

*Supplementary Information for*

**Photoinduced Structural Distortions and Singlet-Triplet Intersystem Crossing in  
Cu(I) MLCT Excited States Monitored by Optically Gated Fluorescence  
Spectroscopy**

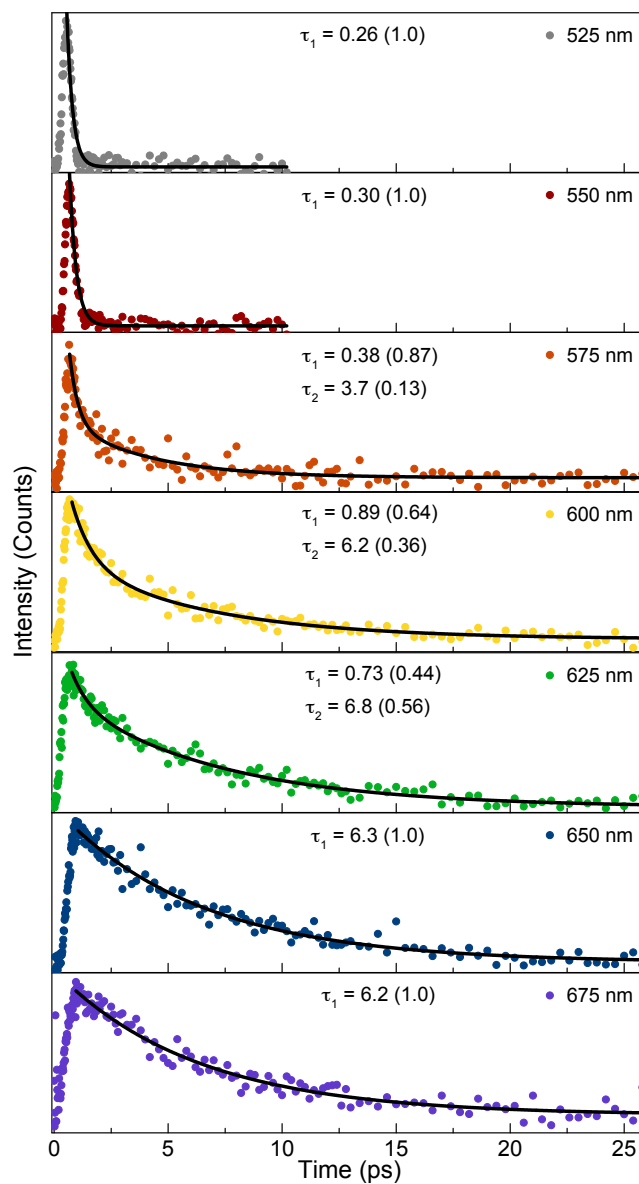
Sofia Garakyaraghi,<sup>1</sup> Petr Koutnik<sup>1</sup> and Felix N. Castellano<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, United States

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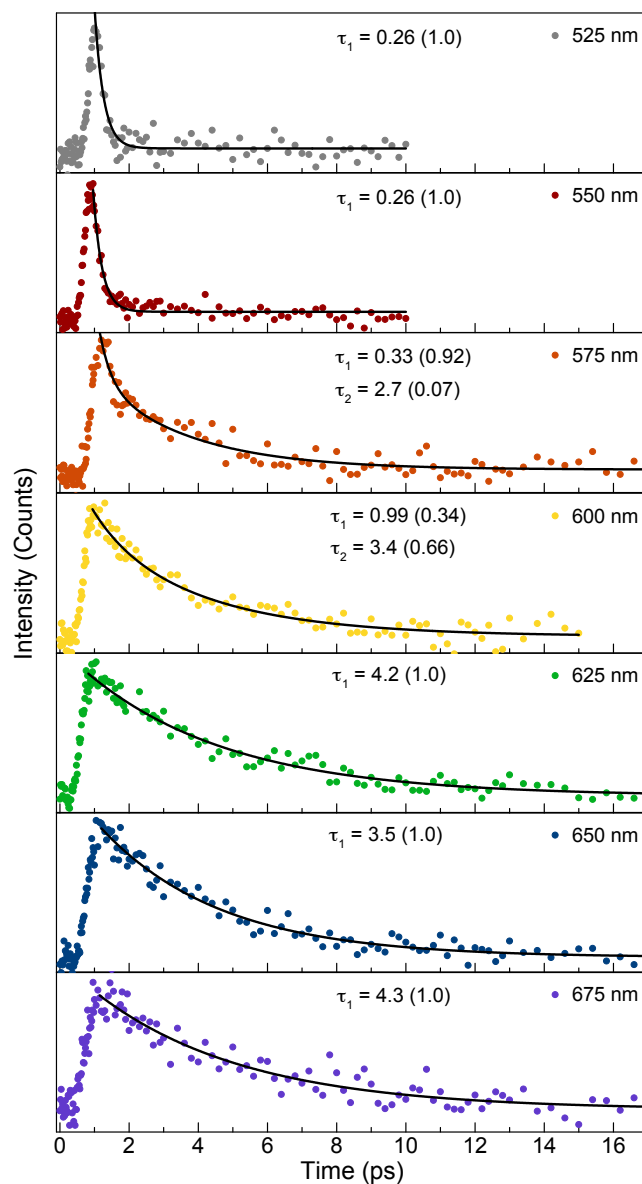
- (1)** Representative sub-picosecond time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{dsbp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.
- (2)** Representative sub-picosecond of time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{dsbtmp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.
- (3)** Representative sub-picosecond of time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{diptmp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.

(1) Representative sub-picosecond time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{dsbp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.



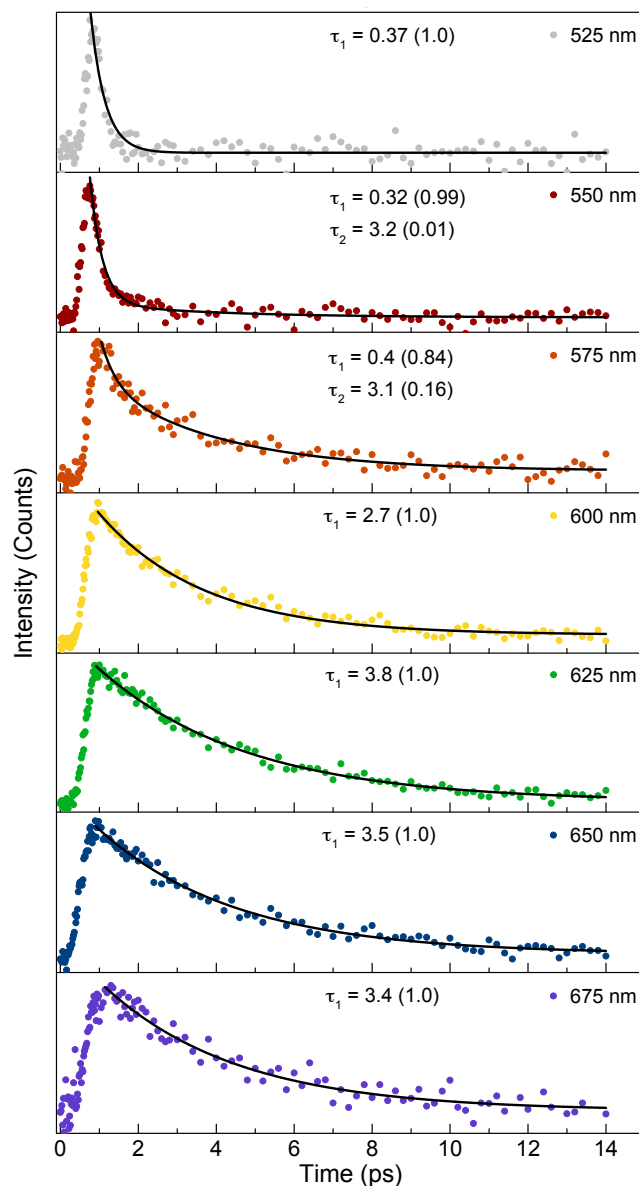
**Figure S1.** Time-resolved PL decay kinetics of  $[\text{Cu}(\text{dsbp})_2]^+$  in dichloromethane measured by fluorescence-upconversion method at room temperature. The black line represents the most adequate fit to a (sum of) exponential function(s), with the time constants (amplitudes) provided in the legend.

(2) Representative sub-picosecond time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{dsbtmp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.



**Figure S2.** Time-resolved PL decay kinetics of  $[\text{Cu}(\text{dsbtmp})_2]^+$  in dichloromethane measured by fluorescence-upconversion method at room temperature. The black line represents the most adequate fit to a (sum of) exponential function(s), with the time constants (amplitudes) provided in the legend.

**(3)** Representative sub-picosecond time-resolved photoluminescence decay kinetics of  $[\text{Cu}(\text{diptmp})_2]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.



**Figure S3.** Time-resolved PL decay kinetics of  $[\text{Cu}(\text{diptmp})_2]^+$  in dichloromethane measured by fluorescence-upconversion method at room temperature. The black line represents the most adequate fit to a (sum of) exponential function(s), with the time constants (amplitudes) provided in the legend.