Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI) FOR: ANTI-STOKES DELAYED FLUORESCENCE FROM METAL-ORGANIC BICHROMOPHORES

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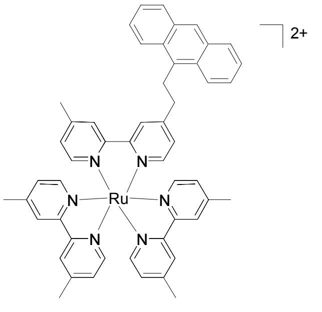
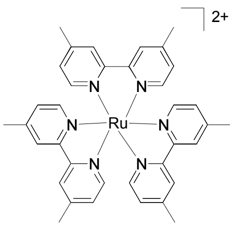
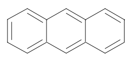
Structures. The structures of the 3 compounds used in this study are presented below. The metal complexes were available from previous studies[1,2a] and anthracene (99.9%, gold label, Aldrich) was used as received.


$[Ru(dmb)_2(bpy\text{-}An)]^{2+}$
1


$[Ru(dmb)_3]^{2+}$


Anthracene

Photophysical Measurements. Static luminescence spectra were obtained with a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). The excitation was accomplished with a 450 W Xe lamp optically coupled to a monochromator (± 2 nm) and the emission was gathered at 90° and passed through a second monochromator (±2 nm). The luminescence was measured with a Peltier-cooled (-30°C), R955 red sensitive photomultiplier tube (PMT). Excitation spectra are corrected with a photodiode mounted inside the fluorimeter that continuously measures the Xe lamp output. Transient emission intensity decays were measured with a nitrogen-pumped broadband dye laser (2-3 nm fwhm) from PTI (GL-3300 N_2 laser, GL-301 dye laser).[2] Coumarin 460 (440–480 nm) dye was used to tune the unfocused excitation. The luminescence is gathered at 90° through a long pass optical filter (> 550 nm), focused through a lens system, and passed through an f/3.4 monochromator (± 4 nm). The emission is detected with a Hamamatsu R928 PMT, mounted in a Products for Research housing. The base of the PMT is wired for fast response and is negatively biased with a Stanford Research PS325 power supply. The PMT signal is terminated through a 50 Ω resistor to a Tektronix TDS 380 digital oscilloscope (400 MHz). The data from the scope, representing an average of 128 laser shots collected at 2-3 Hz, is transferred to a computer and processed using Origin 6.1.

Anti-Stokes Delayed Fluorescence Experiments. Time-resolved photoluminescence experiments were performed as described above[2] with some minor modifications. All samples were deaerated with argon gas for at least 30 minutes prior to measurements and continuously purged throughout the experiments. The 450 ± 2 nm output of the N_2-

pumped dye laser was passed through a 430 nm long pass filter prior to incidence on the sample and the pulse energy was systematically varied through the use of neutral density filters (Rolyn Optics). The pulse energies were measured at the sample position using a Molectron Joulemeter (J4-05). In order to obtain signal intensities sufficient for time-resolved spectra with adequate wavelength resolution (as in Figure 1), the luminescence transients were amplified by terminating the PMT signal into 1 kΩ at the oscilloscope. The anti-Stokes delayed fluorescence kinetic profiles measured by termination into 50 Ω, were averaged over 128 laser shots and the data analyzed and integrated using Origin 6.1. The fluorescence intensities measured for **1** (as in Figure 2) were determined by signal averaging 128 transients at each laser power. The individual transients were integrated over the entire delayed fluorescence profile yielding relative intensities that were each reproducible within 1% of their respective values.

ESI References

(1) T. D. Trouts, D. S. Tyson, R. Pohl, D. V. Kozlov, A. G. Waldron and F. N. Castellano, *Adv. Funct. Mater.,* 2003, **13**, 398.

(2)(a) D. S. Tyson and F. N. Castellano, *J. Phys. Chem. A*, 1999, **103**, 10955. (b) D. S. Tyson, C. R. Luman, X. Zhou and F. N. Castellano, *Inorg. Chem.* 2001, **40**, 4063. (c) D. S. Tyson, K. B. Henbest, J. Bialecki and F. N. Castellano, *J. Phys. Chem. A*, 2001, **105**, 8154.

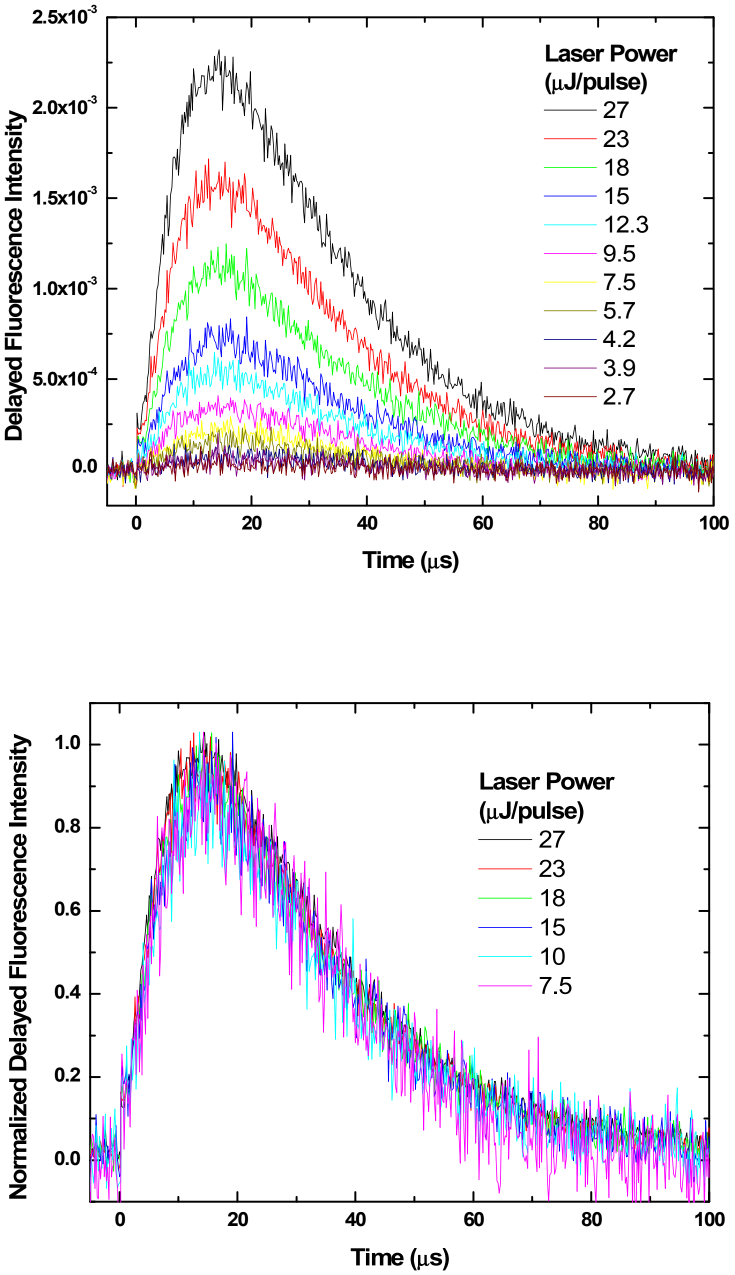


Fig. S1 (a) Delayed fluorescence intensity profile of **1** as a function of 450 ± 2 nm laser power at a concentration of 2.2 x 10^{-5} M in deaerated CH_3CN. (b) Normalized delayed fluorescence intensity profile of **1** illustrating that the dynamics are unaffected by laser power at this concentration.

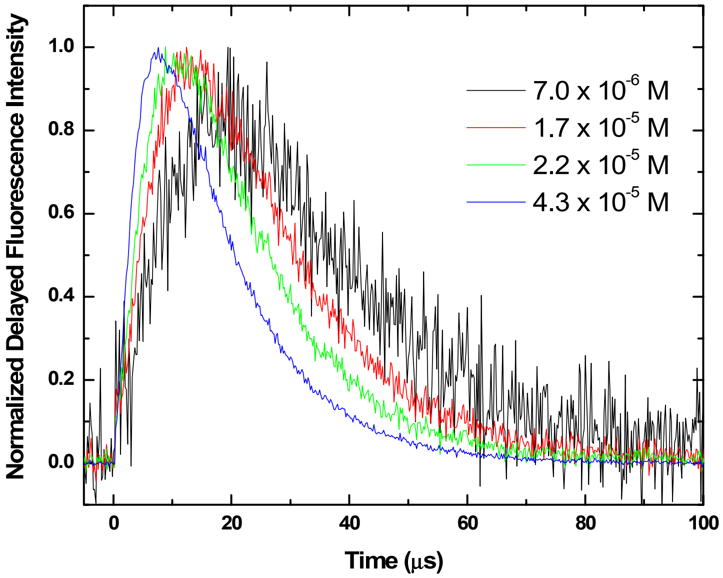


Fig. S2 Concentration dependence of the delayed fluorescence profile of **1** in deaerated CH_3CN. All transients were obtained using 450 ± 2 nm pulsed laser excitation at 65 μJ/pulse.

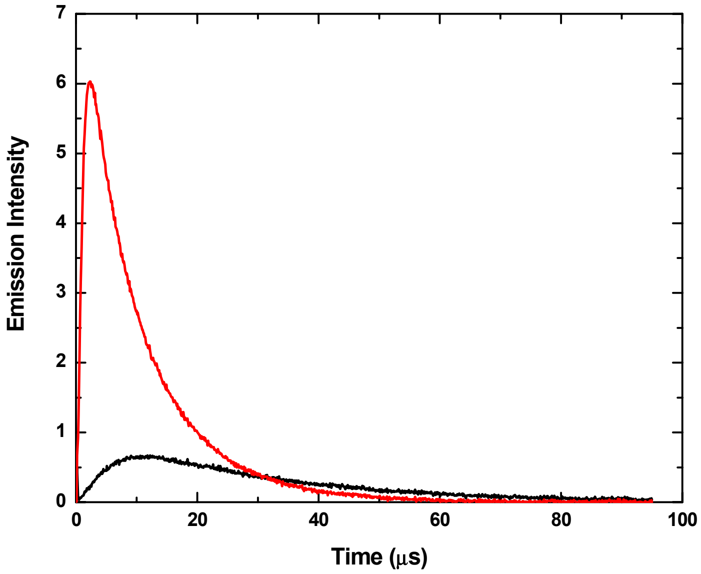


Fig. S3 Comparison of delayed fluorescence intensity and kinetics of bichromophore **1** (black line) and the intermolecular system, $[Ru(dmb)_3]^{2+}$ + anthracene, at equimolar concentration (red line). Integrated areas: 2.38 and 6.98, respectively. Data taken in degassed 3.5 x 10^{-5} M acetonitrile solution with 65 μJ/pulse laser power. Excitation wavelength was 450 ±2 nm; Emission intensity decays observed at 410 ±4 nm.