Electronic Supporting Information

Formation of an Unprecedented (CuBr)$_5$ Cluster and “Zeolite”-type 2D-Coordination Polymer, a Surprising Halide Effect

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Experimental Section

Materials. MeSPr was obtained from Accros. Copper iodide and copper bromide came from Aldrich. These starting materials were used as received.

Synthesis.

Polymer 1. CuBr (0.429 g, 3.00 mmol) was dissolved in neat MeSPr (2.5 mL) and the resulting yellow viscous solution was stirred for further 2 h in a Schlenk tube. Heptane (10 ml) was added in two portions. The Schlenk tube was set into a refrigerator (5° C), where colorless microcrystalline compound 1 crystallized overnight. A second crop was isolated after keeping the filtered solution in freezer at -20°C. Overall yield (61%). Anal. Calcd. for C_{12}H_{30}Cu_5Br_5S_3 • MeSPr (1078.0): C, 17.81, H, 3.71, S, 11.87. Found: C, 16.63; H, 3.16; S, 11.12. The presence of trapped MeSPr molecule inside the cavity of polymer 1 is evidenced by the distinct smell coming from the microcrystalline material.

Preparation of polymer 2. CuI (0.384 g, 2 mmol) was dissolved in neat MeSPr (2 mL) (exothermic reaction) and the resulting yellow viscous solution was stirred for further 2 h in a Schlenk tube. Heptane (10 ml) was added in two portions. During the addition of the last portion, precipitation of a small amount of a colorless solid was noticed. The Schlenk tube was set into a refrigerator (5° C), where colorless crystals of 2 crystallized overnight. A second crop of this air-stable compound was isolated after keeping the filtered solution in freezer at -20°C. Overall yield (72%) Anal. Calcd. for C_{12}H_{30}Cu_4I_4S_3 (1032.5): C, 13.96, H, 2.92, S, 9.32. Found: C, 13.36, H, 2.55, S, 9.02 %.

Apparatus. UV-visible spectra were obtained on an HP-8453 diode array spectrophotometer or on a Varian Cary 300 spectrophotometer. Emission and excitation spectra were measured on a Fluorolog 2 from SPEX or a LS100 from Photon Technology International (PTI). The phosphorescence lifetimes were measured on a LS100 from Photon Technology International, PTI. Thermogravimetric analysis (TGA) measurements were performed on thermal gravimetric analyzer (model Perkin-Elmer TGA-6) under a nitrogen flow at a heating rate of 10 °C/min.
X-ray structures:

**Polymer 1.** X-ray suitable crystals of 1 were obtained by recrystallization from a concentrated MeCN solution. Diffraction data frames for 1 were collected at 100 K on a Bruker Apex Duo and integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS) (T<sub>max</sub>=0.1026, T<sub>min</sub>=0.3033). The structure was solved by direct methods (SIR 92)<sup>1</sup> and refined with SHELXL97.<sup>2</sup> All non–hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and included in final refinement in a riding model with isotropic temperature parameters set to U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C). Crystal data for 1: C<sub>24</sub>H<sub>60</sub>Br<sub>10</sub>Cu<sub>10</sub>S<sub>6</sub>, M=1978.58, monoclinic P<sub>1</sub>, a = 10.5490(6) Å, b = 13.5090(6) Å, c = c = 22.1288(12) Å, α = 88.464(2)°, β = 79.809(2)°, γ = 77.0170(10)°, V = 3024.1(3) Å<sup>3</sup>, Z = 2, D<sub>c</sub> = 2.170 Mg/cm<sup>3</sup>, F<sub>000</sub> = 1880, λ(MoKα) = 1.54178 Å, μ = 13.539 mm<sup>-1</sup>, T = 100(2) K, 15951 refl. collected, 9871 unique (R<sub>int</sub> = 0.037), (R<sub>sig</sub> = 6.51%), 8733 were greater than 2σ(I), R<sub>1</sub>all = 0.0866, wR<sub>2</sub> = 0.1747, R<sub>1</sub>gt = 0.0728, wR<sub>2</sub>gt = 0.1688, GoF = 1.184, ρ<sub>max</sub> = 2.364, ρ<sub>min</sub> = -1.359 e/Å<sup>3</sup>. CCDC 947670.

**Polymer 2.** Diffraction data frames for 2 collected on a Bruker Apex II diffractometer at 115 K were processed with SORTAV software.<sup>3</sup> An empirical multi-scan absorption correction was further applied by using SADABS-2008/1 (T<sub>max</sub>=0.748, T<sub>min</sub>=0.344). The structure was solved by direct methods (SIR 92)<sup>1</sup> and refined with SHELXL97.<sup>2</sup> All non–hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and included in final refinement in a riding model with isotropic temperature parameters set to U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C). Crystal data for 2: C<sub>12</sub>H<sub>30</sub>Cu<sub>4</sub>I<sub>4</sub>S<sub>3</sub>, M=1032.30, monoclinic P<sub>2</sub>1/c, a = 14.2852(7)Å, b = 11.1485(6)Å, c = 21.5737(8)Å, β = 129.284(2)°, V = 2659.4(2) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 2.578 g cm<sup>-3</sup>, F<sub>000</sub> = 1912, λ(MoKα) = 0.71073 Å, μ = 8.031 mm<sup>-1</sup>, T = 115(2) K, 113827 refl. collected, 19030 unique (R<sub>int</sub> = 0.057), 13781 gt. with I > 2σ(I), R<sub>1</sub>all = 0.0719, wR<sub>2</sub> = 0.1150, R<sub>1</sub>gt = 0.0412, wR<sub>2</sub>gt = 0.0957, GoF = 1.078, ρ<sub>max</sub> = 0.880, ρ<sub>min</sub> = -0.976 e/Å<sup>3</sup>. CCDC 947669.

**Computations.** Calculations were performed with Gaussian 09<sup>4</sup> at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT<sup>5-8</sup> and TD-DFT<sup>9-11</sup> were calculated using the crystallographic data with the B3LYP<sup>12-14</sup> method. 3-21G<sup>15-20</sup> basis sets were used for C, H and S, VDZ (valence double ζ) with SBKJC effective core potentials<sup>21-23</sup> for Cu, Br and I. The calculated absorption spectra and related MO contributions were obtained from the TD-DFT/Singlets output file and gausssum2.1.<sup>24</sup> The number of cluster units used for the calculations was 6 and 1 for polymers 1 and 2, respectively, in order to use the same number of crystallographically independent cluster in the unit cells. For polymer 1, the crystallographically independent number of cluster units is three but two were used to represent a full hexagon.

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*Electronic Supplementary Material (ESI) for Chemical Communications*

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References.

22. SBKJC ECP EMST Basis Set Exchange Library.
**Fig. S1.** Representation of the frontier MOs of the cubane unit of polymer 2. H = HOMO, L = LUMO. The MO energies are in eV.
Table S1. Computed energies, oscillator strength (f), and major contributions for the first 5 transitions for 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>v (cm⁻¹)</th>
<th>λ (nm)</th>
<th>f</th>
<th>Major contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29776.58208</td>
<td>335.8343806</td>
<td>0.0505</td>
<td>HOMO→LUMO (40%), H-11→LUMO (5%), H-8→LUMO (2%), H-7→LUMO (5%), H-7→L+1 (2%), H-1→LUMO (6%), H-1→L+1 (4%), HOMO→L+1 (7%)</td>
</tr>
<tr>
<td>2</td>
<td>29948.37936</td>
<td>333.9078846</td>
<td>0.0885</td>
<td>H-1→L+1 (23%), H-13→L+1 (8%), H-10→L+1 (6%), H-9→LUMO (3%), H-9→L+1 (8%), H-7→LUMO (2%), H-7→L+1 (4%), H-3→L+1 (5%), H-2→L+1 (9%), H-1→LUMO (9%), HOMO→L+1 (7%)</td>
</tr>
<tr>
<td>3</td>
<td>30217.7704</td>
<td>330.9311001</td>
<td>0.0022</td>
<td>H-11→LUMO (35%), H-16→LUMO (5%), H-13→LUMO (3%), H-12→LUMO (4%), H-11→L+1 (9%), H-10→LUMO (4%), H-8→LUMO (3%), H-5→LUMO (5%), H-4→LUMO (5%)</td>
</tr>
<tr>
<td>4</td>
<td>30276.64928</td>
<td>330.2875397</td>
<td>0.0005</td>
<td>H-13→LUMO (10%), H-13→L+1 (37%), H-17→L+1 (2%), H-11→L+1 (6%), H-8→L+1 (4%), H-7→L+1 (7%), H-6→L+1 (7%)</td>
</tr>
<tr>
<td>5</td>
<td>31203.38672</td>
<td>320.478033</td>
<td>0.0062</td>
<td>H-8→LUMO (27%), H-4→LUMO (12%), H-11→LUMO (4%), H-10→LUMO (5%), H-9→LUMO (5%), H-8→L+1 (7%), H-7→LUMO (6%), H-5→LUMO (9%), H-5→L+1 (2%), H-4→L+1 (3%)</td>
</tr>
</tbody>
</table>

Table S2. Computed energies, oscillator strength (f), and major contributions for the first 5 transitions for 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>v (cm⁻¹)</th>
<th>λ (nm)</th>
<th>f</th>
<th>Major contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33475.47</td>
<td>298.7262</td>
<td>0.0108</td>
<td>H-1→LUMO (97%)</td>
</tr>
<tr>
<td>2</td>
<td>33526.28</td>
<td>298.2735</td>
<td>0.019</td>
<td>HOMO→LUMO (97%)</td>
</tr>
<tr>
<td>3</td>
<td>33833.58</td>
<td>295.5644</td>
<td>0.0093</td>
<td>H-2→LUMO (98%)</td>
</tr>
<tr>
<td>4</td>
<td>35781.42</td>
<td>279.4746</td>
<td>0.0085</td>
<td>H-4→LUMO (93%)</td>
</tr>
<tr>
<td>5</td>
<td>35838.69</td>
<td>279.0281</td>
<td>0.0274</td>
<td>H-3→LUMO (89%)</td>
</tr>
</tbody>
</table>
Figure. S2. Top: Computed electronic transition (green) of polymer 1 by TDDFT. In red, same electronic transitions but applying a 500 cm\(^{-1}\) thickness to the green lines. Bottom: same as above except a thickness of 1000 cm\(^{-1}\) is applied.
Fig. S3. Top: Computed electronic transition (green) of polymer 2 by TDDFT. In red, same electronic transitions but applying a 500 cm\(^{-1}\) thickness to the green lines. Bottom: same as above except a thickness of 1000 cm\(^{-1}\) is applied.