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Two Halogeno(cyano)cuprates with Long-Lived and Strong Luminescence

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Solvothermal reactions of copper(I) cyanide with tetramethylammonium salts in anhydrous tetrahydrofuran (THF) lead to two novel halogeno(cyano)cuprates, namely, $[Me_4N][Cu_3(CN)_2Br_2]$ (**1**) with a 1-D ribbon motif and $[Me_4N]_2[Cu_4(CN)_5Cl]$ (**2**) with a 3-D nanoporous framework. In **1**, four Cu(I) ions are connected via two μ-Br and two μ_3-Br atoms into a neutral $[Cu_4Br_4]$ cluster, and such clusters are further double bridged by $[Cu(CN)_2]^{2-}$ linkers to form a 1-D ribbonlike chain. While in **2**, Cu(I) ions are connected via μ-CN and μ_3-CN ligands and μ-Cl atoms into a 2-D fluctuant sheet along the *a*–*c* plane, and these sheets are further linked by another kind of μ-CN ligand to form a 3-D nanoporous framework in whose channels reside $[Me_4N]^+$ cations. Results of optical and luminescent studies indicate that both two complexes are potential materials for semiconductors and long-lived highly luminescent materials.

Introduction

Transition metal cyanides[1] have attracted considerable interest, which can be explained, first, by the commercial importance for some of their solutions with the ability to extract precious metals from ores or to be used in precious metal-electroplating applications[2] and, second, by these compounds possessing potential applications as catalysts,[3] high-T_c molecular-based magnets,[4] inclusion compounds,[5] and composite inorganic−organic zeolitic materials.[6] The copper(I) cyanide system has been studied extensively over years,[7] but recent work has shown that there is still much deserving study needed for such systems.[8] For example, copper(I) cyanide has been employed as a precursor in the syntheses of ceramic superconductors,[9] as cyanocuprate reagents in synthetic organic chemistry,[10] and as substructures in synthesizing coordination polymers with special topology, especially in assembling zeolitic frameworks.[11]

Mixed halogeno(cyano)cuprates have attracted great interest because the known types of $[Cu(CN)X]^-$, $[Cu(CN)_2X]^{2-}$, and $[Cu(CN)_3X]^{3-}$ anions in solution were revealed to be

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long-lived and highly luminescent materials with abundant optical transitions,[12,13] in which the association of halide ions with copper cyanide species greatly enhances the lifetime and quantum yield of luminescence. Unfortunately, up to now the research of halogeno(cyano)cuprates luminescence was restricted in solution due to the difficulty of preparing their pure crystalline samples. The only known three halogeno(cyano)cuprates, $[Bu_4N][Cu(CN)X]$ (X = Br, I) with 1-D helical structures[8i] and $KCu_2(CN)_2Br\cdot H_2O$ with a 3-D open framework,[8l] have been reported without their luminescent properties. Herein we report the syntheses, crystal structures, and optical absorption spectra as well as the long-lived and efficient solid-state luminescent properties of the two novel types of halogeno(cyano)cuprates, namely, $[Me_4N][Cu_3(CN)_2Br_2]$ (**1**) with a 1-D ribbon motif and $[Me_4N]_2[Cu_4(CN)_5Cl]$ (**2**) with a 3-D nanoporous framework, in which the solid-state luminescent properties of the mixed halogeno(cyano)cuprates are investigated in detail for the first time.

Experimental Section

Materials and Instrumentation. All chemicals except THF solvent were obtained from commercial sources and used without further purification. THF was 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 disks in the range 4000−400 cm^{-1}. The FT-R spectra were obtained on a Nicolet Raman 950 spectrometer using KBr as diluter in the range 4000−100 cm^{-1}. Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 35 UV−vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectra using the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$,[14] where α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C/min under a nitrogen atmosphere.

Preparation of $[Me_4N][Cu_3(CN)_2Br_2]$ (1). A mixture of CuCN (81 mg, 0.9 mmol) and Me_4NBr (139 mg, 0.9 mmol) in 10 mL of dry and distilled THF was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 80 °C for 3 days and cooled to 30 °C at 2 °C h^{-1}. Pale yellow crystals of **1** were collected in ca. 60% yield (based on copper). Anal. Calcd for **1** ($C_6H_{12}N_3Br_2Cu_3$): C, 15.12; H, 2.54; N, 8.82. Found: C, 15.24; H, 2.68; N, 8.76. FT-IR (KBr, cm^{-1}): 3432 m, 2983 m, 2763 w, 2287 w, 2114 m, 1635 w, 1492 m, 1440 m, 1404 m, 1397 m, 1373 m, 1333 w, 1309 w, 1173 s, 1069 w, 1050 w, 1002 s, 896 m, 799 s, 472 w, 418 w. FT-R (KBr, cm^{-1}): ν(CN) 2115 (m).

Table 1. Crystal and Structure Refinement Data for **1** and **2**

param	**1**	**2**
formula	$C_6H_{12}Br_2Cu_3N_3$	$C_{13}H_{24}ClCu_4N_7$
M_r	476.63	568.00
cryst size (mm^3)	0.18 × 0.16 × 0.10	0.50 × 0.50 × 0.50
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a (Å)	8.407(3)	12.0576(8)
b (Å)	12.569(4)	17.807(1)
c (Å)	13.125(6)	9.7855(7)
β (deg)	111.579(3)	95.306(4)
V (Å^3)	1289.7(9)	2092.1(2)
D_{calc} (Mg m^{-3})	2.455	1.803
Z	4	4
F(000)	904	1136
abs coeff (mm^{-1})	11.065	4.149
reflcns collcd/unique (R_{int})	7915/2252 (0.0308)	6414/1837 (0.0225)
data/params/restraints	1855/127/0	6428/114/0
R^a	0.0594	0.0395
$R_w{}^b$	0.1743	0.1270
goodness-of-fit on F^2	1.000	1.001
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	1.503 and −2.184	0.914 and −0.574

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. ^{b} $R_w = \{[\Sigma(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$.

Preparation of $[Me_4N]_2[Cu_4(CN)_5Cl]$ (2). A mixture of CuCN (81 mg, 0.9 mmol) and Me_4NCl (99 mg, 0.9 mmol) in 10 mL of dry and distilled THF was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel containers under autogenous pressure and then heated at 120 °C for 3 days and cooled to 30 °C at 2 °C h^{-1}. Large orange crystals of **2** were obtained in ca. 75% yield (based on copper). Anal. Calcd for for **2** ($C_{13}H_{24}N_7ClCu_4$): C, 27.49; H, 4.62; N, 17.26. Found: C, 27.60; H, 4.65; N, 17.18. FT-IR (KBr, cm^{-1}): 3472 w, 3019 m, 2959 w, 2784 w, 2577 w, 2465 w, 2117 m, 2079 m, 1487 vs, 1404 s, 1286 w, 948 vs, 455 w. FT-R (KBr, cm^{-1}): ν(CN) 2115(m), 2087(m).

Single-Crystal Structure Determination. Single crystals of **1** and **2** were mounted on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 140 K. The intensity data sets were collected with the ω scan technique and reduced by CrystalClear software.[15] The structures were solved by the direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were located by difference Fourier maps and subjected to anisotropic refinement. Hydrogen atoms were added according to the theoretical models. All of the calculations were performed by the Siemens SHELXTL version 5 package of crystallographic software.[16] Crystallographic data and structural refinements for **1** and **2** are summarized in Table 1. More details on the crystallographic studies as well as atom displacement parameters are given as Supporting Information. Since the C and N atoms of the bridging cyanide groups cannot be distinguished crystallographically,[8i,17] assignments

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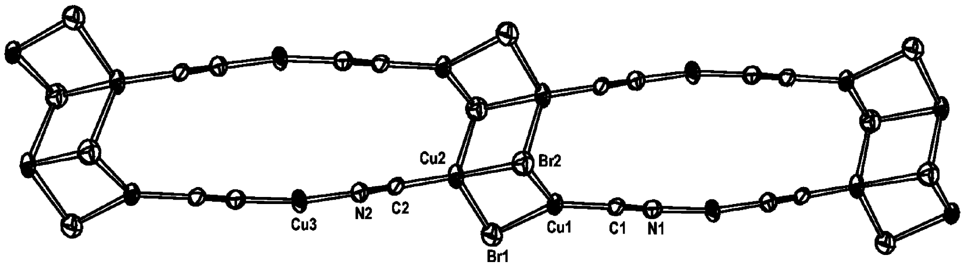

Figure 1. ORTEP representation of **1** with 50% thermal ellipsoids with the atom-labeling scheme.

based on the refinement of their anisotropic thermal parameters[18] have been made in the present complexes.

Results and Discussion

Synthetic Considerations. Two novel complexes with very different structures were obtained in similar reaction procedures except using the relatively subtle change of halogen anions. Reaction temperature does not play a decisive role in the formation of **1** and **2** although it has direct relation to the yields of the products. Complex **1** can be also obtained with a similar procedure under 120 °C in a lower yield. However, only the crystals of Me_4NX ($X =$ halogen) can be obtained when the reaction temperature decreases to 50 °C or lower. At the same time, a trace of water in the solvent would affect the reactions greatly. Lower yields of the targeted products would be achieved accompanied by green byproducts $[Me_4N]_2[CuX_4]$ ($X =$ halogen) if the THF solvent was used without further purification. Considering the above facts, the difference between the structures of **1** and **2** should be ascribed to the different coordination abilities of the halogen anions as well as their sizes.

Crystal Structure Descriptions of 1 and 2. Complex **1** features a 1-D ribbonlike chain in which there are three unique Cu(I) ions in the asymmetric unit (Figure 1). The three-coordinate Cu1 atom is in a distorted trigonal-planar coordination environment and coordinated by one μ-Br, one μ_3-Br, and one cyanide C atom. The four-coordinate Cu2 atom is tetrahedrally coordinated by one μ-Br, two μ_3-Br, and one cyanide C atom, while the two-coordinate Cu3 is approximately linearly connected by two cyanide N atoms to form a subunit of $[Cu(CN)_2]^-$ with the N−Cu−N bond angle of 168.6(1)°. The neutral tetracopper $[Cu_4Br_4]$ clusters with crystallographic inversion center, composed of Cu1, Cu2, μ-Br1, and μ_3-Br2 atoms to form chairlike conformations, are double bridged by $[Cu(CN)_2]^-$ subunits to form a 1-D ribbonlike chain extending along the *b* direction, which is different from the 1-D infinite helical $^\infty{}_1[-Cu^I(X)-CN-]$ chains with the terminal X anions possessing side-on fashion in the two known halogeno(cyano)cuprates.[8i] The Cu−N bond distances within the $[Cu(CN)_2]^-$ subunit varying from 1.840(3) to 1.861(3) Å are in good agreement with those in linear $-CN-Cu^I-CN-$ units [8j,19] although the Cu−N bond length is somewhat shorter than Cu−C bond length according to the C and N assignments based on their refinement of anisotropic thermal parameters. The Cu−μ-Br and Cu−μ_3-Br bond lengths in the $[Cu_4Br_4]$ cluster are in the range 2.3789(8)−2.4920(8) and 2.4227(8)−2.568(1) Å, respectively, which are comparable to those found in Cu_xBr_y clusters.[20] The ribbonlike chains juxtapose to form anionic layers along the *c* direction, between which the $[Me_4N]^+$ cations locate (Figure 2 and S1). Interestingly, two-coordinate, three-coordinate, and four-coordinate Cu(I) atoms are in coexistence in **1**, which is unprecedented according to the survey of the Cambridge Crystallographic Database.

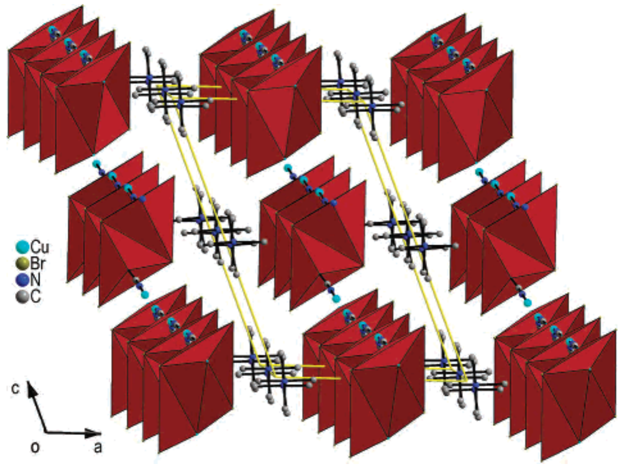

Figure 2. Ribbonlike chains in **1** juxtaposed to form anionic layers along the *c* direction, between which the $[Me_4N]^+$ cations are located. The $[Cu_4Br_4]$ clusters in the chains are represented as red polyhedra.

The structure of **2** exhibits a 3-D nanoporous framework in which there are two unique Cu(I) ions in the asymmetric unit (Figure 3). The Cu1 atom is in a tetrahedral environment consisting of two μ_3-cyanide C3 atoms, one μ-cyanide N1 atom, and one symmetry-related disordered μ-cyanide C(N)2 atom. The Cu2 atom is in a center of approximate trigonal environment and coordinated by one μ-cyanide C1 atom, one μ_3-cyanide N3 atom, and one μ-Cl atom. As shown in Figure 4, the $[Cu1]_2$ dimers are double-bridged by [CN−Cu2−CN] units to form 1-D double-stranded $^\infty_1[Cu_4(CN)_4]$ ribbons extending along the [101] direction, resulting in the formation of fused 12-membered $[Cu_4(CN)_4]$ rings and 4-membered $[Cu_2C_2]$ rings by sharing the Cu1−C3 edges, and the ribbons are further bridged by the μ-Cl atoms on the both sides

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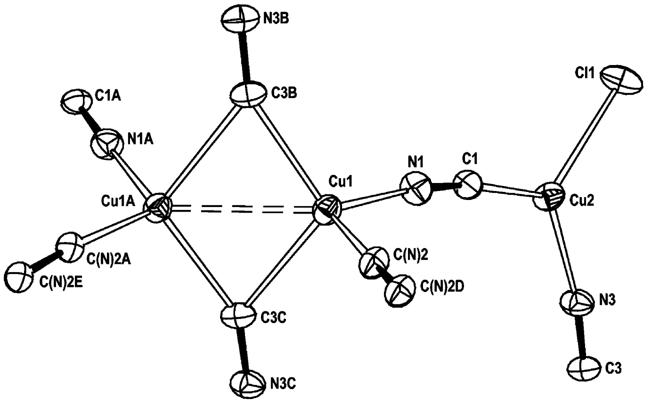

Figure 3. ORTEP representation of **2** with 30% thermal ellipsoids with the atom-labeling scheme. Symmetry codes: (A) $-x, y, 3/2 - z$; (B) $1/2 + x, -1/2 - y, 1/2 + z$; (C) $-1/2 - x, -1/2 - y, 1 - z$; (D) $-x, -1 - y, 1 - z$.; (E) $x, -1 - y, 1/2 + z$.

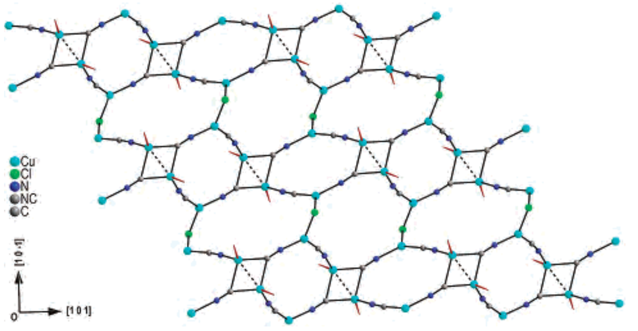

Figure 4. View of 2D fluctuant sheet in **2** containing fused $[Cu_4(CN)_4]$ rings and $[Cu_2N_2]$ rings. The copper−copper interactions are represented as dashed lines, and the red lines represent the symmetry-related disordered cyanide groups bridging the sheets to form a 3D framework.

through the Cu2−Cl1 bonds to form a 2-D wavelike layer along the $[10\bar{1}]$ direction. Interestingly, the Cu···Cu separation in the $[Cu1]_2$ dimers is 2.4853(4) Å, which is much shorter than the sum of van der Waals radii for copper (2.8 Å),[21] suggesting significant copper−copper interactions. These wavelike layers are further linked by symmetry-related disordered cyanide groups along the *b*-axis to form a 3-D nanoporous structure with two kinds of hexagonal channels possessing the effective size of ca. 3×3 Å^2 along the *a*-axis and *b*-axis, respectively (Figure 5 and S2), and the $[Me_4N]^+$ cations are located in the channels along the *a*-axis while the channels along the *b*-axis are almost vacant. It should be noted that the Cu1−N1 bond length in **2** is longer than Cu2−C1 bond length according to the C and N assignments based on their refinement of anisotropic thermal parameters, which is opposed to the model in **1**.

Optical Spectroscopy. Optical diffuse reflectance spectra of **1** and **2** reveal the presence of the optical gaps of 2.43 and 1.96 eV (Figure S3), respectively, suggesting that the two materials are semiconductors. Furthermore, these values are consistent with the color of their crystals. FT-IR spectra exhibit sharp middle bands at 2114 cm^{-1} for **1** and 2117 and 2079 cm^{-1} for **2**, and FT-R spectrum reveal middle bands at 2115 cm^{-1} for **1** and 2115 and 2087 cm^{-1} for **2**, which are comparable to stretching absorption of free CN$^-$ in solution (2080 cm^{-1}) and can be ascribed to that of cyanide group in the complexes. Generally, the ν(C≡N) of a M−C≡N−M group red-shifts if the μ-cyanide group further bridges another metal ion through its C atom into a M_2−C≡N−M group because the coordination of the third metal center will decrease the bonding electrons of the C≡N to weaken the C≡N triple bond. Accordingly, the bands at 2115 cm^{-1} can be assigned to the stretching absorption of the μ-cyanide groups in the two complexes, while the band at 2087 cm^{-1} can be ascribed to the stretching absorption of the μ_3-cyanide groups in **2**.

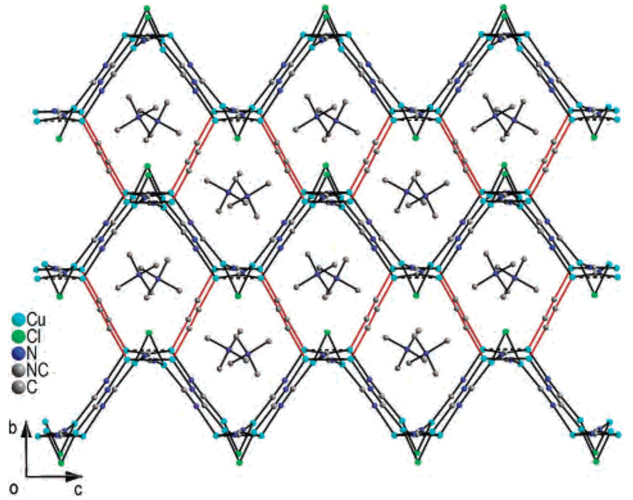

Figure 5. 3D nanoporous framework of **2** constructed from 2D fluctuant sheets linked by symmetry-related disordered cyanide groups drawn in red with the $[Me_4N]^+$ cations being located in the channels along the *a*-axis.

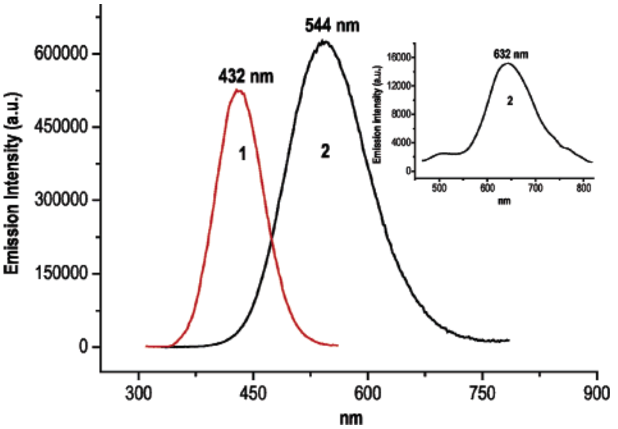

Figure 6. Solid-state electronic emission spectra of **1** (λ_{ex} = 290 nm) and **2** (λ_{ex} = 312 nm and λ_{ex} = 434 nm (inset)) at room temperature.

Luminescent Properties. As shown in Figure 6, complex **1** displays a very strong and sharp blue fluorescent emission band in the solid state at 432 nm upon photoexcitation at 290 nm, while complex **2** exhibits a very strong green emission band at 544 nm upon photoexcitation at 312 nm and a relatively weak orange emission band at 632 nm upon photoexcitation at 434 nm, suggesting both two complexes are efficient luminescent materials. The lifetime of the emission band for **1** was measure to be 31 μs, while the lifetimes of the emission bands at 544 nm and at 632 nm for **2** were 21 μs and 17.9 ms, respectively (Figure S10). The emission peaks at 432 nm for **1** and at 544 nm for **2**

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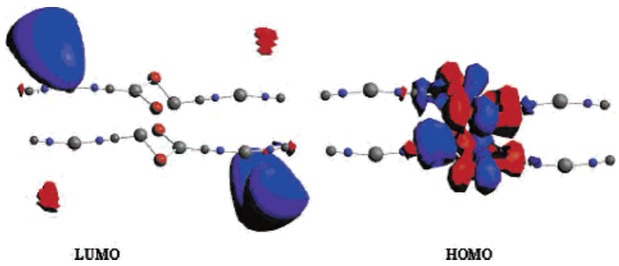

Figure 7. Electron-density distribution of the lowest unoccupied and highest occupied frontier orbitals calculated for **1**.

probably may be assigned to metal-to-ligand charge transfer (MLCT) where the electron is transferred from the copper(I) center to the unoccupied π^* orbital of cyanide ligand according to the literature,[13,22] while the weak band at 632 nm with a long lifetime for **2** reveals phosphorescence characteristics and probably may be ascribed to metal-centered transitions of the type $3d^{10} \rightarrow 3d^9 4s$ and $3d^{10} \rightarrow 3d^9 4p$ on the copper(I) center[22a,23] strongly modified by copper−copper interactions within the $[Cu(1)]_2$ dimers. Time-dependent DFT calculations[24] using the B3LYP functional were performed on the two complexes with their ground-state geometries adapted from the truncated X-ray data. The results indicate that the lowest singlet excitation for **1** is dominated by the HOMO → LUMO transition, in which HOMO is composed of d orbitals of Cu(I) and lone pair orbitals of the bromide atoms and LUMO mainly consists of π^* orbitals of cyanide groups (Figure 7). While for **2**, the lowest singlet excitation is dominated by the combination of HOMO → LUMO and HOMO → LUMO+1 transitions, in which HOMO is mainly composed of d orbitals of Cu(I) and both LUMO and LUMO+1 mainly consist of π^* orbitals of cyanide groups (Figure 8). As a result, the origin of the fluorescence at 432 nm for **1** and at 544 nm for **2** can be ascribed to MLCT transitions. The calculated lifetimes for lowest singlet excitation using a rough function $\tau = 1.499/(fE^2)$ (f, oscillator strength; E, excitation energy) are revealed to be 13 μs for **1** and 0.7 μs for **2**, which are in agreement with the experimental values. More accurate data could be obtained with more sophisticated theoretical approaches to gain detailed insight into the energy correlation among various electronic states for nontruncated structures.

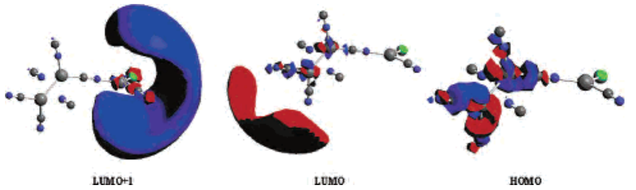

Figure 8. Electron-density distribution of the lowest two unoccupied and highest occupied frontier orbitals calculated for **2**.

TGA Study. The thermogravimetric analysis (TGA) study shows that the two complexes decompose at decomposition point T_{onset} of 237.4 °C for **1** and 292.5 °C for **2** (Figure S4 and S5), indicating the present compounds are stable as luminescent materials. The detailed decomposition mechanisms of the two complexes are too complex to explain at present.

Conclusion

In summary, the investigation of the reaction conditions demonstrates that the relatively subtle change in halogen anions in the similar reaction procedures results in two significantly different halogeno(cyano)cuprates, which exhibit long-lived and strong luminescence with abundant optical transitions supported by the theoretical calculations. Considering the excellent luminescent properties, good thermal stabilities, and the simple preparation methods, both complexes possess tremendous potential applications as efficient luminescent materials. Furthermore, complex **1** is an unprecedented 1-D ribbonlike halogeno(cyano)cuprate with the coexistence of two-coordinate, three-coordinate, and four-coordinate Cu(I) atoms, while complex **2** is the first 3-D halogeno(cyano)cuprate bearing two kinds of intersecting nanosized channels.

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Supporting Information Available: Theoretical approach methodology, optical absorption spectra, TGA spectra, FT-IR spectra, FT-R spectra, and X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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