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Full Length Article

# The temperature dependent luminescent decay kinetics of an emissive copper complex in the single crystalline phase using time-gated luminescence microscopy



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## ABSTRACT

The temperature dependence of the luminescent lifetime of a single crystal of Cu(I) phenanthroline, [Cu(dmp)(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (dmp=2,9-dimethyl-1,10-phenanthroline and PPh<sub>3</sub>=triphenylphosphine), was measured using a fluorescence lifetime imaging microscope utilizing time-gated CCD detection. At all temperatures between 100 K and 292 K, the single crystals exhibited biexponential luminescent decay as well as non-linear Arrhenius luminescent decay kinetics. Variable temperature single-crystal XRD measurements revealed that the observed behavior is likely not the result of a crystallographic phase transition.

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## 1. Introduction

Luminescent transition metal complexes are an important class of compounds that have found use as emissive materials in OLEDs (organic light-emitting diodes) [1–5], phosphorescent oxygen sensors [6–8], and sensitizers in TTA (triplet-triplet annihilation) systems [9–11]. While the luminescent properties of these complexes are often characterized in solution and thin films, measurements on individual single crystals remains relatively rare. By performing measurements on the single crystal phase, the solid-state photophysical properties can be directly compared with their crystal structures to better establish structure–function relationships in these materials [12]. The ability to determine kinetic parameters relevant to these solid-state systems across a variety of temperatures is becoming increasingly important to the development of light-emitting technologies. To that end, we report a novel variable temperature time-resolved imaging microscope capable of quantifying the luminescent lifetimes of solid-state samples on the nanosecond timescale. The time-gated detection utilized in this system offers several advantages: data collection is fast, as all pixels are being acquired at once, and it typically results in simpler data analysis than frequency modulated techniques [13,14]. Another key advantage is the ability to delay the start of the detector gate so as to remove the initial excitation and potential

background fluorescence from other components of the matrix from the sample emission [15].

Luminescent earth-abundant first row transition metal complexes are appealing alternatives for use in light emitting devices compared to rare earth metals due to their lower cost and reduced toxicity [16–18]. Cu(I) bisphenanthrolines continue to be attractive materials for optoelectronic materials [19–22]. Herein we report for the first time the temperature dependence of the luminescent properties of single crystals of an emissive copper complex, Cu(dmp)(PPh<sub>3</sub>)<sub>2</sub>·BF<sub>4</sub> (CuDMP, dmp=2,9-dimethyl-1,10-phenanthroline and PPh<sub>3</sub>=triphenylphosphine). The unusual temperature dependent photophysics of CuDMP in the single-crystal form is compared to previous studies [23,24].

## 2. Experimental procedures

### 2.1. Fluorescence lifetime imaging microscope (FLIM)

A schematic of the FLIM is shown in Fig. 1. The samples are excited using a frequency tripled pulsed Nd:VO<sub>4</sub> diode-pumped solid-state laser (Spectra-physics model T80-YHP70-355Q, 355 nm, pulse width ~35 ns fwhm, 1.0 kHz). Laser output was passed through a solarization resistant bare fiber optic cable (Thorlabs UM22-200) and delivered to the rear port of an inverted microscope (Olympus IMT-2) using a reflective collimator (Thorlabs, RC08SMA-F01). A set of reflective neutral density filters

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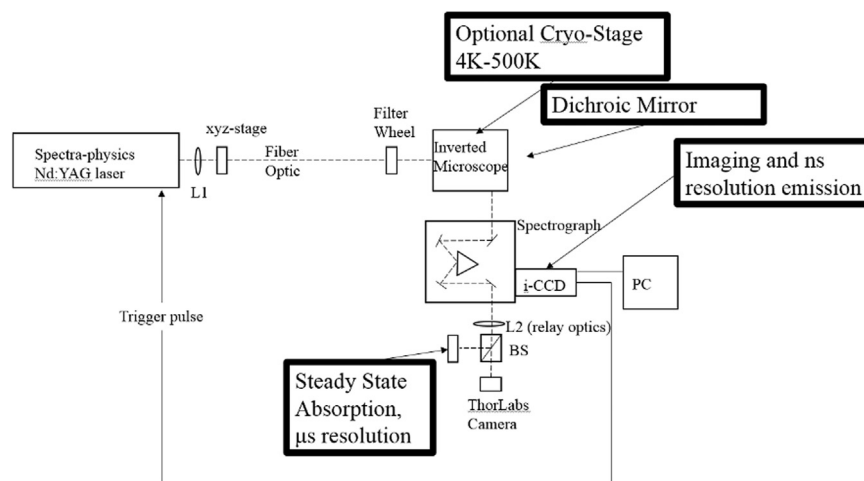


Fig. 1. A simplified schematic of the fluorescence lifetime imaging microscope (not to scale).

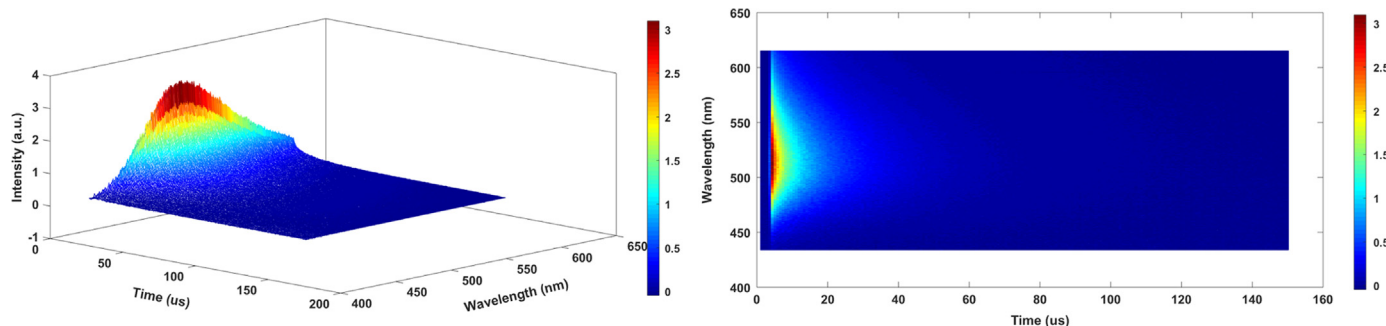


Fig. 2. False color images of the time-resolved emission of CuDMP at 293 K shown as a full 3D plot (a) and a top down plot (b).

(Thorlabs, NDUV10a) mounted on a rotating filter wheel (Thorlabs, FW1) placed between the output of the collimator and the microscope port was used to attenuate laser power. The light is then focused onto the sample using a reflective objective (Newport,  $15\times$ ). Subsequent UV emission is cut off from reaching the eyepieces or detector. Samples are mounted on a traditional microscope stage for room temperature experiments or within a microscopy cryostage (cryoindustries, RC102-CFM) for temperature dependent measurements. Emission from the sample is recollected through the objective and delivered through the microscope imaging port to an imaging spectrograph (Princeton Instruments, Acton SP2750). Time-gated light intensities were recorded using an intensified CCD camera (PIMAX3, Princeton Instruments, Intensifier, Unigen 2,  $1024\times 256$ ). Sample imaging is recorded using a flat mirror within the spectrograph. Spectra are recorded by dispersing a single line of the image using a standard grating ( $150\text{ g/mm}$ ,  $500\text{ nm}$ ). By combining spectra from multiple time delays, traces of emission intensity as a function of time and energy are produced (Fig. 2). All spectra are wavelength and intensity calibrated using Intensical hardware and software (Princeton Instruments, Lightfield ver. 4.7.2.1403).

## 2.2. Chemical synthesis

$[\text{Cu}(\text{CH}_3\text{CN})]\text{BF}_4$  (Sigma-Aldrich), triphenylphosphine (Acros Organics), and 2,9-dimethyl-1,10 phenanthroline hemi hydrate (Alfa Aesar) were used as received. Ethanol (Decon labs, 200 proof) was used as the solvent. The synthesis used was adapted from previous reports [23,24]. A single equivalent of  $[\text{Cu}(\text{CH}_3\text{CN})]\text{BF}_4$  (0.050 g, 0.159 mmol) and 2.1 equivalents of  $\text{PPh}_3$  (0.088 g, 0.336 mmol) were dissolved in warm ethanol. Separately, 1 equivalent of dmp (0.035 g, 0.161 mmol) was dissolved in ethanol. This solution was added

slowly, with stirring, to the first solution. With the addition of the dmp solution, the reaction turned yellow in color and remained yellow upon complete addition of dmp solution. The solution was then left undisturbed and yellow crystals of the desired product were formed.

## 2.3. Time-resolved emission measurements

Crystals were mounted on a quartz coverslip in a thin layer of low-fluorescing oil (IMMOIL-Type F, Olympus) or silver thermal paste (Arctic Silver, polysynthetic silver thermal compound). Normalized decay traces were fit using a biexponential decay function using the Matlab R2012b curve fitting application.

## 2.4. Single crystal X-ray diffraction

A suitable single crystal was selected and mounted on a glass capillary with oil. All structural data was collected using a Bruker SMART APEX2 CCD diffractometer with a  $\text{MoK}\alpha$  source ( $\lambda=0.71073$ ). Samples were cooled using nitrogen gas with an Oxford Cryosystems (Cryostream 700) apparatus. Unit cell parameters were determined using the APEX2 program package. Olex2 was used to solve and refine the structures. Full structure data was collected at 90 K, while indexing scans were performed every 5 K between 170 K and 135 K.

## 3. Results and discussion

Upon excitation with UV light (355 nm), single crystals of CuDMP exhibit broad yellow-orange emission centered at approximately 515 nm at room temperature (Fig. 3). When the

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