

Supplementary Material

A Copper Cyanide Complex with Efficient Red Luminescence

Xi Liu,^{A,B} Yun-Zhi Yang,^A Chun-Hai Wang,^A and Kun-Lin Huang^A

^A College of Chemistry, Chongqing Normal University, Chongqing 400047, P. R. China

^B Author to whom correspondence should be addressed (e-mail: xliu@cqnu.edu.cn).

Additional plot of the structure

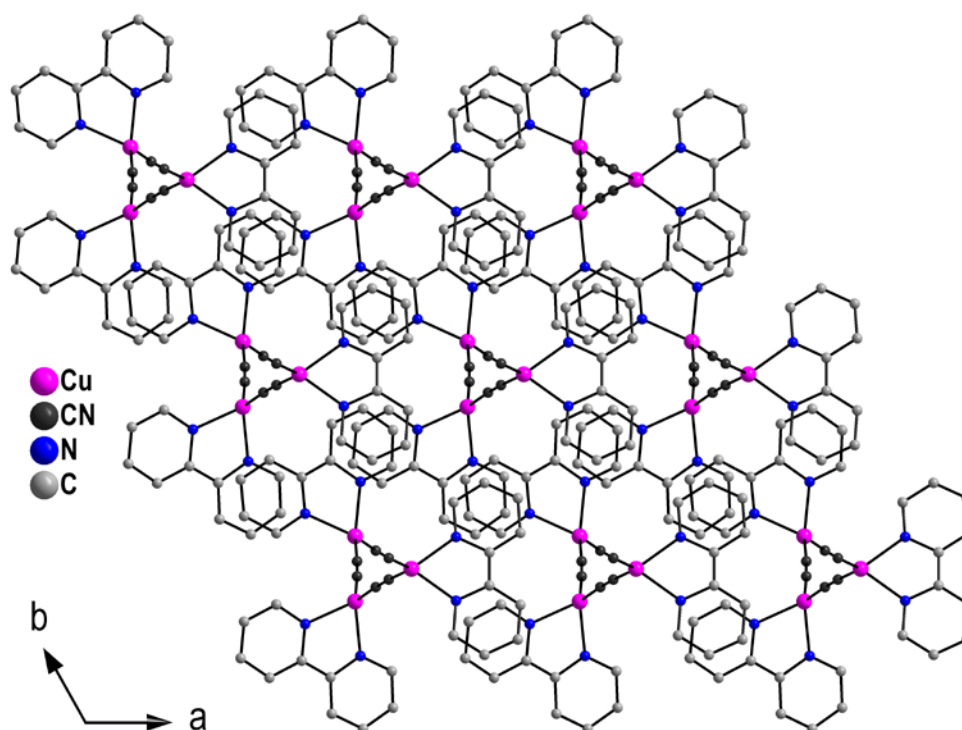


Figure S1. A view of 3-D structure along the *c* direction formed by π - π interactions.

Materials and physical measurement

All chemicals except CH_3CN solvents were obtained from commercial sources and used without further purification. CH_3CN were purified and distilled by conventional methods, and stored under nitrogen before use. Elemental analyses were performed on a Vario EL III elemental analyzer. The FT-IR spectra were obtained on a Perkin Elmer Spectrum using KBr discs in the range 4000 – 400 cm^{-1} . Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. The lifetimes of the emission bands were measured on an Edinburgh

LifeSpec-ps system.

Structure determination

A reddish brown crystal with dimensions of $0.21 \times 0.14 \times 0.12 \text{ mm}^3$ was mounted on a glass fiber for X-ray diffraction analysis. All measurements were performed on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. A total of 5328 reflections were collected, of which 967 were independent ($R_{\text{int}} = 0.0526$). The intensity data were collected in the range of $3.13 < \theta < 25.31^\circ$ with an ω scan technique and reduced by CrystalClear software.^[1] The structure was solved by direct methods and refined by full-matrix least-squares techniques. The structure was refined anisotropically for non-hydrogen atoms; The pyridine ring was constrained to be an ideal aromatic 6-member ring due to its large thermal vibration; The hydrogen atoms were added according to the theoretical models. Structure solution and refinement based on 510 observed reflections with $I > 2\sigma(I)$ and 57 parameters gave $R = 0.0695$, $wR = 0.1826$ ($w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.001$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{max}} = 0.804$ and $(\Delta\rho)_{\text{min}} = -0.435$. All of the calculations were performed with Siemens SHELXTLTM version 5 package of crystallographic software.^[2] The cyanide group was refined as disordered over two symmetry-related sites due to the cyanide group with crystallographic inversion centers.

CCDC-910570 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requwst/cif.

1 Rigaku, CrystalClear Version 1.35, Rigaku Corporation, 2002.

2 Siemens SHELXTLTM Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, U.S.A. 1994.

Time-dependent DFT calculation approach methodology with Gaussian2009 program

Calculations on the excited-state electron-density distribution of the corresponding frontier orbitals for the $^{\infty}_1[\text{Cu}(\text{CN})(\text{bipy})]$ chain in **1** was carried out using Gaussian2009.^[3] “Double- ζ ” quality basis sets were employed for the C, H, N (6-311g) and the Cu (LANL2DZ). The original ground state geometry, $[\text{Cu}_2(\text{CN})_3(\text{bipy})_2]^-$ for **1** was adapted from their truncated X-ray data, and further saturated with H atoms to form $[\text{Cu}_2(\text{HCN})_2(\text{CN})(\text{bipy})_2]^+$ molecular fragment. 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.^[4] More accurate data could be obtained to gain detailed insights into the energy correlation among various electronic states for nontruncated structures.

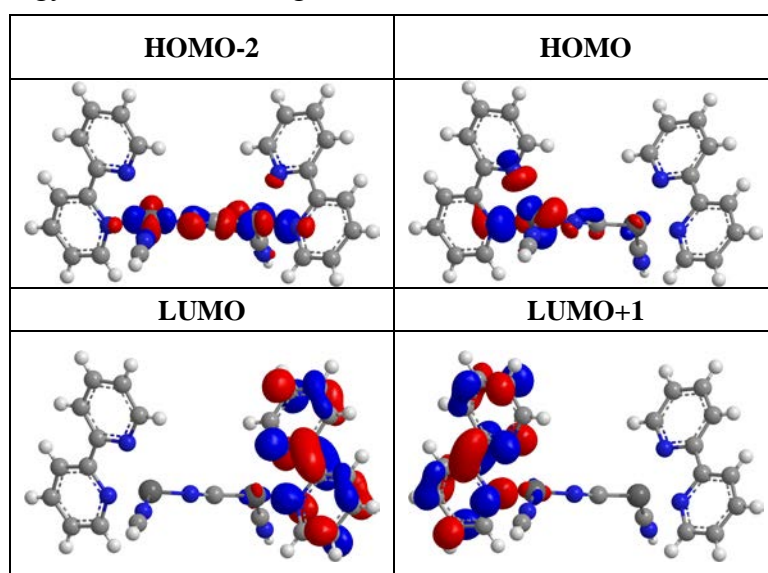


Figure S2 The electron-density distribution of the corresponding frontier orbitals calculated for **1**.

3 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

4 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.

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	569.37	0.0012	HOMO-2→LUMO+1, HOMO→LUMO HOMO→LUMO+1 HOMO→LUMO
T1	637.67	0.0000	HOMO→LUMO+1 HOMO→LUMO+3

DOS calculation approach methodology with CASTEP program

The crystallographic data of the present compound determined by X-ray were used to calculate the electronic band structure. Calculation of the electronic band structure along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradientcorrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,⁵ which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential⁶ for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 880 eV. Pseudoatomic calculations were performed for H-1s¹, C-2s²2p², N-2s²2p³ and Cu-3d¹⁰4s¹. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code,^{5a} e.g., reciprocal space pseudopotentials representations and eigen-energy convergence tolerance 0.2949 E-06 eV. All of calculations were performed by CASTEP program in the Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, USA.

5 (a) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. Materials Studio CASTEP, version 2.2; Accelrys: San Diego, CA, 2002. (b) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. J. Phys.: Condens. Matter 2002, 14, 2717.

6 Hamann, D. R.; Schluter, M.; Chiang, C. Phys. Rev. Lett. 1979, 43, 1494.

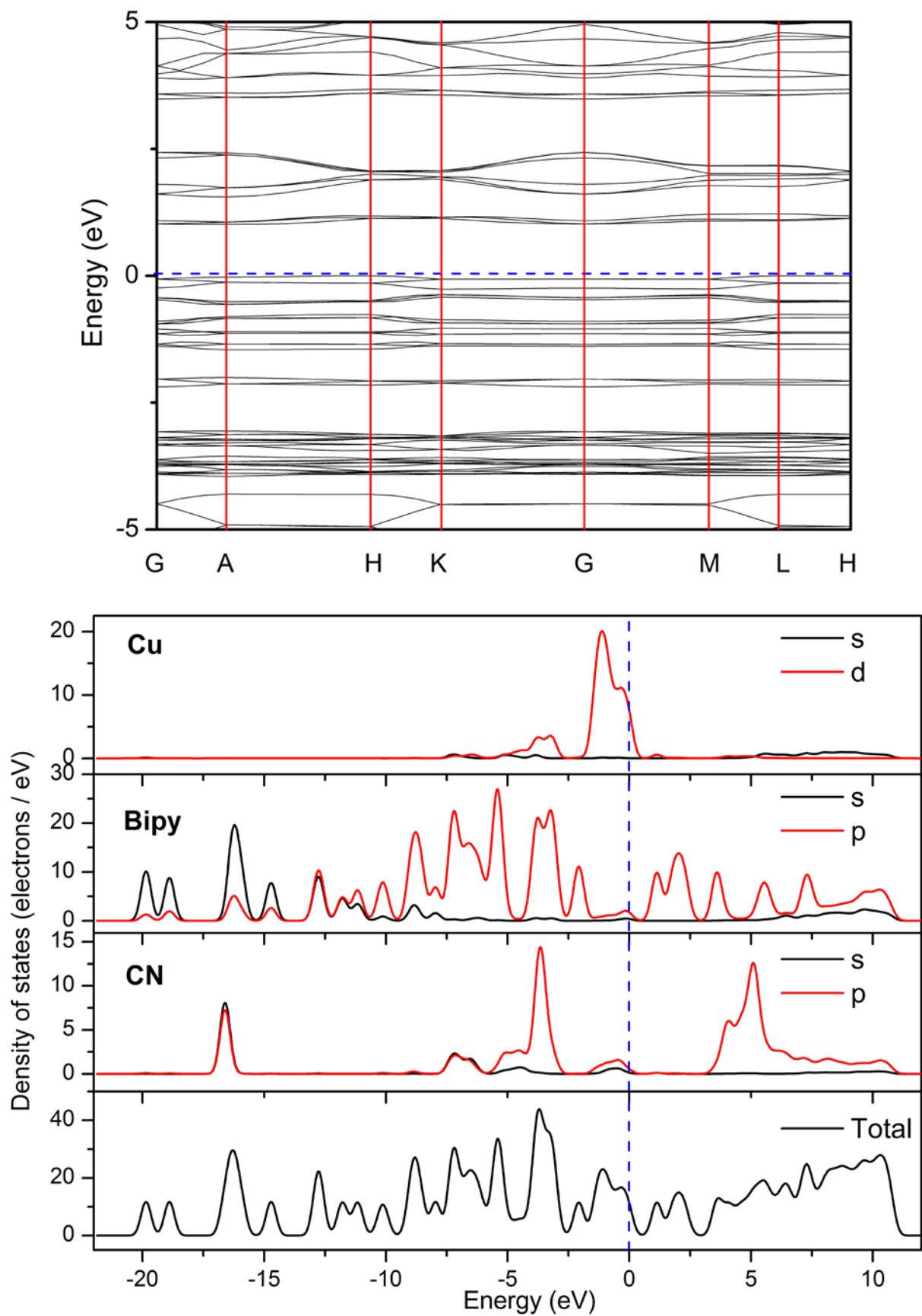


Figure S3. Energy band structures and density of states (total and partial) of **1**. Energy bands are shown only between -5.0 and 5.0 eV for clarity, and the Fermi level is set at 0 eV.

Computational descriptions/explanations

The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure S3, where the labeled k-points are present as G (0, 0, 0), A (0, 0, 0.5), H (2/3, 1/3, 0.5), K (2/3, 1/3, 0), M (0.5, 0, 0), and L (0.5, 0, 0.5). It is observed that the top of valence bands (VBs) appears to be relatively flat and the bottom of conduction bands (CBs) have small dispersion. The lowest energy (1.02 eV) of conduction bands (CBs) is localized at the G point, and the highest energy (0.00 eV) of VBs is localized at the H point, indicating compound **1** shows a semiconductor character with an indirect band gap of 1.02 eV. The bands can be assigned according to total and partial densities of states (DOS). The $C_{\text{bipy-2s}}$, $N_{\text{bipy-2s}}$, $C_{\text{cyanide-2s,2p}}$ and $N_{\text{cyanide-2s,2p}}$ states, mixing with small portion $C_{\text{bipy-2p}}$, $N_{\text{bipy-2p}}$ states, create the VBs localized at about -21.0 and -13.8 eV, while the $C_{\text{bipy-2p}}$, $N_{\text{bipy-2p}}$, mixing with small portion $C_{\text{bipy-2s}}$, $N_{\text{bipy-2s}}$, $C_{\text{bipy-2s,2p}}$, $N_{\text{bipy-2s,2p}}$ states, create the VBs localized at about -13.8 and -4.5 eV. The VBs between energy -4.5 eV and the Fermi level (0.0 eV) are mostly formed by Cu-3d state, $(\text{CN})_{\text{bipy-2p}}$, and $(\text{CN})_{\text{cyanide-2p}}$ states. The CBs between 1.02 and 2.86 eV are almost contribution from $(\text{CN})_{\text{bipy-2p}}$ states, while the CBs between 2.86 and 11.0 eV are mainly consist of the hybridizations of $(\text{CN})_{\text{bipy-2p}}$ and $(\text{CN})_{\text{cyanide-2p}}$ states. Furthermore, we have also calculated the atomic site and angular momentum projected DOS to elucidate the nature of the electronic band structures and chemical bonds. In the top of VBs, the angular momentum projected DOS is much lower for $(\text{CN})_{\text{bipy-2p}}$, and $(\text{CN})_{\text{cyanide-2p}}$ than Cu-3d states, showing that some electrons from $(\text{CN})_{\text{bipy-2p}}$, and $(\text{CN})_{\text{cyanide-2p}}$ transform into the VBs and take part in covalence interactions between C and Cu atoms, N and Cu atoms. This case tells us that the hybridization between Cu-3d and $C_{\text{bipy/cyanide-2p}}$, Cu-3d and $N_{\text{bipy/cyanide-2p}}$ states takes place and covalent bond character appears between Cu and C atoms, Cu and N atoms. Accordingly, the origin of the high-energy emission band at 598 nm of **1** may be mainly ascribe to ligand-to-ligand charge transfer (LLCT) where the electrons are transferred from the occupied π orbitals of 2, 2'-bipy ligands or cyanide groups ($(\text{CN})_{\text{bipy-2p}}$, $(\text{CN})_{\text{cyanide-2p}}$ states, VBs) to the unoccupied π^* orbital of 2, 2'-bipy ligands ($(\text{CN})_{\text{bipy-2p}}$ states, CBs), while the origin of the low-energy emission band at 650 nm of **1** may be mainly ascribe to metal-to-ligand charge transfer (MLCT) where the electrons are transferred from the copper (Cu-3d state, VBs) to the unoccupied π^* orbitals of 2, 2'-bipy ligand ($(\text{CN})_{\text{bipy-2p}}$ states, CBs).