

Accessory Publication

A novel copper cyanide complex with a layered structure

Xi Liu, Guo-Cong Guo*

Single Crystal measurements

Data collection for **1** was performed on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated MoK α radiation. The intensity data set was collected with ω scan technique and corrected by CrystalClear software. The structure was solved by the direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were located by difference Fourier map and subjected to anisotropic refinement. Hydrogen atoms were added according to the theoretical models. All of the calculations were performed by Siemens SHELXTLTM version 5 package of crystallographic software.

Time-dependent DFT calculation Approach Methodology

Calculations on the excited-state electron-density distribution of the corresponding frontier orbitals for the ∞ [Cu(CN)(CH₃CN)] chain in **1** was carried out using Gaussian2003.^[1] “Double- ζ ” quality basis sets were employed for the C, H, N (6-311G) and the Cu (LANL2DZ). The ground state geometries, [Cu₃(HCN)₂(CN)₂(CH₃CN)₃]⁺ for **1** was adapted from their truncated X-ray data. Based on this geometry, time-dependent DFT (TDDFT) calculation using the B3LYP functional was performed. All calculated results can rationally explain the origins of the fluorescent emissions according to the literature.^[2] More accurate data could be obtained to gain detailed insights into the energy correlation among various electronic states for nontruncated structures.

	HOMO-1	HOMO	LUMO
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¹ Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.

² For latest examples, see: (a) Yong, L.; Hoffmann, S. D.; Fässler, T. F.; Riedel, S.; Kaupp, M. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 2092. (b) Zheng, S.-L.; Yang, J.-H.; Yu, X.-L.; Chen, X.-M.; Wong, W.-T. *Inorg. Chem.* **2004**, *43*, 830. (c) Wang, C.-C.; Yang, C.-H.; Tseng, S.-M.; Lin, S.-Y.; Wu, T.-Y.; Fuh, M.-R.; Lee, G.-H.; Wong, K.-T.; Chen, R.-T.; Cheng, Y.-M.; Chou, P.-T. *Inorg. Chem.* **2004**, *43*, 4781.

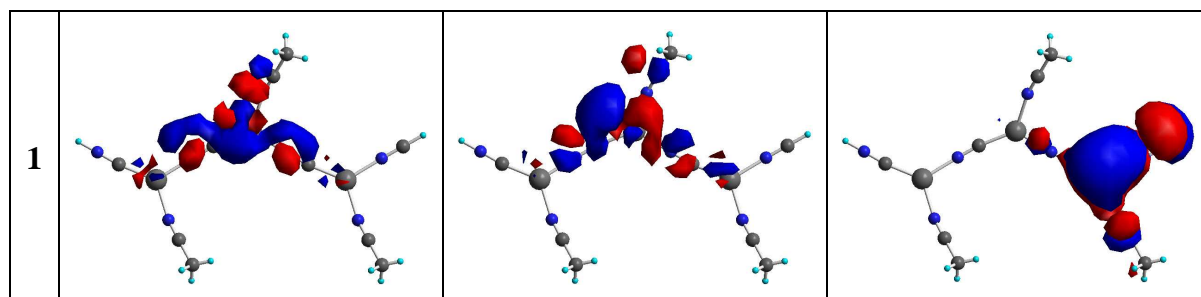


Figure S1 The electron-density distribution of the corresponding frontier orbitals calculated for **1**.

Table S1. The calculated excitation energy (E), oscillator strength (f), and dominant orbital excitation from TD-DFT calculations for the lowest singlet excitation states.

Excited State	E (nm)	f	Dominant configurations
S1	318.24	0.0024	HOMO-1→LUMO, HOMO→LUMO

Table S2. Geometrical characteristics of the C-H...Br hydrogen bonds in **1**.

D-H	H...A (Å)	D...A (Å)	∠(DHA) (°)	D-H...A
0.93(4)	2.52(4)	3.318(4)	145(2)	C(3)-H(3C) ...O(2)