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Temperature-dependent Emission of Copper(I) Phenanthroline Complexes with Bulky Substituents: Estimation of an Energy Gap between the Singlet and Triplet MLCT States

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Temperature dependence of emission from bis(2,9-di-*tert*-butyl-1,10-phenanthroline)copper(I) ($[Cu(dtbp)_2]^+$) as well as several other copper(I) bis(phenanthroline) complexes was measured between 190 and 300 K. An analysis based on a Boltzmann distribution model gives an energy gap between ^{1}MLCT and ^{3}MLCT excited states as $790\,cm^{-1}$ for $[Cu(dtbp)_2]SbF_6$. The contribution of the delayed fluorescence largely depends on the ligand substituents.

Copper(I) bis(diimine) complexes have been of increasing interest not only as powerful candidates for functional materials in utilizing solar energy but also because of *flattening* distortion in excited states.[1] It has been well known that copper(I) bis(phenanthroline) complexes exhibit visible emission from the metal-to-ligand charge-transfer (MLCT) excited states, where copper(II) ion prefers more planer structures due to d^9 electronic configuration. Their emission properties extremely depend on substituents of the ligands, exhibiting complicated temperature dependence.[2–4] For bis(2,9-dimethyl-1,10-phenanthroline)copper(I) ($[Cu(dmp)_2]^+$), steady-state emission at ambient temperatures was found to be mainly delayed fluorescence from ^{1}MLCT state.[4] On the other hand, femtosecond spectroscopy revealed structural change dynamics in the MLCT excited state for $[Cu(dmp)_2]^+$.[5]

Complicated temperature-dependent emission behaviors in copper bis(phenanthroline)s with various substituents are not fully understood since both the conformational change and delayed fluorescence can contribute. It is noted that even an energy gap between ^{1}MLCT and ^{3}MLCT states has not been determined experimentally. More recently, Burstyn et al. synthesized $[Cu(dtbp)_2]BF_4$, in which two phenanthroline ligands are almost perpendicular to each other.[6] Large, bulky substituents at 2,9-positions of the dtbp ligand are expected to suppress flattening distortion from D_{2d} structure toward a D_2 structure. In this study, we report temperature dependence of emission spectra in a series of copper bis(phenanthroline) complexes, in which various extents of distortion are expected. Based on analysis of the data, we estimate an energy gap between ^{1}MLCT and ^{3}MLCT states for $[Cu(dtbp)_2]^+$ and systematically discuss contribution of delayed fluorescence as well as distortion in the excited state in this class of compounds.

Copper(I) bis(phenanthroline) derivatives were prepared in accordance with the literature.[6,7] Compounds were identified by ^{1}H NMR, mass spectroscopy, and elemental analysis.[8] Temperature of the sample solutions was controlled by an Oxford cryostat DN1704. Samples were sealed in quartz cuvettes under vacuum, and CH_2Cl_2 used as solvent was distilled over CaH_2 just before use. Emission spectra were corrected by using standard solutions of *N*,*N*-dimethylamino-*m*-nitrobenzene and 4-dimethylamino-4′-nitrostilbene.[9]

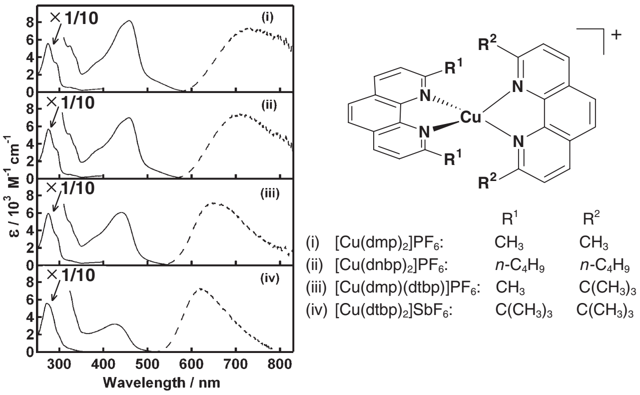

Figure 1. Absorption (solid line) and emission (dashed line) spectra in dichloromethane.

Figure 1 shows absorption and emission spectra of four copper(I) bis(phenanthroline) complexes in CH_2Cl_2 at room temperature. While the absorption bands in the UV region do not much depend on the compounds, those in the visible region largely depend on the phenanthroline ligands. The UV absorption band is due to (π,π^*) transition in the ligand whereas the visible absorption is ascribed to MLCT transition. For $[Cu(dtbp)_2]^+$, the absorption intensity in the visible region is considerably weak, compared with that of $[Cu(dmp)_2]^+$. This phenomenon is consistent with the literature.[6] In addition, the excitation spectrum of $[Cu(dtbp)_2]^+$ at MLCT emission band supports the absorption spectrum over the ultraviolet and visible region. As the substituents become bulky, the MLCT bands decrease in their intensities and shift to blue.

Similarly, emission spectra are shifted to blue as the substituents become bulky. Emission lifetimes at 295 K are 80 ns, 140 ns, 770 ns and 3.2 μs, for $[Cu(dmp)_2]^+$, $[Cu(dnbp)_2]^+$, $[Cu(dmp)(dtbp)]^+$, and $[Cu(dtbp)_2]^+$, respectively. These values are coincident with the literature.[6] Emission intensity becomes larger as the substituents are larger. The quantum yield of $[Cu(dtbp)_2]^+$ was found to be 0.06. All these data suggest that as the substituents become bulky, distortion in the excited states is smaller.

Figure 2a shows emission temperature dependence for the four compounds at 190–300 K. In the figure, emission intensities were corrected taking account of absorbance changes mainly due to temperature dependence of the volume. With decreasing temperature, emission intensities decrease and maxima shift to red in all compounds. This supports that the emission at ambient

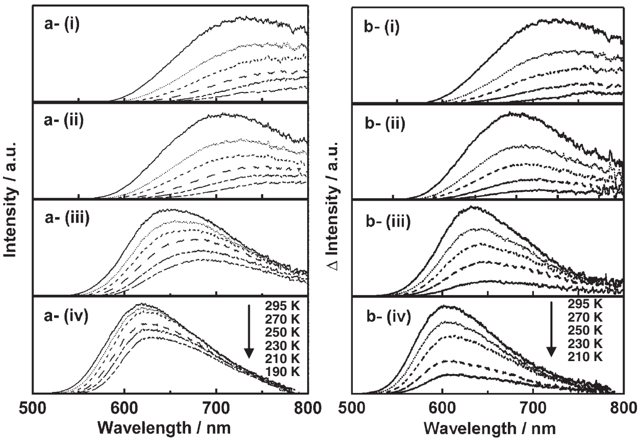

Figure 2. a) Temperature dependence of emission spectra and b) difference spectra (see text) for i) $[Cu(dmp)_2]^+$, ii) $[Cu(dnbp)_2]^+$, iii) $[Cu(dmp)(dtbp)]^+$, iv) $[Cu(dtbp)_2]^+$ (corrected).

temperature involves delayed fluorescence as indicated in the literature.[2,4] However, the extents of the red shift and intensity decrease largely depend on the substituents.[3] The compounds with more bulky substituents show less change in terms of both intensity and red shift. In contrast, lifetimes do not show remarkable temperature dependence between 300 and 190 K.

In order to discuss contribution of delayed fluorescence, difference spectra were made by subtracting the corresponding spectrum at 190 K from those measured at various temperatures in each compound. The results are shown in Figure 2b. While temperature dependence of the maxima of the difference spectra largely depends on the substituents, it should be noted that $[Cu(dtbp)_2]^+$ does not show a significant shift in the difference spectra at 210–300 K. This observation indicates that the observed emission spectra for $[Cu(dtbp)_2]^+$ are just a superposition of the same two components. The two components are highly likely ^{1}MLCT and ^{3}MLCT emission, of which profiles are basically temperature-independent between 300 and 190 K.

Figure 3 shows a semilogarithmic plot of intensity of the difference emission spectrum of $[Cu(dtbp)_2]^+$ versus inverse of temperature. There can be seen a good correlation between the intensity and temperature,

$$I_{(T)} = I_0 \exp\left(-\frac{\Delta E}{k_{\mathrm{B}} T}\right) \qquad (1)$$

Assuming a simple Boltzmann distribution model in which ^{1}MLCT emission is observed as a result of thermal population from ^{3}MLCT state, an energy gap between ^{1}MLCT and ^{3}MLCT states was estimated as 790 cm^{-1}. Here, we assumed that the absorption coefficient of $[Cu(dtbp)_2]^+$ does not change between 190–290 K although concentration changes due to temperature dependence of the volume were took into account.

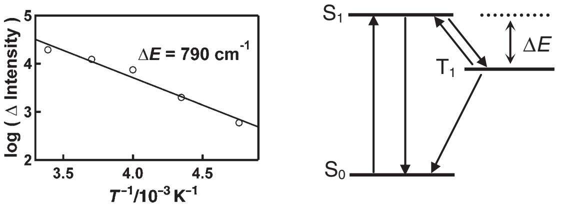

Figure 3. Semilogarithmic plot of emission intensity versus inverse of temperature for $[Cu(dtbp)_2]^+$.

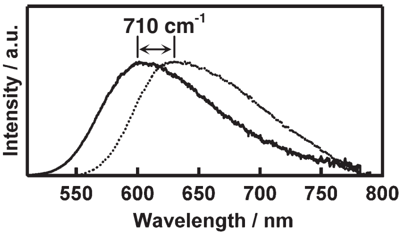

Figure 4. Comparison of the emission spectrum at 190 K (dotted line) emission and difference spectrum at 295 K from 190 K (solid line) for $[Cu(dtbp)_2]^+$.

Figure 4 compares emission spectrum at 190 K and the difference spectrum at 295 K. As can be seen from the figure, an energy difference of the maxima of the two spectra is 710 cm^{-1}. This value agrees well with the energy gap obtained by the above analysis. The fact that the analysis of temperature dependence of the emission intensities and the shifts of emission spectra give much the same values leads to the conclusion that emission of $[Cu(dtbp)_2]^+$ at 190–300 K is a superposition of ^{3}MLCT emission (dotted line in Figure 4) and delayed fluorescence (solid line in Figure 4) from ^{1}MLCT, which should be present at 700–800 cm^{-1} in the upper ^{3}MLCT state. It is noted that thermal equilibrium will be perfectly established with an energy gap of 700–800 cm^{-1} and the lifetime of ca. 3 µs, if we can assume an ISC rate from ^{1}MLCT to ^{3}MLCT states as several ps–several tenth ps.[4,5a] In such situation, contribution of the delayed fluorescence at 190 K is negligibly small.

The obtained value of 700–800 cm^{-1} for an energy gap between ^{1}MLCT and ^{3}MLCT states of $[Cu(dtbp)_2]^+$ is much smaller than that estimated for $[Cu(dmp)_2]^+$, i.e., 1800–2000 cm^{-1}, by theoretical calculation[4] and experimentally.[2] This difference between $[Cu(dtbp)_2]^+$ and $[Cu(dmp)_2]^+$ may come from a difference of molecular structures in the excited state; the dihedral angle between the two phenanthroline ligands in $[Cu(dtbp)_2]^+$ must be closer to 90 degree while that of $[Cu(dmp)_2]^+$ is much smaller in the excited states. If we assumed emission of $[Cu(dtbp)_2]^+$ at 190 K involved delayed fluorescence, an energy gap should be estimated as smaller than 790 cm^{-1}. Thus, the much smaller value in $[Cu(dtbp)_2]^+$ compared with $[Cu(dmp)_2]^+$ is never due to less estimation of contribution of delayed fluorescence at 190 K. Again, the difference energy of the emission maxima shown in Figure 4 supports that our estimation is reasonable.

Although temperature dependence of $[Cu(dtbp)_2]^+$ is interpreted by using a simple Boltzmann model, such analysis is not feasible for the other three compounds. In the these compounds, the difference spectra in Figure 2b considerably shift to red with decreasing temperature. This means that the ^{1}MLCT and ^{3}MLCT states change with temperature. The extent of distortion in these three compounds should be depend on temperature.

Our analysis shows that in the case of $[Cu(dtbp)_2]^+$, the ^{3}MLCT component is the major contribution of the emission. In addition, spectral profiles for the ^{1}MLCT and ^{3}MLCT emission in $[Cu(dtbp)_2]^+$ are to be independent of temperature. These properties are contrast to those of $[Cu(dmp)_2]^+$, in which delayed fluorescence from ^{1}MLCT is the main component. As the substituents become more bulky, the contribution of the delayed fluorescence obviously decreases.

Here, we shall discuss effects of bulkiness of the ligand substituents on the electronic structure as well as the main relaxation pathway from the lowest excited states systematically. It is obvious that when the ligand substituents at 2- and 9-positions are more bulky, distortion toward a planer structure is more inhibited due to steric repulsion. Under the D_{2d} symmetry, the lowest excited singlet state is of forbidden character, since the transitions from two degenerate d orbitals to the degenerate LUMOs of ligand π character cancel each other in their intensity.[4] However, distortion to a planer structure gains transition probability for S_1–S_0 transition, because the D_2 symmetry split energies of the two highest d orbitals and the two transitions do not contribute equally the S_1 excited state.[2,4] At the same time, the excitation energy of S_1–S_0 as well as that of T_1–S_0 transition decreases. Principally such features well agree with the substituent dependence on the lowest visible absorption and emission spectra, although there might be a subtle contradictory in detailed assignments for the second lowest absorption band. In the case of $[Cu(dmp)_2]^+$, the weak absorption shoulder at around 520 nm has been assigned to the lowest absorption band, and the intense absorption band around 460 nm is assigned to the second allowed singlet transition.[4,5] On the other hand, compounds with bulky substituents are expected to exhibit a stronger second absorption band than that of less bulky $[Cu(dmp)_2]^+$; however, such stronger absorption band seems to lack in $[Cu(dtbp)_2]^+$. In $[Cu(dtbp)_2]^+$, Cu–N distances are considerably longer than those of $[Cu(dmp)_2]^+$,[6] and thus transition probability of the second allowed ^{1}MLCT transition may decrease.

A radiative rate constant from T_1 state for $[Cu(dtbp)_2]^+$ is roughly estimated as ca. $10^4\,s^{-1}$ based on its lifetime and quantum yield, and this value is more than one order of magnitude larger than that estimated for $[Cu(dmp)_2]^+$, ca. $10^3\,s^{-1}$.[2] Figure 5 illustrates schematic energy diagram and possible radiative relaxation pathways in copper(I) bis(phenanthroline) complexes in the less-distorted and distorted structures. T_1 state is of more allowed character in a less-distorted structure, probably due to larger spin–orbit coupling with higher singlet excited states. This may come from smaller energy gaps between the higher singlet states and T_1 state in a less-distorted structure, where T_1 state is lifted up. As a result, compounds with more bulky substituents give a less-distorted structure in the excited state and lead to a larger T_1 radiative rate constant as well as a smaller S_1 rate constant. In addition, it is likely that an energy gap between the S_1 and T_1 states is smaller in less-distorted structures. Thus, contribution of delayed fluorescence decreases in less-distorted structures, and the main component of emission is the direct emission from T_1 rather than delayed fluorescence. Longer lifetime in a compound with more bulky substituents can be rationalized by suppressed distortion but also by much smaller contribution of delayed fluorescence.

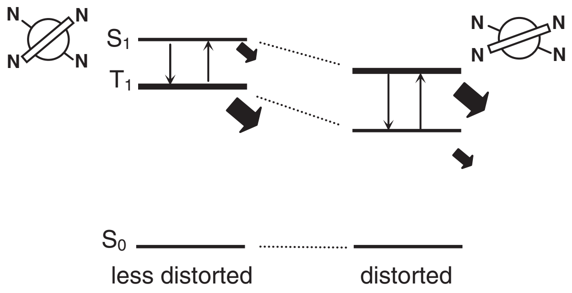

Figure 5. Schematic diagram of radiative relaxation pathways from the excited states for less-distroted and distorted structures in Cu(I) phenanthroline complexes under D_2 symmetry.

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