# 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) ($T_{max}$=0.1026, $T_{min}$=0.3033). The structure was solved by direct methods (SIR 92)[1] and refined with SHELXL97. [2] 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 $U_{iso}(H) = 1.5U_{eq}(C)$. *Crystal data* for **1**: $C_{24}H_{60}Br_{10}Cu_{10}S_6$, $M$=1978.58, monoclinic *P-1*, $a$ = 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$^3$, $Z$ = 2, $D_c$ = 2.170 Mg/cm$^3$, $F_{000}$ = 1880, $\lambda$(MoK$_\alpha$) = 1.54178 Å, $\mu$ = 13.539 mm$^{-1}$, $T$ = 100(2) K, 15951 refl. collected, 9871 unique ($R_{int}$ = 0.037), ($R_{sig}$ = 6.51%), 8733 were greater than 2σ(F$^2$), $R1_{all}$ = 0.0866, $wR2$ = *0.1747*, $R1_{gt}$ = 0.0728, $wR2_{gt}$ = 0.1688, *GoF* = 1.184, $\rho_{max}$ = 2.364, $\rho_{min}$ = -1.359 e/Å$^3$. CCDC 947670

**Polymer 2**. Diffraction data frames for **2** collected on a Bruker Apex II diffractometer at 115 K were processed with SORTAV software.[3] An empirical multi-scan absorption correction was further applied by using SADABS-2008/1 ($T_{max}$=0.748, $T_{min}$=0.344). The structure was solved by direct methods (SIR 92)[1] and refined with SHELXL97. [2] 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 $U_{iso}(H) = 1.5U_{eq}(C)$. *Crystal data* for **2**: $C_{12}H_{30}Cu_4I_4S_3$, $M$=1032.30, monoclinic $P2_1/c$, $a$ = 14.2852(7)Å, $b$ = 11.1485(6)Å, $c$ = 21.5737(8)Å, $\beta$= 129.284(2)°, $V$ = 2659.4(2), $Z$ = 4, $D_c$ = 2.578 g cm$^{-3}$, $F_{000}$ = 1912, $\lambda$(MoK$_\alpha$) = 0.71073 Å, $\mu$ = 8.031 mm$^{-1}$, $T$ = 115(2) K, 113827 refl. collected, 19030 unique ($R_{int}$ = 0.057), 13781 gt. with $I > 2\sigma(I)$, $R1_{all}$ = 0.0719, $wR2$ = *0.1150*, $R1_{gt}$ = 0.0412, $wR2_{gt}$ = 0.0957, *GoF* = 1.078, $\rho_{max}$ = 0.880, $\rho_{min}$ = -0.976 e/Å$^3$. CCDC 947669.

**Computations.** Calculations were performed with Gaussian 09[4] at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT[5-8] and TD-DFT[9-11] were calculated using the crystallographic data with the B3LYP[12-14] method. 3-21G*[15-20] basis sets were used for C, H and S, VDZ (valence double ζ) with SBKJC effective core potentials[21-23] 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.[24] 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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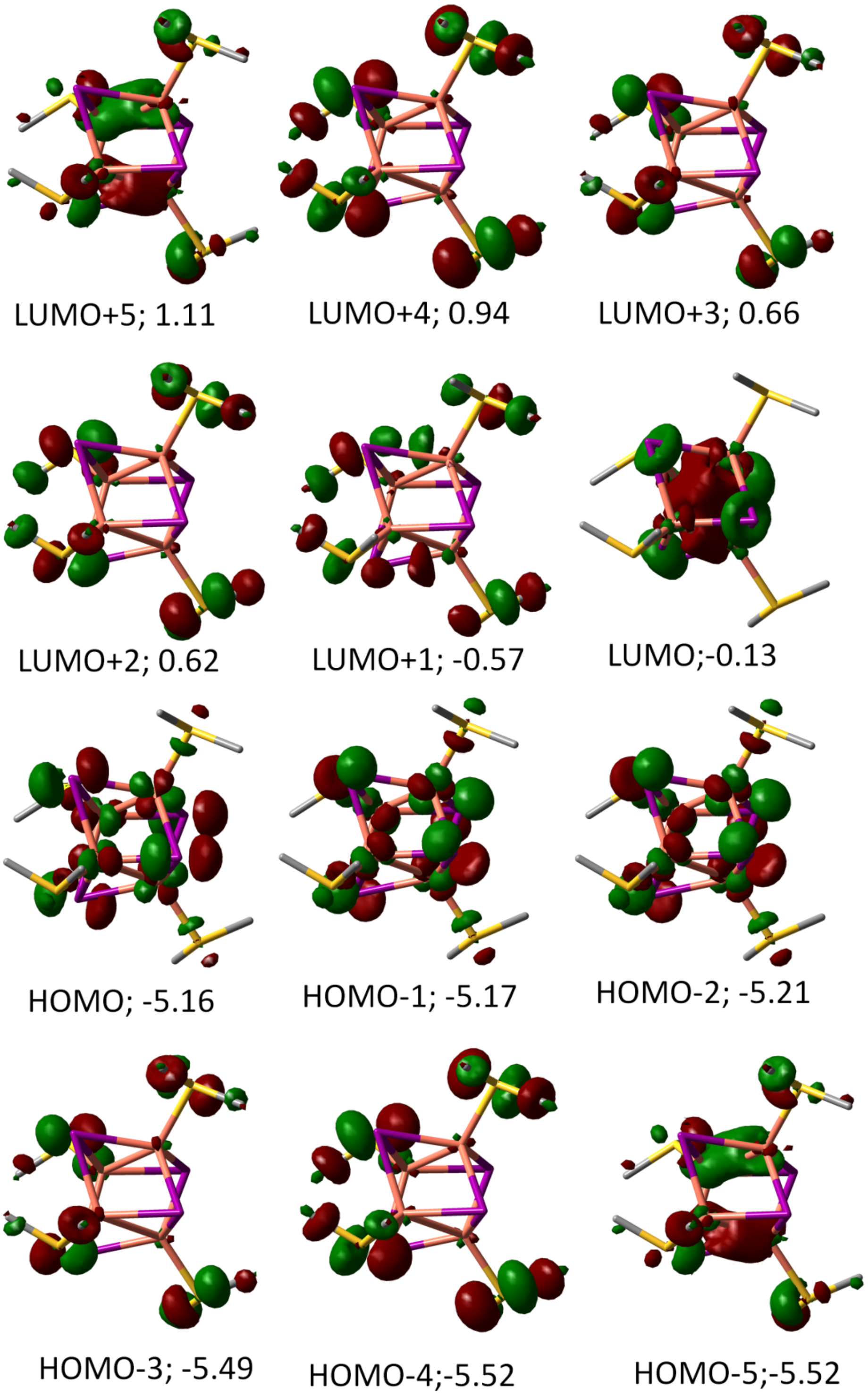


LUMO+5; 1.11 LUMO+4; 0.94 LUMO+3; 0.66

LUMO+2; 0.62 LUMO+1; -0.57 LUMO;-0.13

HOMO; -5.16 HOMO-1; -5.17 HOMO-2; -5.21

HOMO-3; -5.49 HOMO-4;-5.52 HOMO-5;-5.52

**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**.

| No. | $\nu$ (cm$^{-1}$) | $\lambda$ (nm) | f | Major contribution (%) |
|---|---|---|---|---|
| 1 | 29776.58208 | 335.8343806 | 0.0505 | HOMO→LUMO (40%) H-11→LUMO (5%), H-10→LUMO (9%), 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%) |
| 2 | 29948.37936 | 333.9078846 | 0.0885 | 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%) |
| 3 | 30217.7704 | 330.9311001 | 0.0022 | 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%) |
| 4 | 30276.64928 | 330.2875397 | 0.0005 | 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%) |
| 5 | 31203.38672 | 320.478033 | 0.0062 | 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%) |

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

| No. | $\nu$ (cm$^{-1}$) | $\lambda$ (nm) | f | Major contribution (%) |
|---|---|---|---|---|
| 1 | 33475.47 | 298.7262 | 0.0108 | H-1→→LUMO (97%) |
| 2 | 33526.28 | 298.2735 | 0.019 | HOMO→LUMO (97%) |
| 3 | 33833.58 | 295.5644 | 0.0093 | H-2→LUMO (98%) |
| 4 | 35781.42 | 279.4746 | 0.0085 | H-4→LUMO (93%) |
| 5 | 35838.69 | 279.0281 | 0.0274 | H-3→LUMO (89%) |

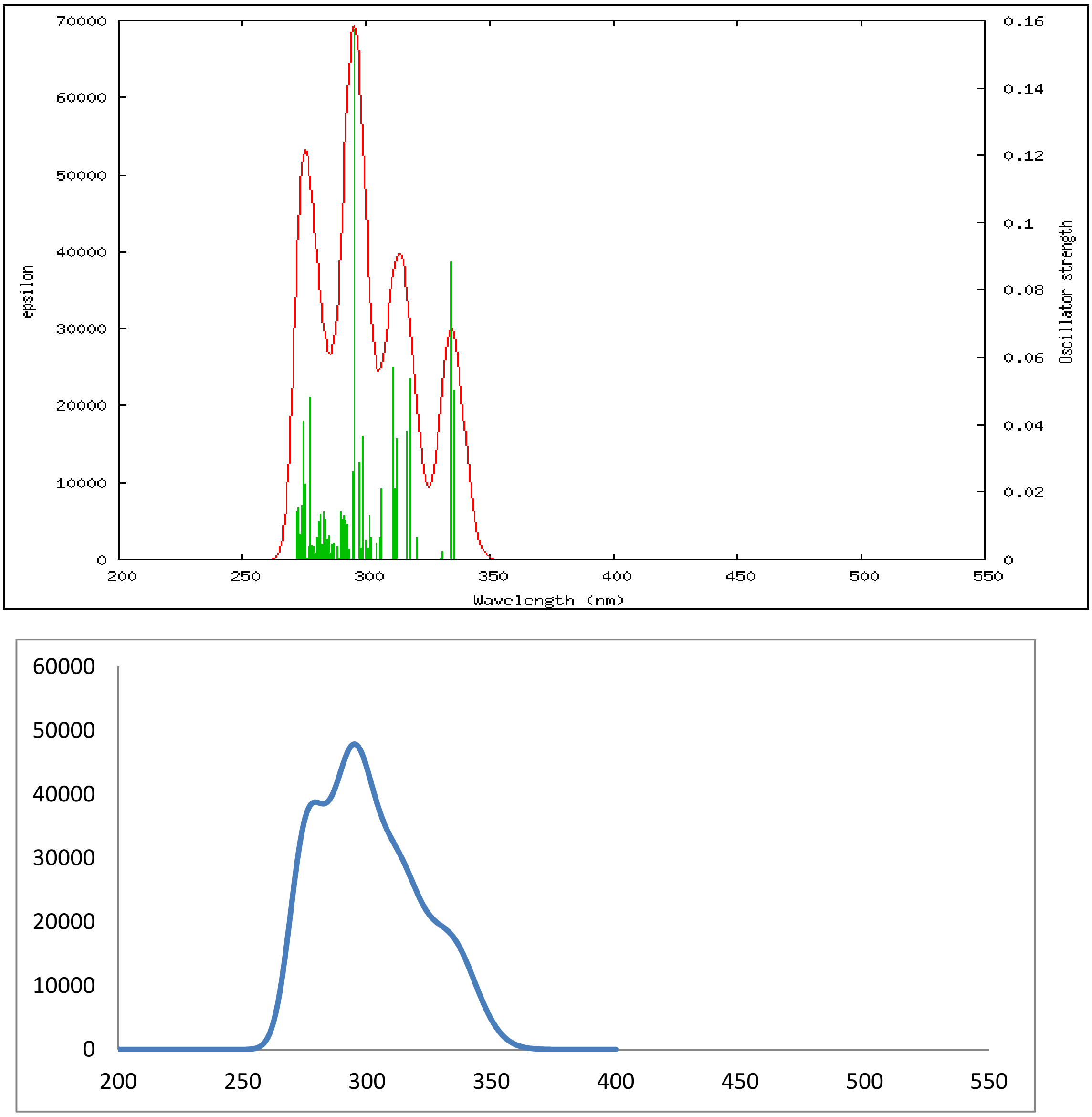
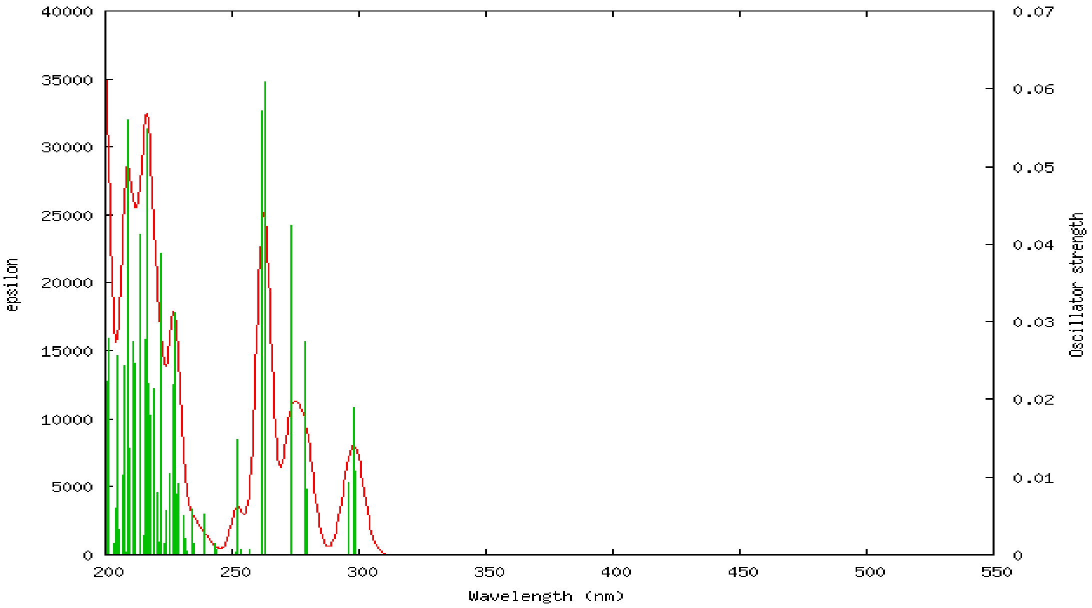


Figure. S2. Top: Computed electronic transition (green) of polymer **1** by TDDFT. In red, same electronic transitions but applying a 500 $cm^{-1}$ thickness to the green lines. Bottom: same as above except a thickness of 1000 $cm^{-1}$ is applied.



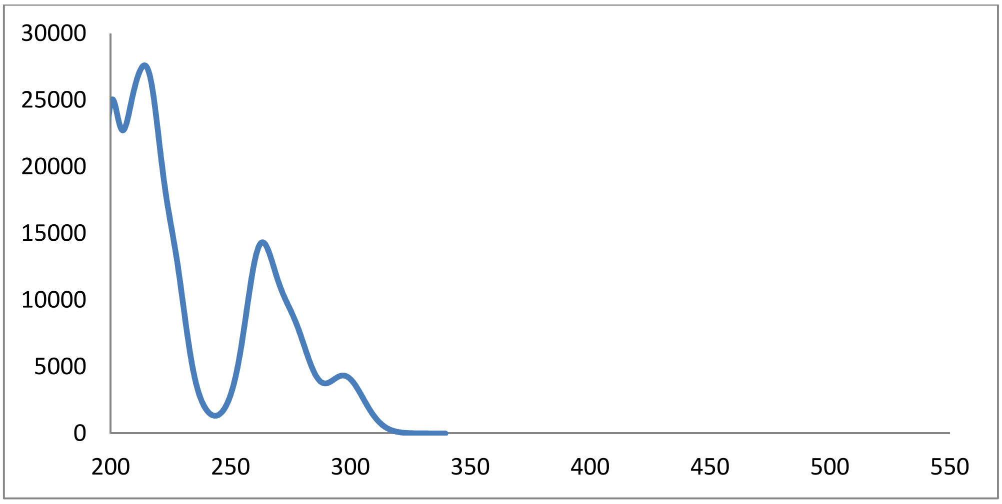


Fig.. S3. Top: Computed electronic transition (green) of polymer **2** by TDDFT. In red, same electronic transitions but applying a 500 cm$^{-1}$ thickness to the green lines. Bottom: same as above except a thickness of 1000 cm$^{-1}$ is applied.