Orange-to-Blue and Red-to-Green Photon Upconversion with a Broadband Absorbing Copper(I) MLCT Sensitizer

Catherine E. McCusker* a and Felix N. Castellano* a

Materials
The dpp ligand1 and [Cu(dpp)]PF 6 (I) were synthesized and purified as previously reported. Spectrophotometric grade dichloromethane (Aldrich), perylene (2) (Aldrich) and pyrrmethene 546 (3) (Exciton) were purchased and used without further purification.

Spectroscopic Measurements
All samples were prepared in a custom 1 cm 2 quartz optical cell with a side arm round bottom flask and deoxygenated with a minimum of three freeze-pump-thaw cycles. Static absorption spectra were measured with a Cary 50 Bio UV-Vis spectrophotometer (Varian). Steady-state emission spectra were obtained on a FL/FS920 (Edinburgh Instruments). The emission signal was detected with a Peltier cooled, red sensitive PMT (R2658P Hamamatsu). For quenching experiments, a 450 W Xe arc lamp was used as the excitation source and for power dependence measurements, either a 593.5 nm (OEM laser systems) or 635 nm (Lasermate) CW laser diode was used as the excitation source. For the power dependence measurements, the excitation power was measured using a Nova II/PD300-UV power meter/detector head (Ophir) and the excitation power was varied using a series of neutral density filters. The Parker-Rees correction was applied to all spectra when converting from wavelength to energy units.3 Time resolved emission decays were collected with an LP920 laser flash photolysis system (Edinburgh Instruments). The excitation source was the Vibrant LD 355 II Nd:YAG/OPO system (OPOTEK). Data acquisition was controlled by the LP900 software program (Edinburgh Instrument). Kinetic traces were collected with a PMT (R928 Hamamatsu) and fit with single exponential functions using IGOR Pro.

Stern-Volmer Quenching
The Stern-Volmer (K SV) and the bimolecular quenching constants (k q) were obtained according to the dynamic Stern-Volmer relation, \( \tau_0/\tau = 1 + K_{SV}[Q] \), where \( \tau_0 \) and \( \tau \) are the [Cu(dpp)]PF 6 lifetimes in the absence or presence of the quencher, respectively. K SV is the Stern-Volmer constant, K SV = k q \( \tau_0 \), and [Q] is the molar concentration of quencher, either 2 or 3. The slope of the Stern Volmer plot was linear over the entire range of measured quencher concentrations.

Power Dependence
For this experiment, an appropriate longpass filter (550 nm or 590 nm) was used to filter the excitation beam to prevent direct excitation of the acceptor, and solutions of the acceptors alone showed no emission. Emission intensities at the maxima of the upconverted emission (470 or 540 ± 10 nm) were recorded over one minute in time-based mode and averaged. These values were used in Figures 2b and 3b. For higher excitation powers, the use of neutral density filters...
before the detector was necessary to prevent PMT saturation. The final emission intensities in these samples were corrected for the filter transmittance at 470 or 540 nm.

Figure S1: Bimolecular quenching of 1 by 2 in deoxygenated dichloromethane solution. (a) Time resolved emission decay traces of 1 (0.7 mM) at 720 nm with increasing concentrations of 2. (b) Stern-Volmer plot of this data.
Figure S2: Bimolecular quenching of 1 by 3 in deoxygenated dichloromethane solution. (a) Time resolved emission decay traces of 1 (0.7 mM) at 720 nm with increasing concentrations of 3. (b) Stern-Volmer plot of this data.

$$K_{SV} = 326.15 \pm 24.4 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_q = 1.38 \times 10^9 \text{ s}^{-1}$$
Figure S3: Upconverted emission intensity of a deoxygenated dichloromethane solution of 1 (1.1 mM) and 2 (10 mM). Emission intensity at 470 nm was probed as the excitation power at 593.5 nm was varied.

Figure S4: Upconverted emission intensity of a deoxygenated dichloromethane solution of 1 (3.7 mM) and 3 (21 mM). Emission intensity at 540 nm was probed as the excitation power at 635 nm was varied.
References