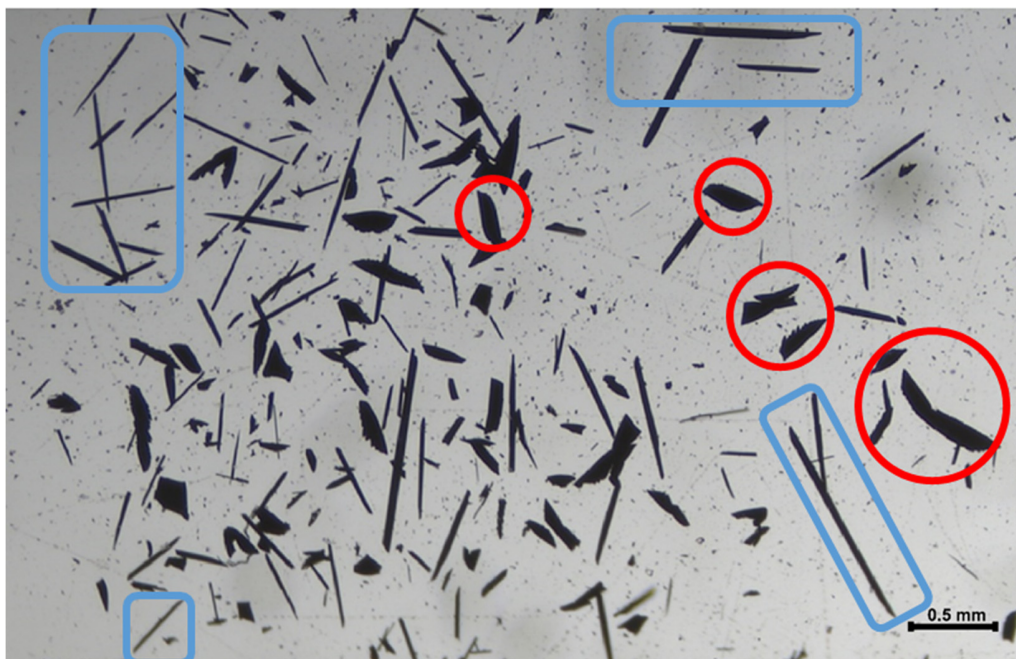


Figure S1. Optical images of a mixture of (a) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$ (plate-shaped crystals, highlighted in red circle) and (b) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$ (rod-shaped crystals, highlighted in blue rectangular).

III. Single Crystal X-ray Crystallography

[Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₃

Single crystal data of [Co₁₂Se₁₆(PEt₃)₁₀][C₁₄₀][toluene]₃ was collected on an Agilent SuperNova diffractometer using a mirror-monochromated Cu K α radiation. The rod-shaped crystal was picked up from solution and mounted on a MiTeGen Kapton loop (polyimide). These were cooled to 100 K with an Oxford Cryosystems nitrogen flow apparatus. Data integration, scaling (ABSPACK) and absorption correction was performed in CrysAlisPro.2. The structure solution was obtained using ShelXT². Subsequent refinement was performed by full-matrix least-squares on F² in ShelXL. Olex2³ was used for viewing and to prepare CIF files. Details of crystallographic data and refinement parameters are given in Table S1.

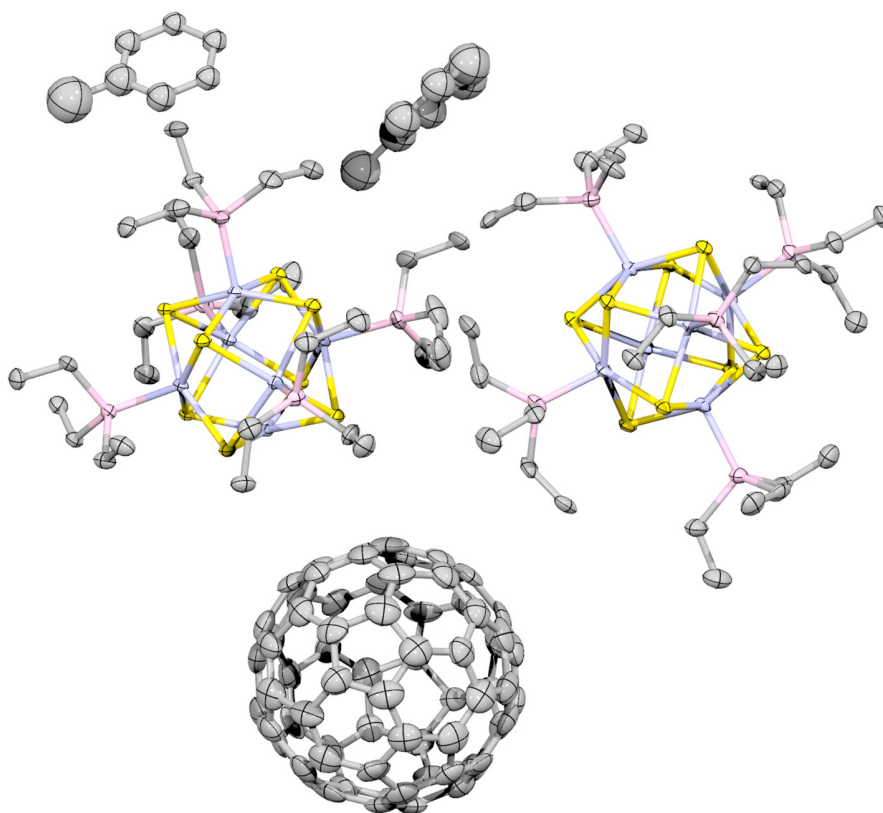


Figure S2. Asymmetric unit of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$, Thermal ellipsoids with 50% probability.

H atoms are omitted for clarity; Co in purple, Se in yellow, P in pink, C in grey.

Table S1. Crystallographic Data of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$

Compound	$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$
Chemical formula	$\text{Co}_{24}\text{Se}_{32}\text{P}_{20}\text{C}_{281}\text{H}_{324}$
Formula mass	8261.82
Crystal system	Triclinic
Space group	$P\bar{1}$
λ (Å)	1.54184
a (Å)	17.0365(10)
b (Å)	21.2529(9)
c (Å)	21.8288(6)
α (°)	98.346(3)
β (°)	75.384(4)
γ (°)	70.305(5)
Z	1
V (Å ³)	6966.9(6)
Temperature (K)	100(2)
Size /mm ³	$0.03 \times 0.11 \times 0.21$
Density (g/cm ⁻³)	1.969
Measured reflections	54794
Unique reflections	27223
Parameters	1702
R_{int}	0.065

θ range (°)	3.4-72.8
R_1 , wR_2	0.0622, 0.1718
S (GOF)	1.00
Max/min res. dens. (e/Å ³)	1.60/-1.40

[Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]₂

Single crystal data of [Co₁₂Se₁₆(PEt₃)₁₀][C₁₄₀][toluene]₂ was collected on an Agilent SuperNova diffractometer using a mirror-monochromated Cu K α radiation. The rod-shaped crystal was picked up from solution and mounted on a MiTeGen Kapton loop (polyimide). These were cooled to 100 K with an Oxford Cryosystems nitrogen flow apparatus. Data integration, scaling (ABSPACK) and absorption correction was performed in CrysAlisPro.2. The structure solution was obtained using ShelXT². Subsequent refinement was performed by full-matrix least-squares on F² in ShelXL. Olex2³ was used for viewing and to prepare CIF files. Details of crystallographic data and refinement parameters are given in Table S2.

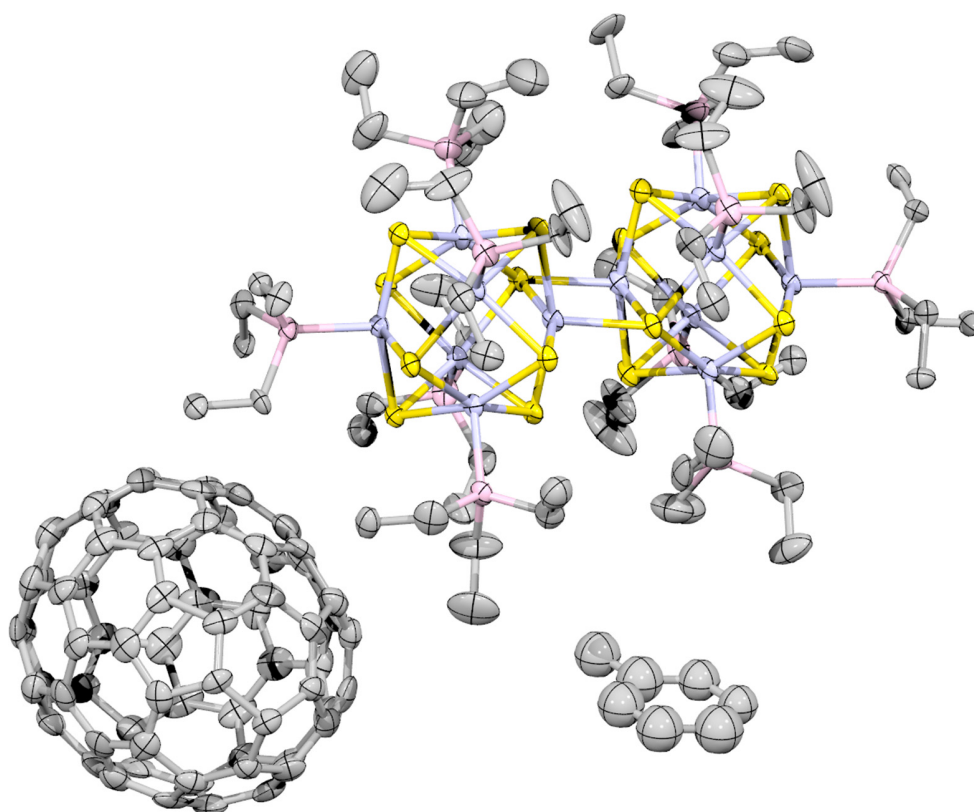


Figure S3. Asymmetric unit of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$, Thermal ellipsoids with 50% probability. H atoms are omitted for clarity; Co in purple, Se in yellow, P in pink, C in grey.

Table S2. Crystallographic Data of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$

Compound	$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$
Chemical formula	$\text{Co}_{24}\text{Se}_{32}\text{P}_{20}\text{C}_{274}\text{H}_{316}$
Formula mass	8169.69
Crystal system	Monoclinic
Space group	$P2_1/c$
λ (Å)	1.54184
a (Å)	18.2929(5)
b (Å)	30.5739(13)

c (Å)	24.8492(12)
β (°)	100.706(4)
Z	2
V (Å ³)	13655.9(10)
Temperature (K)	100(2)
Size /mm ³	$0.06 \times 0.08 \times 0.53$
Density (g/cm ³)	1.987
Measured reflections	59109
Unique reflections	26807
Parameters	1711
R_{int}	0.071
θ range (°)	3.4-73.2
R_1, wR_2	0.0883, 0.2695
S (GOF)	1.021
Max/min res. dens. (e/Å ³)	2.46/-1.85

[Co₁₂Se₁₆(PEt₃)₁₀]₂[C₁₄₀][toluene]_{1.44}

Single crystal data of [Co₁₂Se₁₆(PEt₃)₁₀][C₁₄₀][toluene]_{1.44} was collected on an Agilent SuperNova diffractometer using a mirror-monochromated Cu K α radiation. The rod-shaped crystal was picked up from solution and mounted on a MiTeGen Kapton loop (polyimide). These were cooled to 100 K with an Oxford Cryosystems nitrogen flow apparatus. Data integration, scaling (ABSPACK) and absorption correction was performed in CrysAlisPro.2. The structure solution was obtained using ShelXT². Subsequent refinement was performed by full-matrix least-squares on F² in ShelXL. Olex2³ was used for viewing and to prepare CIF files. Details of crystallographic data and refinement parameters are given in Table S3.

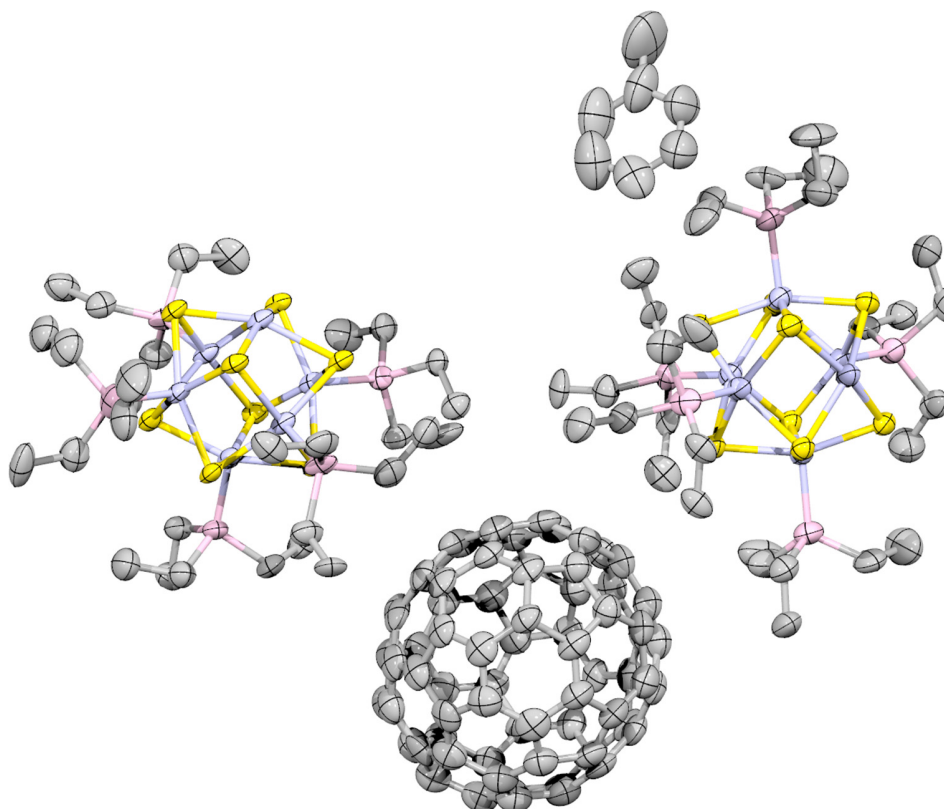


Figure S4. Asymmetric unit of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$, Thermal ellipsoids with 50% probability. H atoms are omitted for clarity; Co in purple, Se in yellow, P in pink, C in grey.

Table S3. Crystallographic Data of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$

Compound	$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$
Chemical formula	$\text{Co}_{24}\text{Se}_{32}\text{P}_{20}\text{C}_{270}\text{H}_{311}$
Formula mass	8116.64
Crystal system	Triclinic
Space group	$P\bar{1}$
λ (Å)	1.54184
a (Å)	17.4495(14)
b (Å)	21.1944(10)

c (Å)	21.2677(16)
α (°)	89.406(5)
β (°)	68.636(7)
γ (°)	70.146(6)
Z	1
V (Å ³)	6831.7(10)
Temperature (K)	100(2)
Size /mm ³	$0.03 \times 0.13 \times 0.33$
Density (g/cm ⁻³)	1.973
Measured reflections	45812
Unique reflections	26336
Parameters	1746
R_{int}	0.075
θ range (°)	4.1-73.3
R_1, wR_2	0.0996, 0.3094
S (GOF)	1.039
Max/min res. dens. (e/Å ³)	2.38/-1.46

IV. Charge States Analysis

Here, we analyzed the Co-Co distances (at the trans-position) in $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ clusters with neutral, 1+, and 2+ oxidation states. We also analyzed the interfullerene C–C distances in C_{140} clusters. The results are summarized in Table S4 below.

Table S4. Comparison of trans Co-Co distances in compounds containing the $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ cluster with different oxidation states and interfullerene C–C distances in compounds containing the C_{140} cluster.

Compound	Trans- Co-Co distance (Å)	Inter-fullerene C–C distance (Å)	Reference
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^0$	10.46	N/A	(4)
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^+[\text{PF}_6]^-$	10.19	N/A	(4)
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{2+}[\text{PF}_6]_2^{2-}$	10.29	N/A	(4)
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^+_2[\text{C}_{140}]^{2-}[\text{toluene}]_3$	10.23	1.63	This work
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^+_2[\text{C}_{140}]^{2-}[\text{toluene}]_2$	10.24	1.58	This work
$[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^+_2[\text{C}_{140}]^{2-}[\text{toluene}]_{1.44}$	10.25	1.58	This work
$[(\text{MDABCO})_2 \cdot \text{MnTPP}]^{2+}(\text{MDABCO})_2[\text{C}_{140}]^{2-}$	N/A	1.59	(5)
$[\text{Ni}_3(\mu_3\text{-I})_2(\mu_2\text{-dppm})_3]^{2+}[\text{C}_{140}]^{2-}$	N/A	1.59	(6)
$[\text{Co}_6\text{Te}_8(\text{PEt}_3)_6]^+[\text{C}_{70}]^0[\text{C}_{140}]^{2-}_{1/2}$	N/A	1.59	(7)

V. Structural Analysis

Intermolecular interactions analysis

Orientations of the nanoclusters are fixed by multiple intermolecular interactions between these building blocks and the toluene crystal modulator. In the $[C_{140}][\text{toluene}]_x$ layers, we observed π to π distances between adjacent C_{140} 's of 4.1 Å, 7.2 Å, and 3.8 Å for crystals with $x = 3, 2, 1.44$, respectively (Figure S5a,d,g). C_{140} 's interact with toluene through C–H $\cdots\pi$ interactions (3.2 Å, 2.9 Å, and 2.6 Å when $x = 3, 2, 1.44$, Figure 3a,d,g). In the $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ layers, we noted that $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ packed densely with short H \cdots H contacts (2.5-2.8 Å, 2.3-2.8 Å, and 2.3-2.8 Å when $x = 3, 2, 1.44$) (Figure S5b,e,h). We attribute these differences to the soft, flexible alkyl shells of the nanoclusters. $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ layers and $[C_{140}][\text{toluene}]_x$ layers are linked through C–H $\cdots\pi$ interactions between $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ and C_{140} nanoclusters with distances of 2.9 Å, 2.9 Å, and 2.8 Å when $x = 3, 2, 1.44$, respectively (Figure S5c,f,i). Interestingly, we also find extra C–H $\cdots\pi$ interaction sites between $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ and toluene when $x = 1.44$ (Figure S5i). This phenomenon, along with other observations – shorter $\pi\cdots\pi$ and H \cdots H interaction distances, suggests that the structure shrinks upon loss of the toluene crystal modulator, which result in shorter intermolecular distances and stronger interactions.

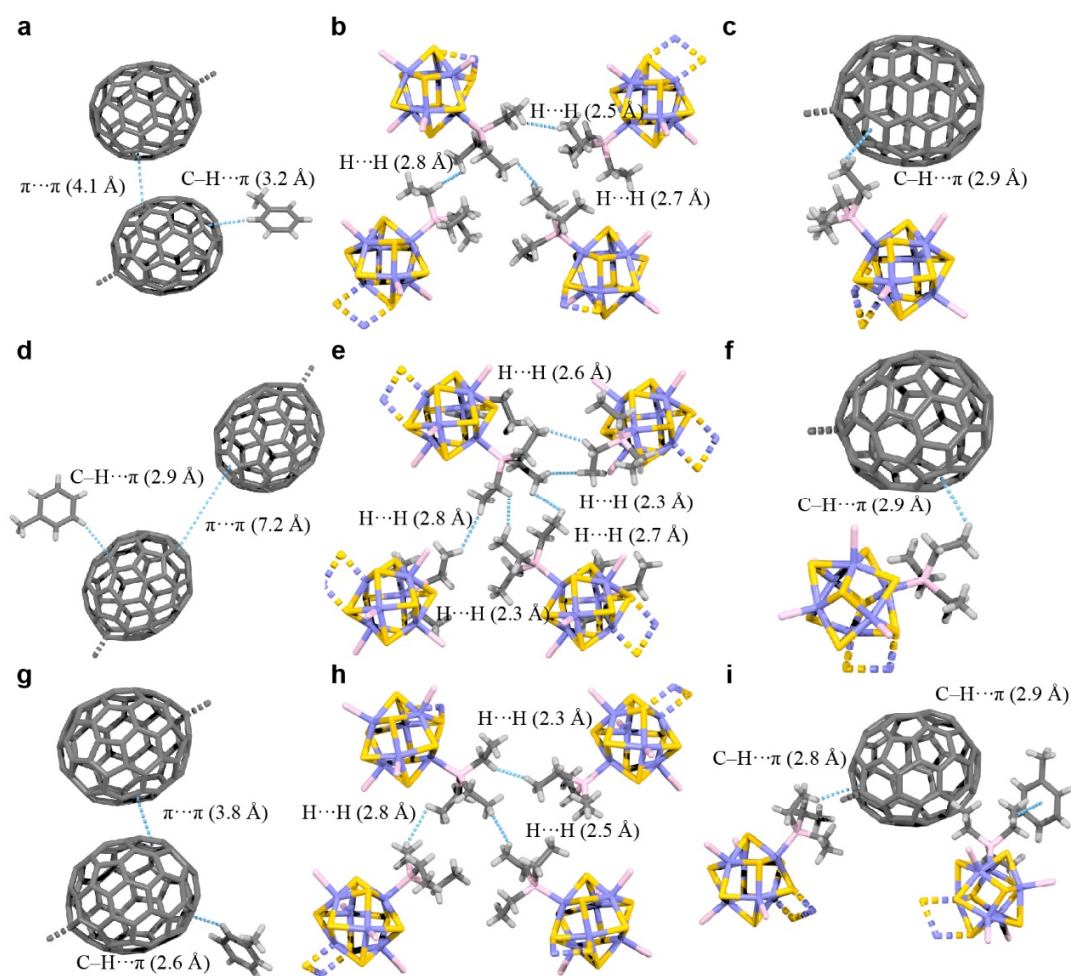


Figure S5. Intermolecular interactions within (a-c) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$, (d-f) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$, and (g-i) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$. (a,d,g) depict $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions in $[\text{C}_{140}][\text{toluene}]_x$ layers. (b,e,h) depict H \cdots H interactions in $\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}$ layers. (c,f,i) depict C-H $\cdots \pi$ interactions between the two layers. Co in purple, Se in gold, P in pink, C in black, H in grey.

An alternative view of crystal packings

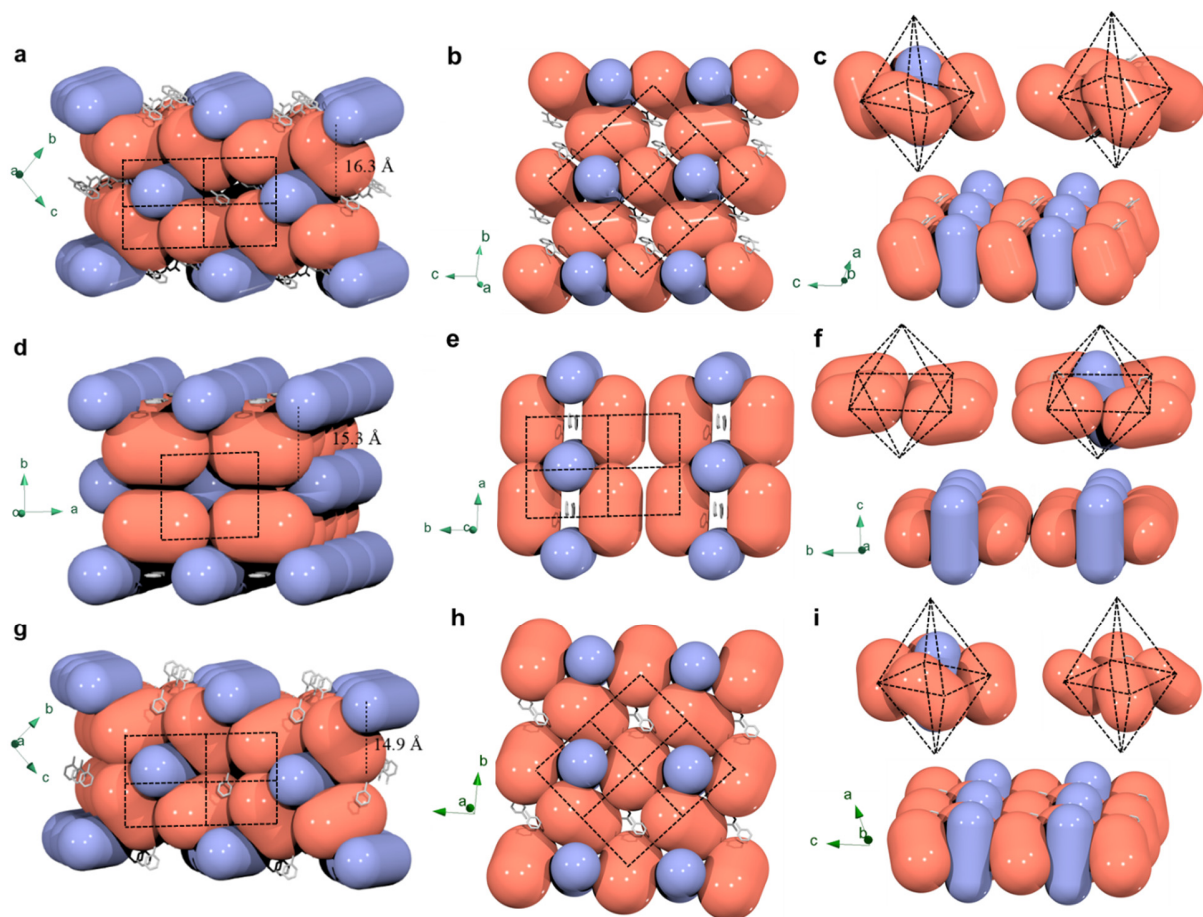


Figure S6. Crystal packings of (a-c) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$, (d-f) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$, and (g-i) $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$. The two superatoms are presented as solid rods – $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]$ in red, $[\text{C}_{140}]$ in blue, and toluene in grey. (b,e,h) depict the arrangements in the mixed superatomic layers $\{(b,c)\}$ layers for $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$ and $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$; and $\{a,b\}$ layer for $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$. (c,f,i) (top) depict the truncated pseudo- O_h sites within the above-mentioned mixed superatomic (b,c) , (a,b) , and (b,c) layers, and (bottom) depict the side views of the mixed superatomic layers.

VI. Mid-IR Electronic Absorption Measurements

The optical absorption in the mid-IR range was measured by a Nicolet 6700 FTIR with Everglo IR light source and a Continuum IR microscope in reflectance mode. A 15x reflective objective, a KBr beam splitter and a nitrogen-cooled MCT-A detector were used to collect the spectrum. The samples were made on Au-Si substrates and sealed in a gas-tight cell with 1 mm ZnSe window in the glovebox. Six measurements on both sample crystal and substrate reference were conducted and averaged to improve accuracy. Reflectance contrast was considered proportional to absorption and then used to Tauc plot analysis for a direct bang gap model. In Figure 4, the linear fitting region of [0.785 1.022], [0.539 0.888] and [0.883 1.015] was selected for the black, red and green curves with R^2 value of 0.995, 0.999 and 0.979, respectively.

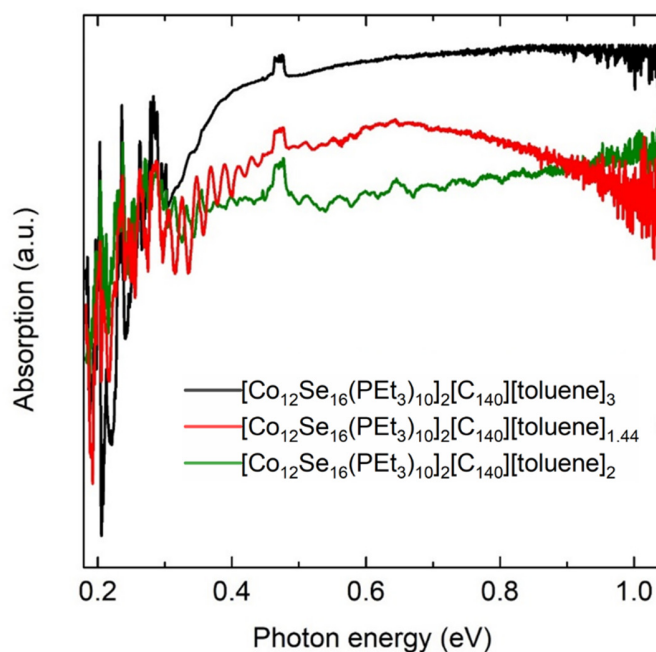


Figure S7. Mid-IR electronic absorption spectrum of $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_3$, $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_2$, and $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$ crystals.

VII. Electrical Conductance Measurements

The room temperature electrical conductivity measurements were tested on the Agilent 4155C semiconductor parameter analyzer in a N₂ protected glove box. A voltage sweep from –2 to 2 V was applied and the current was measured to obtain current-voltage (I-V) curves. To create the devices, single crystals were selected and adhered to a glass slide using silver paste (DuPont 4929N), forming two contacts. Resistivity was then calculated by measuring the dimensions of each sample with a microscope. Four devices are fabricated and tested for each compound to ensure accuracy and reproducibility.

Temperature-dependent electrical conductance measurements were realized in a Cryo Industries Cryogen Free Superconducting Magnet System cryostat, cooled with helium. The device was prepared as above and adhered to a chip carrier. The crystal was covered with PARATONE® oil in a N₂ protected glove box and transferred to the cryostat. Using a Keithley 2400, voltage was applied at a constant 5 V and current was simultaneously measured to obtain resistance. The temperature was swept down from 298 to 210 K at a rate of 0.65 K/min. The thermal activation energy was then calculated from the slope of the Arrhenius plot ($\ln G$ vs $1/T$) indicated by the linear fitting.

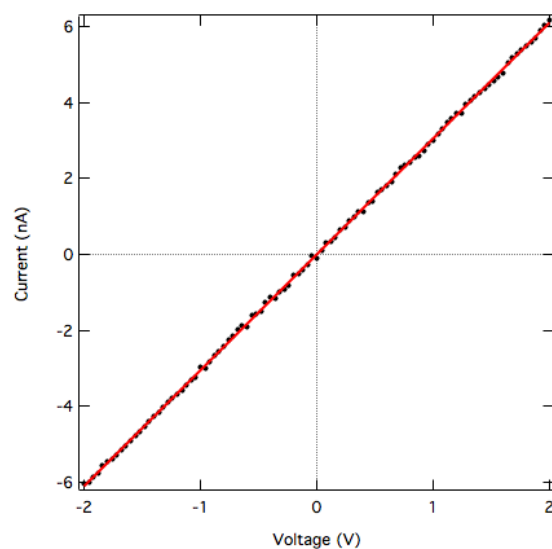


Figure S8. Measured I-V curve of one $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$ crystal. The calculated room-temperature conductivity is $1.25 \times 10^{-4} \text{ S/m}$ ($\pm 0.24 \times 10^{-4} \text{ S/m}$).

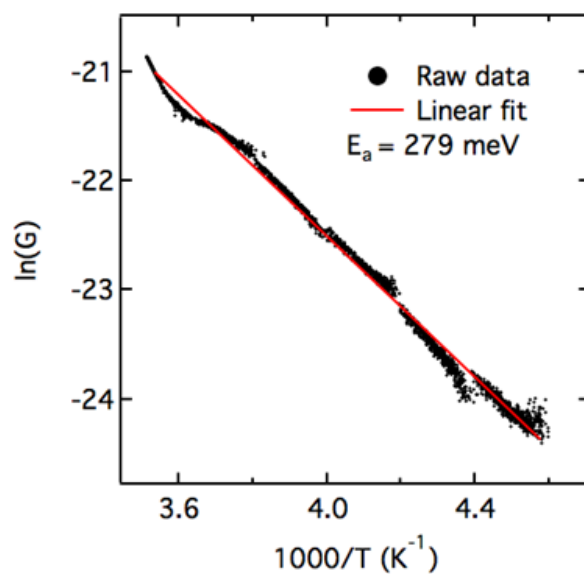


Figure S9. Plot of the conductance (G) vs. $1/T$ for $[\text{Co}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]_2[\text{C}_{140}][\text{toluene}]_{1.44}$. The thermal activation energy E_a is calculated to be 279 meV.

VIII. References:

- (1) Champsaur, A. M.; Hochuli, T. J.; Paley, D. W.; Nuckolls, C.; Steigerwald, M. L., Superatom Fusion and the Nature of Quantum Confinement. *Nano Lett.* **2018**, *18* (7), 4564-4569.
- (2) Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallogr. Section C* **2015**, *71* (1), 3-8.
- (3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339-341.
- (4) Champsaur, A. M.; Hochuli, T. J.; Paley, D. W.; Nuckolls, C.; Steigerwald, M. L., Superatom Fusion and the Nature of Quantum Confinement. *Nano Lett.* **2018**, *18* (7), 4564-4569.
- (5) Konarev, D. V.; Khasanov, S. S.; Otsuka, A.; Saito, G.; Lyubovskaya, R. N., Formation of Antiferromagnetically Coupled C₆₀^{•-} and Diamagnetic (C₇₀⁻)₂ Dimers in Ionic Complexes of Fullerenes with (MDABCO⁺)₂·MIITPP (M = Zn, Co, Mn, and Fe) Assemblies. *Inorg. Chem.* **2007**, *46* (6), 2261-2271.
- (6) Shott, J. L.; Freeman, M. B.; Saleh, N.-A.; Jones, D. S.; Paley, D. W.; Bejger, C., Ball and Socket Assembly of Binary Superatomic Solids Containing Trinuclear Nickel Cluster Cations and Fulleride Anions. *Inorg. Chem.* **2017**, *56* (18), 10984-10990.
- (7) O'Brien, E. S.; Russell, J. C.; Bartnof, M.; Christodoulides, A. D.; Lee, K.; DeGayner, J. A.; Paley, D. W.; McGaughey, A. J. H.; Ong, W.-L.; Malen, J. A.; Zhu, X. Y.; Roy, X., Spontaneous Electronic Band Formation and Switchable Behaviors in a Phase-Rich Superatomic Crystal. *J. Am. Chem. Soc.* **2018**, *140* (46), 15601-15605.