ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2022. Том 63, № 1 *Январь* *DOI: 10.26902/JSC_id84800*

SUPPLEMENTARY MATERIALS TO: A COPPER(I) COORDINATION COMPOUND WITH RED PHOTOLUMINESCENCE

Y.-L. Tao, C.-H. Wang, H.-Y. Xiang, G.-R. Li, C.-H. Li, X. Liu

Chongqing Key Laboratory of Green Synthesis and Applications, College of Chemistry, Chongqing Normal University, Chongqing, People's Republic of China
E-mail: xliu@cqnu.edu.cn

Additional plots of the crystal structure

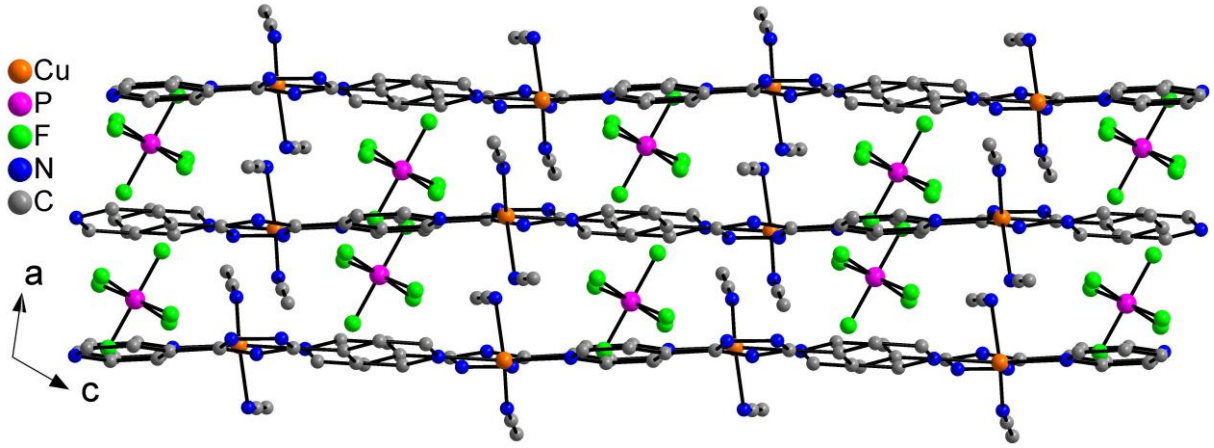


Fig. S1. A view of the packing diagram of the cationic $[Cu(Hbpt)(CH_3CN)_2]_n$ chains and anionic PF_6^- in **1** along the *b* axis. Hydrogen atoms are omitted for clarity.

© Tao Y.-L., Wang C.-H., Xiang H.-Y., Li G.-R., Li C.-H., Liu X., 2022

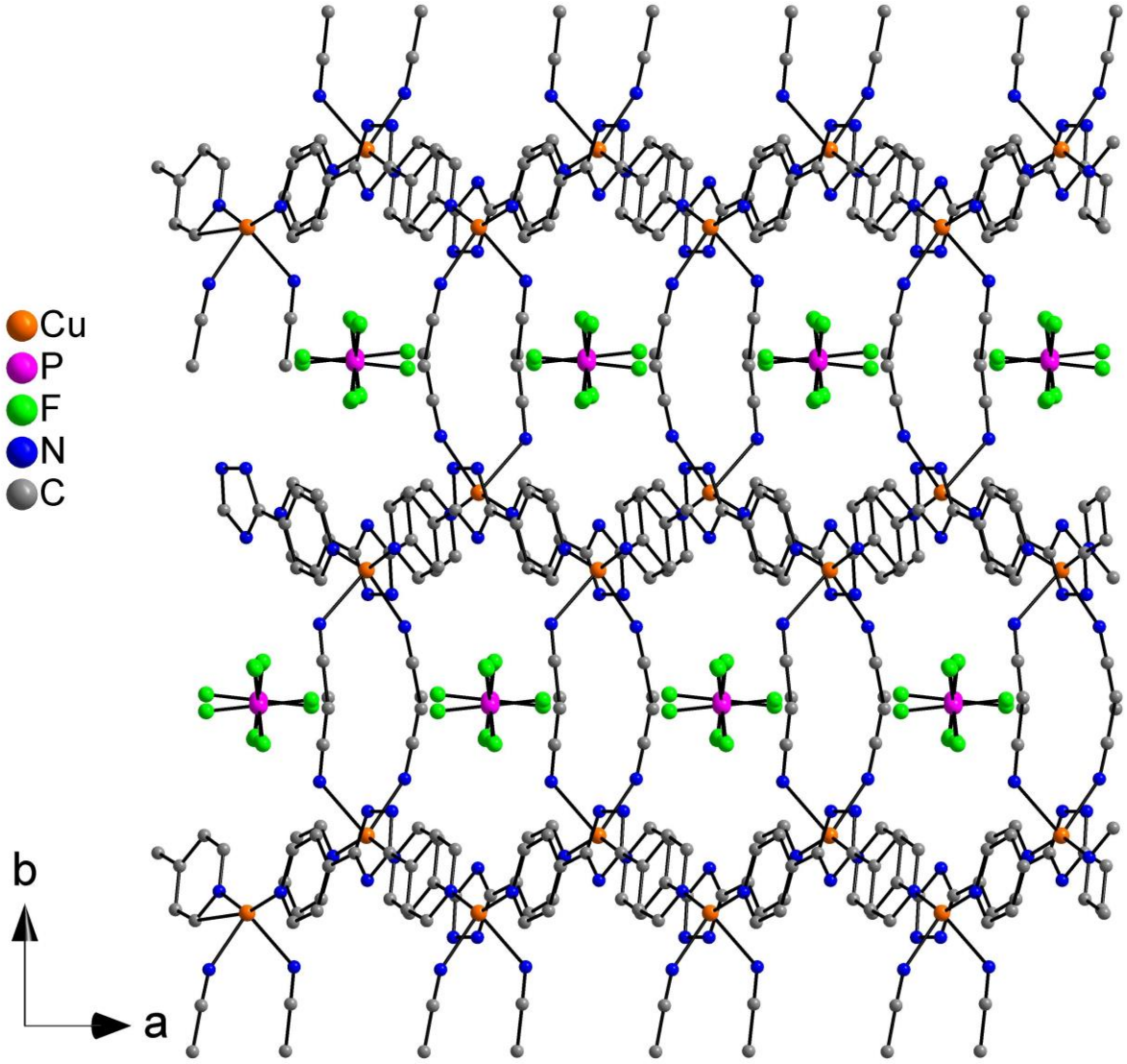


Fig. S2. A view of the packing diagram of the cationic $[Cu(Hbpt)(CH_3CN)_2]_n$ chains and anionic PF_6^- in **1** along the *c* axis. Hydrogen atoms are omitted for clarity.

DFT Calculation Approach Methodology

The crystallographic data of the present complexes determined by X-ray diffraction were used to calculate the electronic band structure. Calculations of the electronic band structure along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three non-local gradient-corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,[1] which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential[2] for the core electrons. The number of plane waves included in the basis was determined by a cut-off energy Ec of 940 eV. Pseudoatomic calculations were performed for H-$1s^1$, C-$2s^2 2p^2$, N-$2s^2 2p^3$, F-$2s^2 2p^5$, P-$3s^2 3p^3$, and Cu-$3d^{10} 4s^1$. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code, e.g., reciprocal space pseudopotentials representations, total energy convergence tolerance of 5×10^{-7} eV, eigen-energy convergence tolerance of approximate 2.67×10^{-7} eV. All of calculations were performed by CASTEP program in Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

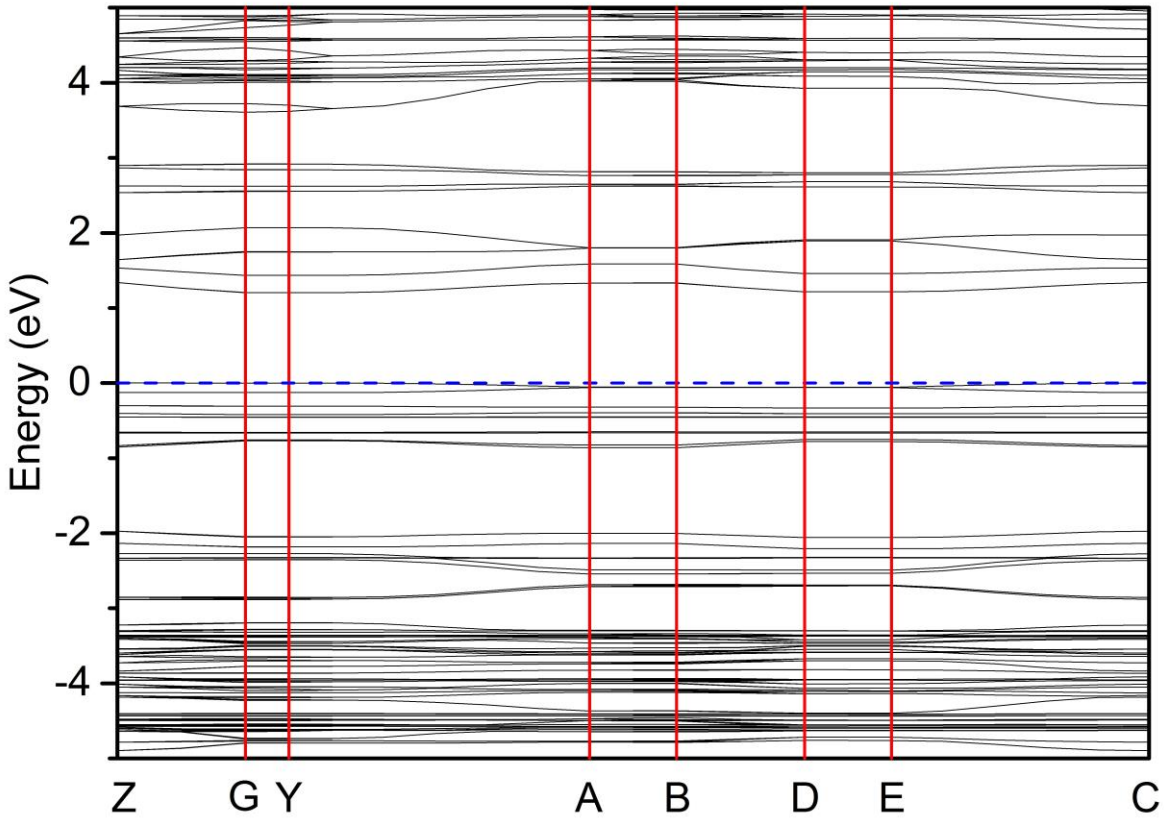


Fig. S3. Energy band structures of **1**. Energy bands are shown only between –5.0 and 5.0 eV for clarity.

(1) (a) Segall M., Linda P., Probert M., Pickard C., Hasnip P., Clark S., Payne M. *Materials Studio CASTEP*, version 5.5; Accelrys: San Diego, CA, **2010**. (b) Segall M., Linda P., Probert M., Pickard C., Hasnip P., Clark S., Payne M. *J. Phys.: Condens. Matter* 2002, *14*, 2717–2744.

(2) Hamann D. R., Schluter M., Chiang C. *Phys. Rev. Lett.* 1979, *43*, 1494–1497.

Computational Descriptions/Explanation

The calculated band structure of compound **1** along high symmetry points of the first Brillouin zone is plotted in Figure S3, where the labeled k-points are present as Z(0, 0, 0.5), G(0, 0, 0), Y(0, 0.5, 0), A(-0.5, 0.5, 0), B(-0.5, 0, 0), D(-0.5, 0, 0.5), E(-0.5, 0.5, 0.5), and C(0, 0.5, 0.5). It is observed that the top of the valence bands (VBs) appears to be relatively flat and the bottom of the conduction bands (CBs) has small dispersion. The lowest energy (1.20 eV) of the conduction bands (CBs) is localized at the G point, and the highest energy (0.00 eV) of the VBs is also localized at the Z point, indicating compound **1** shows a semiconductor character with an indirect band gap of 1.20 eV. The bands can be assigned according to total and partial densities of states (DOS).

The PF_6^--2s, Hbpt-2s, and CH_3CN-2s states, mixing with small Hbpt-2p, and CH_3CN-2p states, create the VBs localized at about -25.0 and -10.0 eV, while the PF_6^--2p, Hbpt-2p, and CH_3CN-2p states mixing with small Hbpt-2s, and CH_3CN-2s states, create the VBs localized at about -10.0 and -1.40 eV. The VBs between energy -1.40 eV and the Fermi level (0.00 eV) are mostly formed by the Cu-3d states (41.5 electrons/eV). The CBs between 0.80 and 2.20 eV are almost contribution from the Hbpt-2p states (15.8 electrons/eV), while the CBs between 2.20 and 7.77 eV are almost formed by BptH-2p states (25.1 electrons/eV) and PF_6^--2p states (26.4 electrons/eV). Together with the structural features of **1**, the origin of the emission band of **1** may be mainly ascribed to metal-to-ligand charge transfer (MLCT) where electrons are transferred from Cu(I) cations (Cu-3d states, VBs) to the unoccupied π^* orbitals of the Hbpt ligands (Hbpt-2p states, CBs).

IR spectra

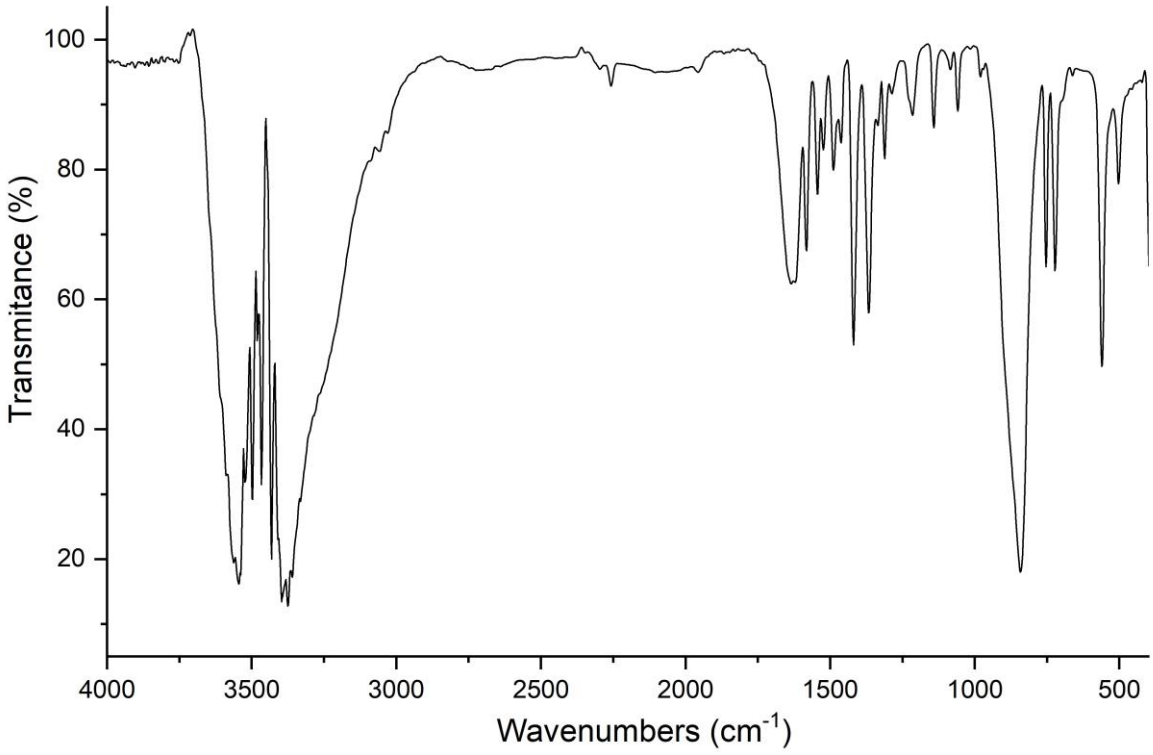


Fig. S4. The FT-IR spectrum of **1** at room temperature.