

# On the Biexponential Decay of the Photoluminescence of the Two Crystallographically-Independent Molecules in Crystals of $[\text{Cu}(\text{I})(\text{phen})(\text{PPh}_3)_2][\text{BF}_4]$

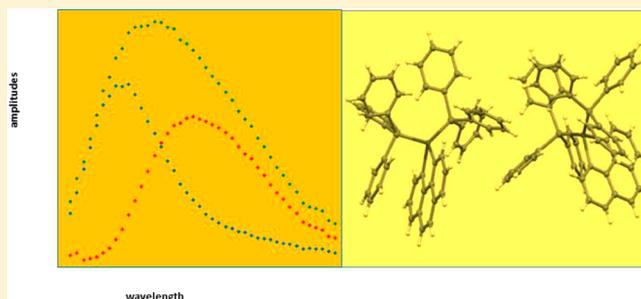
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## S Supporting Information

**ABSTRACT:**  $[\text{Cu}(\text{I})(\text{phen})(\text{PPh}_3)_2][\text{BF}_4]$  crystallizes with two nonsymmetry-related molecules in the asymmetric unit. Synchrotron time-resolved X-ray diffraction experiments have shown that the two independent molecules distort differently on MLCT excitation. The luminescence decay of the crystals is biexponential with two different Stokes-shifts, the more rapid decay corresponding to the shorter wavelength emission. Its amplitude diminishes rapidly with an increase in temperature, indicating that this emission is not due to a thermal activation to a higher state. The double emission is attributed to the presence of two independent molecules with drastically different packing environments. It is concluded that the solid-state environment must be analyzed whenever photochemical properties of molecular solids are reported.

**SECTION:** Spectroscopy, Photochemistry, and Excited States



It is well-known that photochemical processes involving charge separation and recombination are generally accompanied by geometry changes in the donor–acceptor system. In pioneering studies, McMillan and co-workers showed that intramolecular interligand steric repulsion can strongly affect the lifetime of the luminescence following metal-to-ligand charge transfer (MLCT).<sup>1,2</sup> The effect was shown to be pronounced for solutions of 2,9 alkyl substituted Cu(I) phenanthroline complexes. It can be understood in terms of the energy-gap law, which states that a larger energy gap between the photoinduced excited state and the ground state leads to longer lifetimes because of the reduction of nonradiative relaxation processes involving the vibrational energy levels.<sup>3,4</sup> The energy gap theory is strongly supported by subsequent direct experimental observations on the decay of charge-transfer excited states of a solutions of substituted Os complexes,<sup>5</sup> and of 2,9 substituted Cu(I) phenanthrolines.<sup>4</sup> Evidence is now accumulating that a similar effect is due to intermolecular interactions induced by the constraining effect of the molecular environment, leading to crystal-environment dependent photochemical properties. Hoshino and co-workers described the difference in luminescence properties of two polymorphs of  $[\text{AuCl}(\text{PPh}_3)_2]$  with blue and green emission, respectively.<sup>6</sup> More recently, Su and co-workers attributed a luminescence enhancement of  $[\text{Cu}(\text{N}-\text{N})(\text{P}-\text{P})]\text{BF}_4$  complexes in the solid state to  $\pi$ - $\pi$  stacking, although no crystallographic evidence was presented.<sup>7</sup> A further example is our recent study,<sup>8</sup> which revealed microsecond-lifetime emission on MLCT of the Cu(I) phenanthroline complex lacking 2,9-substitution in crystals, discussed in the current

paper. Such emission had not been observed in earlier work on solutions.<sup>4</sup>

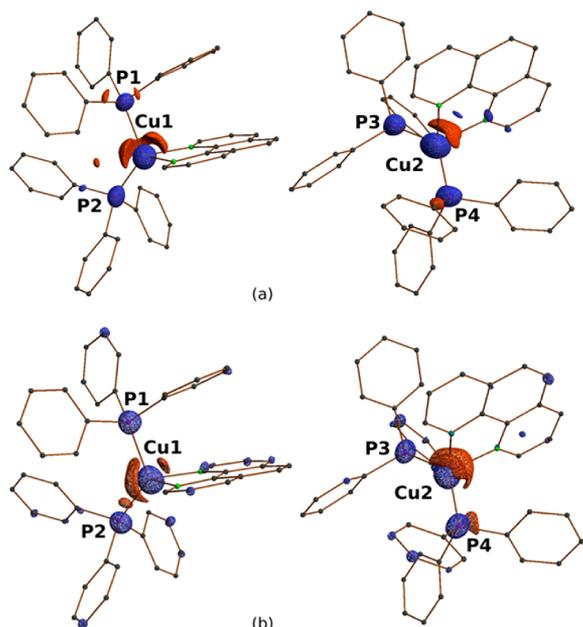
We here present detailed evidence based on time-resolved crystallographic studies of the molecular changes on photoexcitation of the complex, (1,10-phenanthroline-*N,N'*) bis-(triphenylphosphine) copper(I) tetrafluoroborate,  $[\text{Cu}(\text{I})(\text{phen})(\text{PPh}_3)_2][\text{BF}_4]$ . The complex crystallizes with two molecules in the asymmetric unit, one of which, with Cu(1) at its center, shows  $\pi$ -stacking of adjacent molecules, whereas the second (with Cu(2)) is much less constrained.<sup>8</sup> Photo-difference maps,<sup>9</sup> synthesized from the difference between the light-on and light-off structure factors at both 90 and 180K, show very different distortions of the two molecules as illustrated in Figure 1. As tabulated in ref 8, in both cases, the molecules flatten and the distances from the Cu atom to the phenanthroline nitrogen atoms shorten, but the changes are significantly smaller in the constrained Cu(1) complex. A third experiment performed at room temperature was inconclusive as the number of reflections that could be observed was severely limited by thermal motion.

The Cu(2) moves toward the phenanthroline, according to the time-resolved crystallographic experiments and evident in Figure 1.<sup>8</sup> This is in agreement with the energy-gap law as the less restricted configuration is predicted to correspond to a

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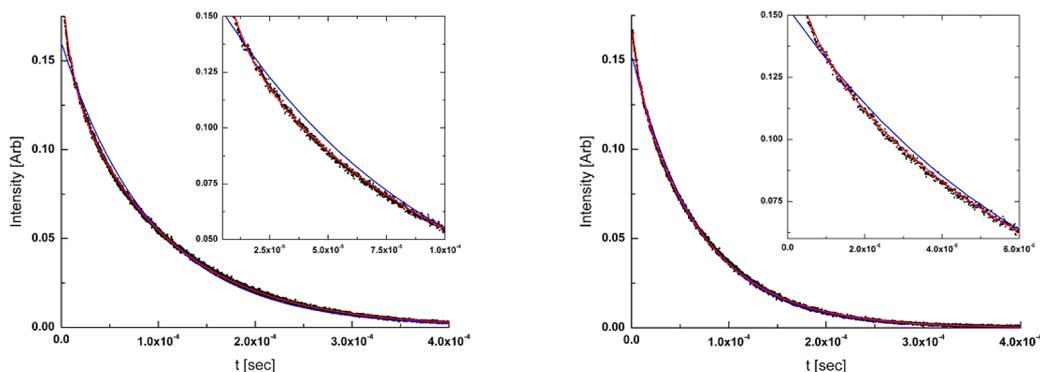
**Figure 1.** Photodifference maps with isosurfaces of  $\pm 0.25 \text{ e}\text{\AA}^{-3}$  (red, positive; blue, negative) at 180K (a) and 90K (b). Cu(1) and Cu(2) are on the right and the left side of each of the graphs, respectively (from ref 8). Calculated with XDGRAPH of the XD program set.<sup>10</sup>

lower energy of the excited state and will thus have a more rapid relaxation of the excited state.<sup>3</sup>

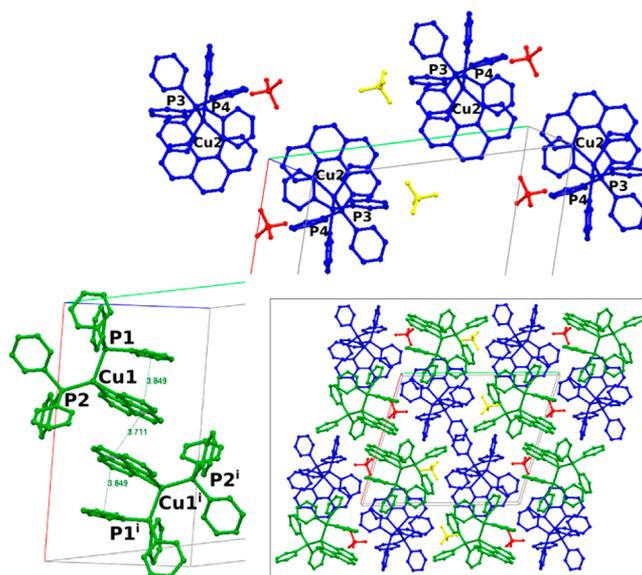
Additional information is obtained by spectroscopic analysis of the crystals. Proper fitting of their time-resolved luminescence requires a biexponential function, as shown in Figure 2.

Comparison with the photodifference maps at 90 and 180 K suggests that the faster decay originates from the Cu(2) complex (B), which is less constrained in the crystal. The Cu(2) complex shows a larger distortion, and is less constrained than the Cu(1) molecule (A), which is  $\pi$ -stacked as is evident in the molecular packing diagrams shown in Figure 3.<sup>8</sup>

Measurements of the emission as a function of wavelength and temperature are shown in Figure 4. The faster decay is represented by the blue curve in the figures. It shows a stronger temperature dependence and is almost absent at room temperature.

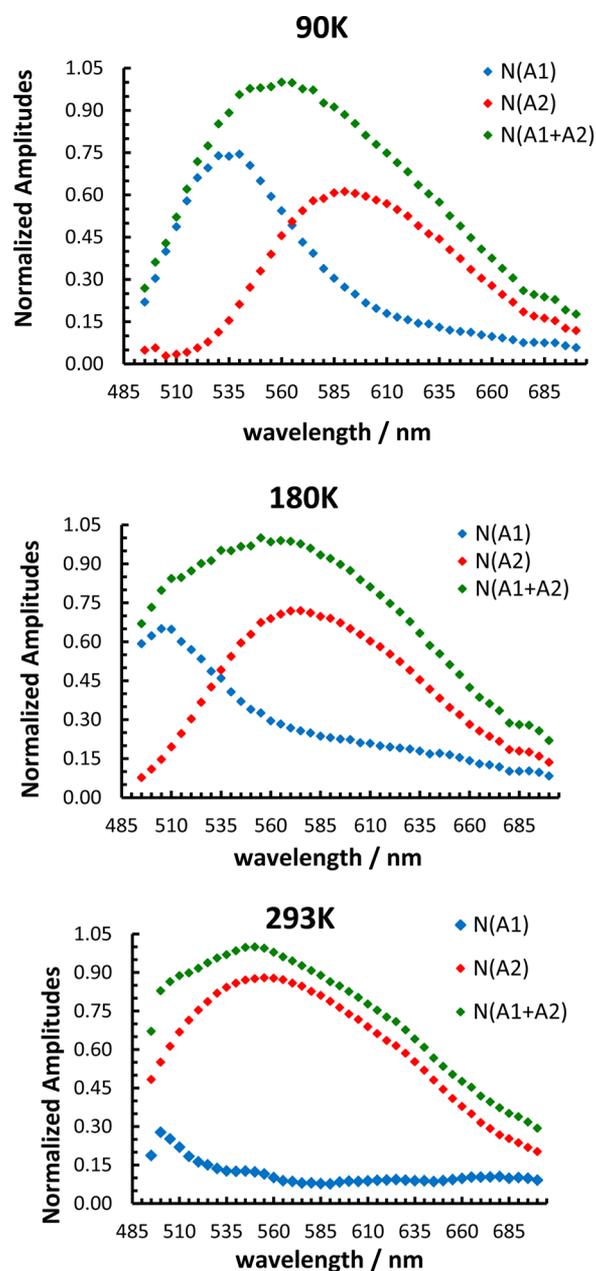


**Figure 2.** Time-dependence of the emission decay of (2) at 90 K (left) and 180 K (right). The blue and red lines represent the single exponential and biexponential fits to the data points (black), respectively. The insets show the region with the largest differences between the two fits. Lifetimes are 10 and 102  $\mu\text{s}$  at 90 K and 8 and 72  $\mu\text{s}$  at 180 K (from ref 8).  $\lambda(\text{excitation}) = 366 \text{ nm}$ ;  $\lambda(\text{emission}) = 595 \text{ nm}$  (90 K), 585 nm (180 K).



**Figure 3.** Comparison of the crystal-packing of the two independent molecules in the cell: (top in blue) packing of molecules B; (lower left in green)  $\pi$ -stacking of molecules A; (lower right) combined packing of all molecules in the crystal.<sup>8</sup>

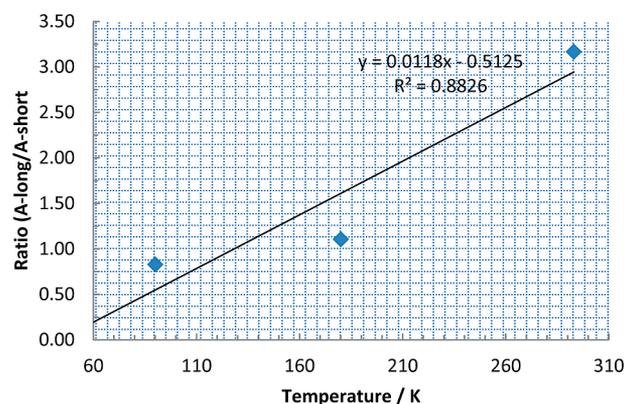
However, the measurements also show that the faster decay occurs with an emission at shorter wavelength, i.e., shows a smaller Stokes-shift, which corresponds to a larger triplet-energy. This observation appears to violate the energy gap law according to which a larger band gap corresponds to a longer lifetime.<sup>3</sup> An alternative explanation would be that the shorter lifetime corresponds to thermally activated delayed fluorescence from the  $S^1$  singlet state, which would not be forbidden as no spin-flip occurs and would correspond to a larger energy difference,  $S^1$  being higher in energy than  $T^1$ .<sup>11,12</sup> However, in that case, the short lifetime emission would increase with temperature, which is not the case (Figure 5), contradicting this alternative explanation. A 2-fold emission has been reported for luminescence of Cu(I)-substituted-phenanthroline complexes in a rigid matrix, but in those cases the second emission has a lifetime of milliseconds and was attributed to intraligand  $\pi$ - $\pi^*$  excitation.<sup>13,14</sup> For the present case, such an explanation is also not compatible with the shortening of the observed Cu-N distances on excitation for both complexes.



**Figure 4.** Wavelength dependence of the emission at three different temperatures. Green: total emission; blue: short-lifetime emission; red: long-lifetime emission.

The temperature dependence of the emission ratio (Figure 5) may be attributed to temperature-dependent intermolecular energy transfer from complex B to complex A. Such a matrix effect would contribute to shortening of the observed lifetime of B.

Information on the energy levels and the singlet–triplet energy gap of the two crystallographically independent molecules in the crystal can be obtained with QMMM calculations on the triplet and singlet states of the two complexes in the crystal environment.<sup>15</sup> Since the Cu(1) complex is  $\pi$ -stacked, it was treated as a dimer in the calculations. There are no strong interactions for the more loosely packed Cu(2) complex (Figure 3). The B3LYP-6-31G(d) results are shown in Table 1.



**Figure 5.** The ratio of the long and short emission amplitudes at the wavelength-maxima of each of the emissions at three different temperatures.

**Table 1.** Calculated Triplet Singlet Energy Gaps (QMMM-UFF Force Field, B3LYP/6-31G(d))

	isolated molecule	QMMM dimer Cu(1) (A)	QMMM monomer Cu(2) (B)	QMMM $\Delta$ GS (H) dimer/2-monomer
excited triplet (H)	-4284.3745	-8568.7366 (-4284.3683/ molec)	-4284.3529	-0.0154
ground state (H)	-4284.4450	-8568.8114 (-4284.4072/ molec.)	-4284.4315	0.0258
$\Delta$ (H) (ES-GS)	0.0705	0.0748	0.0786	-0.00412
$\Delta$ (eV)	1.9184	2.0354	2.1388	
$\lambda$ (nm)	646	609	580	$\Delta\lambda = 29$
experimental (crystal) (90K)		590	535	$\Delta\lambda = 55$

The QMMM results indicate that the triplet/singlet energy difference of the  $\pi$ -stacked Cu(1) complexes is smaller than that of Cu(2) complex by an amount in qualitative agreement with the observed bathochromic (red) shift of the longer-lifetime emission of former complex. This is in agreement with the assignment of the fast and slow emission decays. However, the observations and the calculations do not agree with the energy gap law, which would predict a longer lifetime for the state with the larger energy gap.<sup>3</sup>

A possible explanation for this discrepancy is related to the differences in geometry and atomic displacement parameters between the ground state structures of the two complexes. As summarized for the two copper atoms in Tables 2 and 3, complex 2 is significantly contracted, and its Cu atom has

**Table 2.** Cu Coordination Distances ( $\text{\AA}$ , 90 K) for the Two Independent Molecules in Crystals of  $[\text{Cu}(\text{I})(\text{phen})(\text{PPh}_3)_2][\text{BF}_4]$  (Ref 8)

CuN		CuP	
Complex 1			
2.074	2.132	2.241	2.292
Complex 2			
2.069	2.073	2.229	2.234
$\Delta$			
0.005	0.059	0.012	0.058

**Table 3. Principal Elements of the Cu Atomic Displacement Tensor ( $\text{\AA}^2$ , 90 K) of the Two Independent Molecules in Crystals of  $[\text{Cu}(\text{I})(\text{phen})(\text{PPh}_3)_2][\text{BF}_4]$  (Ref 8)**

$A_{11}$	$A_{22}$	$A_{33}$
	Complex 1	
0.0130	0.0131	0.0155
	Complex 2	
0.0123	0.0113	0.0135
	$\Delta$	
0.0007	0.0018	0.0020

smaller observed thermal displacement parameters, thus affecting the vibronic energy levels. The analyses at 180 K and 90 K are in full agreement (Tables S1 and S2). The two complexes are not identical, which would affect the interpretation in terms of the energy gap law.

We conclude that the solid-state environment of luminescent molecules must be analyzed whenever photophysical properties of solids are reported. Packing forces in the crystals significantly reduce distortions on excitation and thus affect photochemical properties, as demonstrated by the observed phosphorescence of a Cu(I) phenanthroline without 2.9 substitution, contrary to earlier experience, and by the anomalous relation between the emission lifetime and the Stokes-shift. The strong decrease of the emission of the Cu(2) (B) complex with increasing temperature may be attributed to energy transfer from complex B to A. The broadening of the luminescence due to the presence of two nonidentical emitters, evident in Figure 4, may have technical applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

Cu coordination distances for the two independent molecules in the crystals and principal components of the Cu atomic displacement parameters (180K). This material is available free of charge via the Internet <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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