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Anti-Stokes delayed fluorescence from metal–organic bichromophores†

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Long wavelength excitation of $[Ru(dmb)_2(bpy\text{-}An)]^{2+}$ (dmb is 4,4′-dimethyl-2,2′-bipyridine and bpy-An is 4-methyl-4′-(9-anthrylethyl)-2,2′-bipyridine) in CH_3CN solution produces upconverted delayed singlet anthracene fluorescence *via* bimolecular triplet–triplet annihilation.

The generation of ultraviolet and blue light from molecular systems offers significant challenges for device technologies such as organic light-emitting diodes.[1] Short-wavelength light production ultimately requires new molecules, concepts, and methods for the efficient creation of blue and UV-light from low energy sources. We propose a possible route to this goal utilizing sensitized anti-Stokes delayed fluorescence from chromophore–triplet energy transfer quencher molecules. In essence, the energy from two separately absorbed quanta on two different molecules can be transferred to one molecule *via* triplet–triplet annihilation, resulting in delayed singlet fluorescence having a higher frequency than that of the exciting light, *i.e.* upconverted fluorescence. This strategy was first explored by Parker and Hatchard over 40 years ago in non-covalent aromatic systems.[2] Further extensions of the upconversion *via* the annihilation concept have been used to generate S_2 delayed fluorescence in metalloporphyrins[3] and S_1 delayed fluorescence in a diplatinate(II) pyrophosphate complex at 4.2 K.[4]

Over the past 15 years several chromophore-quencher metal–organic systems have been purposely designed to efficiently sensitize the long-lived triplet state of the covalently appended quencher.[5–14] Interestingly, their Jablonski diagrams meet the requirements for sensitized anti-Stokes delayed fluorescence, suggesting immediate widespread applicability of this concept to a range of molecular systems. One particular class includes Ru(II) diimine metal-to-ligand charge transfer (MLCT) chromophores bearing pendant anthracene(s), where the ^{3}MLCT excited state is higher in energy than the triplet state of anthracene (^{3}An*), while the anthracene singlet state (^{1}An*) lies above that of the ^{1}MLCT state.[8–12,14] It has been shown that ^{3}An* is sensitized with a quantum yield of unity in $[Ru(bpy)_2(bpy\text{-}An)]^{2+}$, where bpy-An is 4-methyl-4′-(9-anthrylethyl)-2,2′-bipyridine, following excitation of the MLCT fragment.[12] Delayed singlet fluorescence has never been reported in this or any associated chromophore-quencher molecules although Wilson and coworkers noted efficient triplet–triplet quenching of $[Ru(bpy)_2(bpy\text{-}^3An^*)]^{2+}$ in degassed methanol, implying that triplet–triplet annihilation was responsible for this observation.[12] Since the annihilation process is expected to yield highly fluorescent singlet anthracene molecules,[15,16] we propose that such systems are suitable candidates for photon upconversion.

The current work examines the supra-nanosecond anti-Stokes photoluminescence of $[Ru(dmb)_2(bpy\text{-}An)]^{2+}$ (**1**), where dmb is 4,4′-dimethyl-2,2′-bipyridine, in fluid solutions at room temperature. Contrary to all previous studies on related systems, we decided to focus our investigation on the triplet–triplet annihilation processes in RT solutions of these molecules by observing the anti-Stokes delayed fluorescence. Visible excitation of dilute solutions of **1** in CH_3CN produces anti-Stokes delayed singlet fluorescence of anthracene in the near-visible region and this annihilation process is completely shunted in glycerol where diffusion is significantly impeded. Our data are consistent with a reaction sequence where visible light exclusively produces the MLCT excited state yielding triplet anthracene with a quantum yield of unity.[10–12] Two excited chromophore-quencher molecules diffuse to form an encounter complex leading to triplet–triplet annihilation, yielding one ground and one excited state chromophore. The latter decays radiatively to the ground state by the emission of UV and blue light whose spectrum is unmistakably that of the singlet fluorescence of anthracene. Although intramolecular singlet energy transfer provides an efficient nonradiative deactivation pathway,[10–13] upconverted fluorescence was easily detected in our apparatus.

Compound **1** was synthesized in a previous study and its structural characterization as well as its photophysical properties have been reported.[10,11] Excitation of **1** in deaerated CH_3CN (10 to 80 μM) using the 450 ± 2 nm output of a N_2-pumped dye laser with pulse energies varying from 5 to 60 μJ per pulse (500 ps fwhm) yields a clearly observable delayed fluorescence signal at shorter wavelengths. Since delayed fluorescence is produced by long-wavelength sensitization, the signal is free from artifacts such as prompt singlet fluorescence. Fig. 1 displays the delayed fluorescence spectrum of **1** measured 9 μs after a 60 μJ laser pulse. The residual ^{1}An fluorescence in **1** resulting from UV excitation in our steady-state fluorimeter is also included in Fig. 1 for comparative purposes. These data illustrate that the delayed fluorescence signal emanates from singlet anthracene moieties which are produced *via* triplet–triplet annihilation. Under the same experimental conditions the free bpy-An ligand in deaerated CH_3CN does not produce any delayed fluorescence signal. The dependence of the intensity of the anti-Stokes delayed fluorescence on incident laser pulse energy was also evaluated, Fig. 2. The integrated intensity of the delayed fluorescence signal measured subsequent to each laser pulse was proportional to the square of the excitation power over the range of

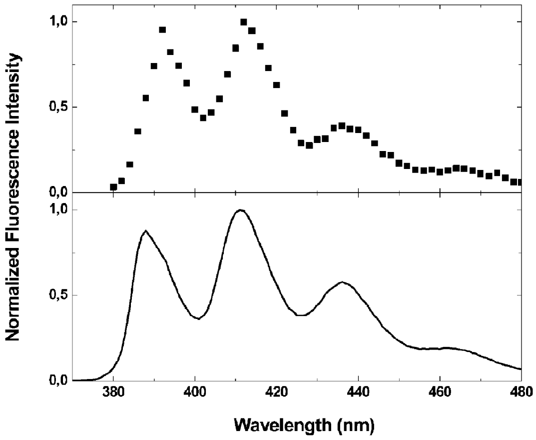

Fig. 1 Delayed fluorescence spectrum of **1** (solid squares) in deaerated CH_3CN (3.5×10^{-5} M) measured 9 μs after a 450 ± 2 nm, 60 μJ laser pulse and residual anthracene emission from **1** (black line) using 360 ± 2 nm lamp excitation.

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† Electronic supplementary information (ESI) available: experimental details and kinetic traces of the anti-Stokes delayed fluorescence signals. See http://www.rsc.org/suppdata/cc/b4/b412681e/

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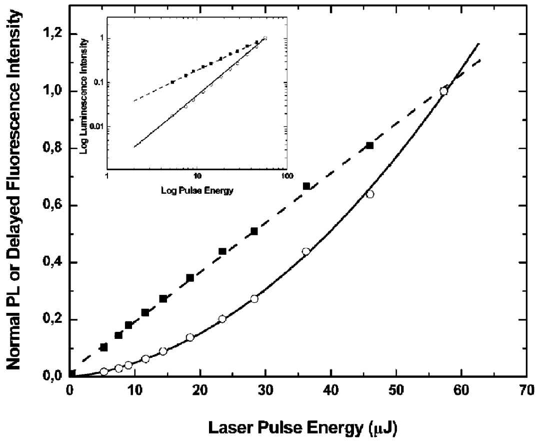

Fig. 2 Delayed integrated fluorescence intensity of **1** at 410 nm (open circles) and prompt photoluminescence intensity of an optically matched sample of $[Ru(bpy)_3]^{2+}$ at 610 nm (solid squares) measured as a function of 450 ± 2 nm incident pulse energy in deaerated CH_3CN. The data are normalized to the highest incidence intensity. The dashed line is the best linear fit to the $[Ru(bpy)_3]^{2+}$ data and the solid line is the best quadratic fit to the delayed anti-Stokes emission data for **1**. Inset: double logarithm plot of the same data; the slopes are 0.96 for $[Ru(bpy)_3]^{2+}$ and 1.88 for **1**.

5–60 μJ per pulse. This result would be expected if the delayed fluorescence signal was produced *via* triplet–triplet annihilation under our experimental conditions.[15] The double logarithm plot in the inset of Fig. 2 yields a straight line with a slope of 1.88 which is indicative of the quadratic dependence of the annihilation process, *i.e.* the delayed fluorescence intensity is proportional to the square of the incident light power and hence to the square of the triplet concentration. Control experiments verified that under the same experimental conditions and instrument dynamic range, the photoluminescence intensity of $[Ru(bpy)_3]^{2+}$ at 610 ± 2 nm generated with 450 ± 2 nm excitation displayed a linear power dependence and the plot of prompt photoluminescence intensity *versus* pulse energy yielded a slope of 0.96, Fig. 2.

It is important to note that the delayed fluorescence signal indirectly probes the triplet anthracene dynamics which decays by parallel first- and second-order processes.[15,17] Although we do not analyze the kinetics in detail, we have identified at least 3 pathways for triplet decay which nominally include triplet state decay and triplet–triplet annihilation. The third pathway involves reaction of the excited triplets with ground state molecules which markedly influences the dynamics of the delayed fluorescence. The delayed fluorescence signal substantially shortens as a function of increasing ground state species while incident light intensity, which influences the number density of triplets, has no apparent effect on the delayed fluorescence dynamics as a function of concentration (see ESI†). These data provide evidence for non-luminescent exciplex formation which is competitive with bimolecular triplet–triplet annihilation and first-order triplet decay.

Although **1** produces a reasonable anti-Stokes fluorescence, we cannot measure a quantum yield for the process since it results from upconversion and the method of standardization is unclear at this time. Since the MLCT ground state can serve as an intramolecular singlet state quencher of the anthracene fluorescence we decided to look at the intermolecular process using equimolar concentrations of $[Ru(dmb)_3]^{2+}$ and anthracene (3.5×10^{-5} M). We believed that this modification would help suppress the intramolecular singlet transfer thereby enhancing the relative yield of the upconverted singlet fluorescence. The direct comparison between **1** and the intermolecular system under identical experimental conditions revealed that the relative efficiency of the upconversion process was ~2.9-fold higher in the latter case (see ESI†). In essence, the simpler (and unoptimized) noncovalent system was superior in generating anti-Stokes fluorescence and suggests new approaches for the utilization of MLCT excited states in optical devices.

The present contribution demonstrates the observation of upconverted delayed singlet fluorescence from **1** as well as a noncovalent donor–acceptor system in dilute solutions resulting from bimolecular triplet–triplet annihilation. Although there are efficient competing kinetic pathways for the sensitized triplets, detection of the anti-Stokes delayed fluorescence was possible under experimental conditions where normal photophysical processes would typically be evaluated. Moreover, related chromophore-quencher molecules and bimolecular assemblies will likely be susceptible to the same upconversion processes, permitting triplet state access to higher-lying fluorescent singlet states, potentially yielding new materials with blue and/or UV emission properties.

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