[60] Fullerene Metal Complexes with Large Effective Two-photon Absorption Cross-section

Fangfang Jian,1,2* Jing Wang,2 Hailian Xiao,2 Pusu Zhao2, Pingping Sun2, Lihua Huang2

1Microscale Science Institute, Weifang Colledge, Weifang 261061, P. R. China.
2New Materials & Function Coordination Chemistry Lab., Qingdao University of Science & Technology Qingdao, 266042, P.R. China.

E-mail: wj_crystal@qust.edu.cn

Supporting information

Table of contents

1. Crystal Analyst for 2d and 2g S-1 ~ S-4
2. UV-vis spectra S-5 ~ S-6
3. IR spectra S-7 ~ S-13
4. 1H, 13C, and 31P NMR spectroscopy S-14 ~ S-18
5. Open-aperture Z-scan data in o-dichlorobenzene solution S-19 ~ S-20
6. Open-aperture Z-scan data in solid state S-21 ~ S-22
7. The frontier molecular orbitals of [(MeO)2PS2]2Ni·2C60 S-23
1. Crystal Analyst for \{[(\text{EtO})_2\text{PS}_2]\text{Ni}\}_2\cdot2\text{C}_{60} \ 2d \text{ and } \{[(\text{EtO})_2\text{PS}_2]\text{Pd}\}_2\cdot2\text{C}_{60} \ 2g

Crystallographic Data Collection. The diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatic Mo-K$_\alpha$ ($\lambda = 0.71073$ Å, $T = 293$K) radiation. Empirical absorption correction was carried out by using the SADABS program. Their structures were solved by direct methods and refined by least squares on $F_{\text{obs}}^2$ with SHELXTL software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*. A summary of the key crystallographic information for 2d and 2g was given in Table S1. Due to many disorder atoms, the structure refinement has not properly converged.

![ORTEP diagram with ellipsoids drawn at 50% probability for 2d {[(EtO)$_2$PS$_2$]$_2$Ni}·2C$_{60}$ (Left) and for 2g {[(EtO)$_2$PS$_2$]$_2$Pd}·2C$_{60}$ (Right).](S-1)

**Fig. S0** ORTEP diagram with ellipsoids drawn at 50% probability for 2d {[(EtO)$_2$PS$_2$]$_2$Ni}·2C$_{60}$ [Left] and for 2g {[(EtO)$_2$PS$_2$]$_2$Pd}·2C$_{60}$ [Right].
Table S1 A summary of the key crystallographic information for 2d and 2g

<table>
<thead>
<tr>
<th></th>
<th>[(EtO)$_2$PS$_2$]$<em>2$Ni·2C$</em>{60}$ (2d)</th>
<th>[(EtO)$_2$PS$_2$]$<em>2$Pd·2C$</em>{60}$ (2g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{128}$H$</em>{20}$NiO$_4$P$_2$S$_4$</td>
<td>C$<em>{128}$H$</em>{20}$O$_4$P$_2$PdS$_4$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1870.33</td>
<td>1918.02</td>
</tr>
<tr>
<td>T(K)</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C$_2/m$</td>
<td>C$_2/m$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>31.509(6)</td>
<td>31.488(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.407(3)</td>
<td>16.491(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.668(2)</td>
<td>10.072(2)</td>
</tr>
<tr>
<td>beta, deg</td>
<td>108.64(3)</td>
<td>108.62(3)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>5225.7(17)</td>
<td>4956.3(18)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Dc (Mg/m$^3$)</td>
<td>1.189</td>
<td>1.285</td>
</tr>
<tr>
<td>Absorption coefficient (mm$^{-1}$)</td>
<td>0.350</td>
<td>0.360</td>
</tr>
<tr>
<td>F(000)</td>
<td>1884</td>
<td>1920</td>
</tr>
<tr>
<td>Theta range for data collection (°)</td>
<td>1.42 to 24.49</td>
<td>1.36 to 26.97</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-34 ≤ h ≤ 36</td>
<td>-38 ≤ h ≤ 40</td>
</tr>
<tr>
<td></td>
<td>-19 ≤ k ≤ 19</td>
<td>-20 ≤ k ≤ 20</td>
</tr>
<tr>
<td></td>
<td>-11 ≤ l ≤ 0</td>
<td>-12 ≤ l ≤ 0</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>9119/ 4471  [R_{(int)} = 0.1844]</td>
<td>11370/5594  [R_{(int)} = 0.1107]</td>
</tr>
<tr>
<td>Completeness to theta</td>
<td>99.0%</td>
<td>100%</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4471 / 0 / 449</td>
<td>5594 / 0 / 442</td>
</tr>
<tr>
<td>GOF</td>
<td>0.957</td>
<td>1.158</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>$R_1$ = 0.0912, $wR_2 = 0.2060$</td>
<td>$R_1$ = 0.0869, $wR_2 = 0.2220$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1$ = 0.2659, $wR_2 = 0.2963$</td>
<td>$R_1$ = 0.1609, $wR_2 = 0.2564$</td>
</tr>
<tr>
<td>Largest diff. peak and hole( e.Å$^{-3}$)</td>
<td>0.480 and -0.823</td>
<td>0.796 and -0.922</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
<td></td>
</tr>
</tbody>
</table>
Fig. S1. The view of crystal packing along the c axis; A) 2d $\{[(\text{EtO})_2\text{PS}_2]_2\text{Ni}\}\cdot2\text{C}_{60}$; B) 2g $\{[(\text{EtO})_2\text{PS}_2]_2\text{Pd}\}\cdot2\text{C}_{60}$
Fig. S2. Van der Waals contacts in the crystal structures of 2d and 2g: A) along the c axis; B) along a axis
2. UV-vis spectra

Fig. S3-1 Solid UV-vis spectra of metal dialkyldithiophosphate complexes: 1D, [(MeO)₂PS₂]₂Ni; 1E, [(MeO)₂PS₂]₂Cu; 1G, [(MeO)₂PS₂]₂Pd; 2D, [(EtO)₂PS₂]₂Ni; 2E, [(EtO)₂PS₂]₂Cu; 2G, [(EtO)₂PS₂]₂Pd;

Fig. S3-2 Solid UV-vis spectra of metal fullerene complexes for 1d, 1e, 1g, 2d, 2e and 2g.
Fig. S3-3 UV-vis spectra of metal dialkyldithiophosphate complexes in o-dichlorobenzene: 1D, [(MeO)₂PS₂]₂Ni; 1E, [(MeO)₂PS₂]₂Cu; 1G, [(MeO)₂PS₂]₂Pd; 2D, [(EtO)₂PS₂]₂Ni; 2G, [(EtO)₂PS₂]₂Pd;

Fig. S3-4 UV-vis spectra of metal fullerene complexes in o-dichlorobenzene for 1d, 1e, 1g, 2d, 2e and 2g.
3. IR spectra

Fig. S4-1 The IR spectra of 1a

Fig. S4-2 The IR spectra of 1b

S-7
**Fig. S4-3** The IR spectra of 1c

**Fig. S4-4** The IR spectra of 1d

S-8
Fig. S4-5 The IR spectra of 1e

Fig. S4-6 The IR spectra of 1f

S-9
Fig. S4-7 The IR spectra of 1g

Fig. S4-8 The IR spectra of 2a

S-10
Fig. S4-9 The IR spectra of 2b

Fig. S4-10 The IR spectra of 2c
Fig. S4-11 The IR spectra of 2d

Fig. S4-12 The IR spectra of 2e
Fig. S4-13 The IR spectra of 2e

Fig. S4-14 The IR spectra of 2g
4. $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy

Fig. S5-1 $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy of complexes 1d

S-14
Fig. S5-2 $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy of complexes 1g

S-15
Fig. S5-3 $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy of complexes 2d S-16
Fig. S5-4  $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy of complexes 2e
Fig. S5-5 $^1$H, $^{31}$P and $^{13}$C NMR spectroscopy of complexes 2g

S-18
5. Open-aperture Z-scan data in o-dichlorobenzene solution

\( \beta = 0.02253 \text{ cm/GW} \)
\( \sigma = 9317 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Mn} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1a)

\( \beta = 0.02018 \text{ cm/GW} \)
\( \sigma = 6260 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Fe} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1b)

\( \beta = 0.02222 \text{ cm/GW} \)
\( \sigma = 6892 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Co} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1c)

\( \beta = 0.02469 \text{ cm/GW} \)
\( \sigma = 9573 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Ni} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1d)

\( \beta = 0.02364 \text{ cm/GW} \)
\( \sigma = 7332 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Cu} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1e)

\( \beta = 0.02323 \text{ cm/GW} \)
\( \sigma = 7206 \text{ GM} \)
\[ \text{[(MeO)$_2$PS$_2$]$_2$Zn} \cdot 2\text{C$_6$H$_4$O$_2$} \] (1f)

\( \beta = 0.02355 \text{ cm/GW} \)
\( \sigma = 6353 \text{ GM} \)
\[ \text{[(EtO)$_2$PS$_2$]$_2$Mn} \cdot 2\text{C$_6$H$_4$O$_2$} \] (2a)
Fig. S6. Open-aperture Z-scan data in o-dichlorobenzene solution: normalized transmittance of the complexes of fullerene C_{60} with metal dialkyldithiophosphate. Scatter points are experimental data, and solid curves are theoretical fitting results.
6. Open-aperture Z-scan data in solid state

\[
\beta = 0.04382 \text{cm/GM} \\
\sigma = 271344 \text{ GM}
\]

\[
\beta = 0.04091 \text{cm/GW} \\
\sigma = 253790 \text{ GM}
\]

\[
\beta = 0.04767 \text{cm/GW} \\
\sigma = 295728 \text{ GM}
\]

\[
\beta = 0.04681 \text{cm/GW} \\
\sigma = 290392 \text{ GM}
\]

\[
\beta = 0.04022 \text{cm/GW} \\
\sigma = 249512 \text{ GM}
\]

\[
\beta = 0.04267 \text{cm/GW} \\
\sigma = 264710 \text{ GM}
\]

\[
\beta = 0.04669 \text{cm/GW} \\
\sigma = 289648 \text{ GM}
\]

\[
\beta = 0.04298 \text{cm/GW} \\
\sigma = 266632 \text{ GM}
\]

\[
\beta = 0.0469 \text{cm/GW} \\
\sigma = 289648 \text{ GM}
\]
Fig. S7. Open-aperture Z-scan data in solid state: normalized transmittance of the complexes of fullerene C_{60} with metal dialkyldithiophosphate. Scatter points are experimental data, and solid curves are theoretical fitting results.
7. \([(\text{CH}_3\text{O})_2\text{PS}_2]_2\text{Ni}\cdot2\text{C}_{60}\) 1d is calculated by density functional method at B3LYP/6-31G level of theory.

HOMO = -0.22141 a.u.  
LUMO = -0.12790 a.u.

HOMO-1 = -0.22224 a.u.  
LUMO+1 = -0.12783 a.u.

HOMO-2 = -0.22869  
LUMO+2 = -0.12765 a.u.

HOMO-3 = -0.23266 a.u.  
LUMO+3 = -0.12762 a.u.

**Fig. S8** The frontier molecular orbitals of 1d