Supplementary Materials for

Nanoscale Atoms in Solid-State Chemistry


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I. Synthetic Details

**General Information**

Triethylphosphine, selenium and tellurium powders, bis(cyclooctadiene)nickel, chromium(II) chloride and dicobalt octacarbonyl were obtained from STREM Chemicals. C\textsubscript{60} was purchased from BuckyUSA. Allylmagnesium bromide and 1-methylnaphthalene were obtained from Sigma-Aldrich. Dry and deoxygenated solvents were prepared by elution through a dual column solvent system (Glass Contour Solvent Systems). 1-Methylnaphthalene was stirred over sodium at 100 °C and then distilled under vacuum.

All reactions and sample preparations were carried out under nitrogen using standard schlenk techniques or in an argon-filled glovebox. Clusters Co\textsubscript{6}Se\textsubscript{8}(PEt\textsubscript{3})\textsubscript{6} (1), Cr\textsubscript{6}Te\textsubscript{8}(PEt\textsubscript{3})\textsubscript{6} (2) and Ni\textsubscript{9}Te\textsubscript{6}(PEt\textsubscript{3})\textsubscript{8} (3) were synthesized according to published protocols (4-6).

**Compound 1•2C\textsubscript{60}**

Cluster 1 (17.5 mg, 10.3 µmol) was dissolved in 5 mL of toluene and filtered with a 0.2 µm syringe filter. C\textsubscript{60} (14.8 mg, 20.6 µmol) was dissolved in 5 mL of toluene and filtered with a 0.2 µm syringe filter. The two solutions were combined in a vial. Black crystals were obtained overnight. The supernatant was decanted, the solid was washed with toluene and dried under vacuum for ~12 h. Yield: 25.1 mg, 78 %.

**Compound 2•2C\textsubscript{60}**

Cluster 2 (21.0 mg, 10.3 µmol) was dissolved in 5 mL of toluene and filtered with a 0.2 µm syringe filter. C\textsubscript{60} (14.8 mg, 20.6 µmol) was dissolved in 5 mL of toluene and filtered with a 0.2 µm syringe filter. The two solutions were combined in a vial. Black crystals were obtained overnight. The solid was centrifuged, rinsed with toluene and dried under vacuum for ~12 h. Yield: 29.5 mg, 82 %.
**Compound 3•C₆₀**

Sample 1

C₆₀ (18.9 mg, 8.4 μmol) was dissolved in 5 mL of toluene and filtered with a 0.2 μm syringe filter into a vial. Cluster 3 (6.1 mg, 8.5 μmol) was dissolved in 5 mL of toluene, filtered with a 0.2 μm syringe filter and added dropwise to the stirred C₆₀ solution. A dark brown precipitate formed instantly. The slurry was stirred for 5 min. The solid was centrifuged, rinsed with toluene and dried under vacuum for ~12 h. Yield: 24 mg, 96 %.

Sample 2

C₆₀ (10 mg, 13.8 μmol) was dissolved in 2 mL of 1-methylnaphthalene and filtered with a 0.2 μm syringe filter into a vial. 1-Methylnaphthalene (1 mL) and toluene (1 mL) were successively layered on top of the C₆₀ solution. Cluster 3 (37 mg, 16.5 μmol) was dissolved in 5 mL of toluene filtered with a 0.2 μm syringe filter and layered on top of the C₆₀ solution. The vial was placed in a freezer at −30 °C for 2 weeks. The supernatant solution was decanted and the remaining black solid was centrifuged, rinsed with toluene and dried under vacuum for ~12 h. Yield: 35.1 mg, 88 %.
II. Measurements

*Raman Spectroscopy*
Raman spectra were recorded on a custom-made apparatus (see Section V for more details). The sample was loaded in a quartz cuvette sealed under an atmosphere of Ar.

*Electronic Absorption spectroscopy*
Electronic absorption spectra were taken on an Agilent Technologies Cary 5000 UV-vis-NIR spectrophotometer. The sample was ground with KBr and pressed into a pellet. A background spectrum collected using a pristine KBr pellet was subtracted.

*Magnetometry*
The magnetic data were collected on a Quantum Design SQUID magnetometer. The sample was encapsulated in a gel capsule under an atmosphere of Ar. The capsule was mounted using a clear plastic straw.

*X-ray Diffraction*
The single crystal x-ray diffraction data of 1•2C_{60} was collected using an Oxford Diffraction Xcalibur-2 CCD diffractometer with graphite monochromatized MoKα radiation. The crystal was mounted in a cryoloop under Paratone-N oil and cooled to 100K with an Oxford Diffraction Cryojet system. The collected frames were analyzed using the Crysalis program package, and integrated intensities were corrected for absorption using the Gaussian integration method.

The single crystal x-ray diffraction data of 2•2C_{60} was collected on a Bruker SMART CCD APEX II diffractometer with graphite monochromated CuKα radiation. The crystal was mounted in a Cryoloop using Paratone-N oil and cooled to 100 K with an Oxford Cryosystems 700 Series Cryostream Plus unit. Data were collected and integrated using the Bruker SAINT software package, and integrated intensities were corrected for absorption using a multi-scan technique (SADABS).

High resolution powder x-ray diffraction (PXRD) measurements of 3•C_{60} were collected on the X16C beam line at the National Synchrotron Light Source, Brookhaven National
Laboratory. A Si(111) channel-cut monochromator selected a parallel 0.70007 Å incident beam. The diffracted x-rays were analyzed by a Ge(111) crystal and detected using a NaI scintillation counter. The powder was sealed in a glass capillary of 1 mm nominal diameter, which was spun at several Hz during data collection to improve particle statistics. Data were collected over a 2θ range 1° to 30° in steps of 0.005°, with count time increasing from 10 to 30 sec per point over that range.

Electrical Transport Measurements

Single crystals of 1•2C₆₀ were grown directly onto a prefabricated device assembled on a Si substrate with a 300 nm SiO₂ layer. Prior to the crystal growth, Au electrodes separated by a 10 µm gap were deposited on the substrate by evaporating the metal through a shadow mask. Compounds 1•2C₆₀ and 2•2C₆₀ were also sintered into pellets. The material was loaded into a 6 mm vacuum pellet die and pressed under a load of 4 tons. Electrical contact was made with silver paste. The electrical transport measurements of 1•2C₆₀ and 2•2C₆₀ were performed using a continuous flow cryostat system (Janis Research Company Inc.). The electrical conductance in both two probes and four probes configurations was measured using a source meter (Yokogawa GS200 DC voltage/current source) and an electrometer (Keithley 6514 programmable electrometer).
III. X-Ray Diffraction

The single crystal data of 1•2C₆₀ and 2•2C₆₀ were first analyzed with the NRCVAX program package (22). For all subsequent calculations and refinements, the program CRYSTALS was used (23). The merohedral twinning in space group $P\overline{3}$ was addressed by introducing twin conditions, with the two possible twin volumes refining to values close to 0.5. Data for 1•2C₆₀ allowed full refinement of all individual atoms in the structure, whereas for 2•2C₆₀, the data quality did not allow an unconstrained refinement. There, restraints were introduced to keep carbon-carbon bonds in the C₆₀ clusters within an acceptable range. Furthermore, anisotropic refinements of the carbon atoms in the C₆₀ clusters indicated sizeable rotational motion of the C₆₀ cluster, even at 100K, leading to non-elliptical atomic displacement parameters. Where possible, hydrogen atoms were placed geometrically and constrained to the connecting carbon atom. For 2•2C₆₀, only the main cluster atoms, Cr, Te, and P could be refined anisotropically, whereas all other atoms were refined with isotropic displacement parameters.

3•C₆₀

We collected synchrotron powder x-ray diffraction data on two samples of 3•C₆₀ (samples 1 and 2). We saw interesting magnetic behavior in sample 1 but also noted that the broad peak centered at $2\theta \sim 2^\circ$ ($d \sim 20$ Å) in the powder diffraction pattern suggest the presence of disordered material (Fig. S1A), likely composed of 3 and C₆₀. We then improved the synthesis to decrease the fraction of disordered material (Fig. S1B shows the pattern for sample 2). While it is difficult to determine the ratio of crystalline to amorphous material for a given sample on an absolute basis, one can compare the ratio of crystalline to amorphous for the two samples through the Rietveld scale factors divided by the intensity of the ~2 degree amorphous peak. The ratio of scale factors S2/S1 = 1.9, and the ratio of amorphous peaks is A2/A1 = 0.55, so one infers that the crystalline / amorphous ratio increased by roughly a factor of 3.5 in the second synthesis. Fig. S1C shows the temperature dependence of the zero-field cooled and field cooled magnetizations ($M$) of samples 1 and 2. Both samples exhibit the same magnetic behavior but the magnitude of the magnetization of sample 2 is about three times that of sample 1.
This is strong evidence that the magnetic behavior observed in $3 \cdot C_{60}$ indeed arises from the crystalline lattice that we report.

Visual inspection of the powder x-ray diffraction pattern of $3 \cdot C_{60}$ suggested a FCC structure, subsequently confirmed by Rietveld refinement using TOPAS-Academic software (24). The structure was refined from models based on the published literature (6). The Rietveld fit (Fig. S1, A and B) cannot distinguish the orientation of the fullerene; for the purpose of illustration, we have placed it with two-fold axes along the lattice translations, but it may well be orientationally disordered.
**Fig. S1.** Rietveld refinement of two different samples of 3•C₆₀. (A) shows sample 1 and (B) shows sample 2. Black dots are data, red trace is fit. The lower black trace is the difference, to the same scale. Note vertical scale expanded by a factor of 10 above 5.5°. (C) Temperature dependence of the ZFC and FC magnetization ($M$) of 3•C₆₀ in an applied external field $H = 200$ Oe. In the ZFC experiment, the sample was cooled from room temperature to 2 K in zero-field prior to the measurement of $M$ from 2 K to 10 K.
Table S1. Selected crystallographic data.

<table>
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<th>Compound</th>
<th>1•2C&lt;sub&gt;60&lt;/sub&gt;</th>
<th>2•2C&lt;sub&gt;60&lt;/sub&gt;</th>
<th>3•C&lt;sub&gt;60&lt;/sub&gt;</th>
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<td>C&lt;sub&gt;156&lt;/sub&gt;H&lt;sub&gt;90&lt;/sub&gt;Cr&lt;sub&gt;6&lt;/sub&gt;P&lt;sub&gt;6&lt;/sub&gt;Te&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;108&lt;/sub&gt;H&lt;sub&gt;120&lt;/sub&gt;Ni&lt;sub&gt;9&lt;/sub&gt;P&lt;sub&gt;8&lt;/sub&gt;Te&lt;sub&gt;6&lt;/sub&gt;</td>
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<td>Fm&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>16.1818(3)</td>
<td>21.6623(7)</td>
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<tr>
<td>b (Å)</td>
<td>15.7500(8)</td>
<td>16.1818(3)</td>
<td>21.6623(7)</td>
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<tr>
<td>c (Å)</td>
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<td>120</td>
<td>90</td>
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<td>10165(1)</td>
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<td>R&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; [F&lt;sup&gt;2&lt;/sup&gt; &gt; 2σ(F&lt;sup&gt;2&lt;/sup&gt;)]</td>
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<td>0.0932</td>
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</table>

\[
\begin{align*}
R_i &= \frac{\sum |F_i| - |F_c|}{\sum |F_i|} \\
R_w &= \frac{1}{\sum w(F^2 - F_c^2)^2} \left( \sum w(F^2 - F_c^2)^2 \right)^{1/2} \\
R_{wp} &= \frac{\sum (y_{20}^{obs} - y_{20}^{calc})^2 / \sigma_{20}^2}{\sum (y_{20}^{obs} - y_{20}^{calc})^2 / \sigma_{20}^2} \\
\chi^2 &= \frac{\sum (y_{20}^{obs} - y_{20}^{calc})^2 / \sigma_{20}^2}{N - P}
\end{align*}
\]
IV. Molecular Structure of $2 \cdot 2C_{60}$

**Fig. S2.** Space filling molecular structure of $2 \cdot 2C_{60}$ showing the crystal packing looking down the $c$-axis. The centroid-to-centroid distance between two adjacent $C_{60}$’s is 10.3 Å. Carbon, black; Chromium, purple; phosphorus, orange; tellurium, teal. The ethyl groups on the phosphines were removed to clarify the view.

**Fig. S3.** Space filling molecular structure of $2 \cdot 2C_{60}$ showing the crystal packing looking down the $ab$ plane. The $C_{60}$ layers are 12.3 Å apart. Carbon, black; Chromium, purple; phosphorus, orange; tellurium, teal. The ethyl groups on the phosphines were removed to clarify the view.
V. Raman Spectroscopy

For Raman measurements, an Ar-Ion laser generates 514.5 nm light. The light enters an inverted microscope where a 40X/0.6 N.A. objective focuses it to a 1 µm² spot size on the sample, which is inside a sealed, 1 cm thick cuvette. Scattered light is focused through a 50 µm pinhole, recollimated, and refocused into a 0.27 m monochromator, where the light strikes a CCD array detector with 4 cm⁻¹ resolution. Typical 514.5 nm powers range from 10 to 80 µW, and collection times range from 15 minutes to 1 hour. We perform consecutive scans on the same spot, and we perform some scans at 10 µW to ensure there is no sample degradation or photoproduct buildup. At relatively low power densities (less than 100 W/cm²) pure C₆₀ can produce oligomers with the A₂g pentagonal pinch mode at 1459 cm⁻¹ (25). The absence of a peak at this energy shows that we are not generating this photoproduct even at our much higher power densities. Control spectra taken with the cluster only produced no signal.

Fig. S4. Raman spectra of 1•2C₆₀ and 2•2C₆₀. The 1•2C₆₀ spectrum was taken with 78 µW and averaged for 1 hour (7.8 kW/cm² power density). The 2•2C₆₀ spectrum was taken with 46 µW and averaged for 15 minutes (4.6 kW/cm² power density). The A₂g pentagonal pinch mode of C₆₀ is centered at 1463 cm⁻¹ and 1462 cm⁻¹ in 1•2C₆₀ and
$2\times2C_{60}$, respectively. The peak position error is $\pm 1 \text{ cm}^{-1}$, reflecting the peak position of spectra taken with different samples on different days. The spectra are offset for clarity.

**Fig. S5.** Raman spectrum of $3\times C_{60}$. The spectrum was taken with 30 $\mu$W laser power averaged for 1 hour (3.0 kW/cm$^2$ power density). The broad main peak is centered at $1454 \pm 3 \text{ cm}^{-1}$, with the error reflecting the peak position of different samples on different days.
VI. Electronic Absorption Spectroscopy

Fig. S6. Solid-state electronic absorption spectrum of $1 \cdot 2C_{60}$ dispersed in KBr.

Fig. S7. Solid-state electronic absorption spectrum of $2 \cdot 2C_{60}$ dispersed in KBr.
VII. Electrical Transport Properties

Fig. S8. Optical micrograph of a single crystal device used to measure the electrical transport properties of $1\cdot2C_{60}$. The scale bar is 100 µm.

Fig. S9. Plot of the conductance ($G$) vs. $1/T$ for $2\cdot2C_{60}$. The two probes conductance measurements were done on a pressed pellet. The thermal activation energy of ~100 meV is calculated from the slope of the Arrhenius plot indicated by a dashed line.
VIII. References


18. Materials and methods are available as supplementary materials on *Science* Online.


