

Femtosecond photorelaxation dynamics in halogen-bridged dinuclear copper(I) complexes in solid-state thin films

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Halogen-bridged dinuclear Cu(I) complexes, $[\text{Cu}(\mu\text{-X})_2]_2$, have been paid attention as thermally activated delayed fluorescence (TADF) materials. Tsuboyama reported highly emissive $[\text{Cu}(\mu\text{-X})\text{dppb}]_2$ (Figure 1) exhibits TADF with luminochromism responding to the microscopic viscosity of matrix: green emission at around 510nm in a rigid matrix such as block crystals and yellow emission at around 550nm in fluid solutions.¹ The emitting state for the former is assigned as (X+M)LCT while the latter is MLCT with flattened Cu(I) coordination.¹ In this work, the photorelaxation dynamics in XLCT and MLCT of $[\text{Cu}(\mu\text{-X})\text{dppb}]_2$ in neat films have been studied by time-resolved emission spectroscopy.

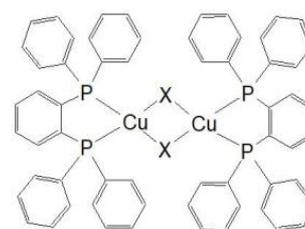


Fig.1 $[\text{Cu}(\mu\text{-X})\text{dppb}]_2$ (X=I) (**1**)

Figure 2 shows absorption and emission spectra for a neat film prepared on a quartz glass by vacuum evaporation of **1** at 350 °C. The spectrum exhibited yellow broad emission at around 550 nm (Figure 2) assignable to MLCT, indicating the neat film of **1** is not so rigid as to suppress the flattening distortion of the Cu(I) coordination. Upon 405 nm-excitation of the neat film a fluorescence band with the peak at around 520 nm appeared within 100 fs, indicating structural relaxation in (X+M)LCT occurs very rapidly. The 520 nm fluorescence decayed with the lifetime of 20 ps, slightly faster than for the block crystal (~50 ps). These lifetimes correspond to the intersystem crossing rate in (X+M)LCT. After the decay of the fluorescence, the emission band was red-shifted to 550 nm with the time constant of 200~400 ns and then decayed with 2 μs. Consequently, the transition from ³(X+M)LCT to ³MLCT accompanied by flattening of the Cu(I) coordination occurs in the sub-microsecond region in neat films, much faster than that in block crystals (>4 μs) and much slower compared for fluid 2-methyl tetrahydrofuran solutions (2~3 ns).

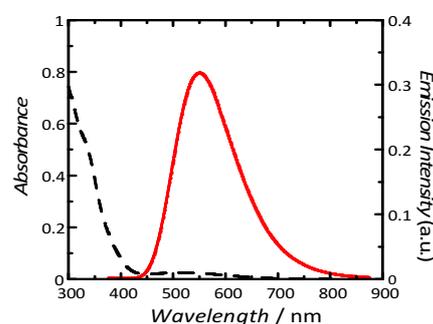


Fig. 2 Absorption and Emission spectra for a vapor-deposited neat film of **1**.

1) Tsuboyama, A., *et al.*, *Inorg. Chem.*, **2007**, 46, 1992-2001.