

Low power upconversion using MLCT sensitizers†

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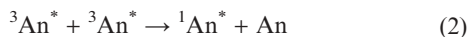
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Selective low energy excitation of the metal-to-ligand charge transfer (MLCT) transition in $[\text{Ru}(\text{dmb})_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) in the presence of anthracene or 9,10-diphenylanthracene yields easily visualized upconverted singlet fluorescence resulting from triplet–triplet annihilation at low excitation power.

The efficient generation of ultraviolet and blue light in molecular systems remains challenging for device technologies such as organic light-emitting diodes.¹ A plausible and economic strategy towards fulfilling this goal involves harnessing *sequential* highly allowed one-photon absorptions to create higher energy excited states. This can be easily accomplished using triplet–triplet annihilation reactions where the energy stored in two separate excited triplet molecules is combined to generate a higher energy excited singlet state and a corresponding ground state species.^{2–4} In order to observe upconverted light in this scenario, the annihilating triplets must be sensitized using photons of significantly longer wavelength than those required to afford direct excitation of the singlet state. We propose that the judicious selection of an appropriate *inorganic* triplet sensitizer (where the intersystem crossing yield is unity)⁵ in concert with an aromatic hydrocarbon energy acceptor, may lead to efficient photon upconversion at low excitation power.

In a recent contribution, we reported the observation of sensitized anti-Stokes delayed fluorescence from anthracene in Ru(II)–anthracene bichromophores resulting from bimolecular triplet–triplet annihilation.⁶ Since the covalent bichromophores are also poised for efficient singlet–singlet energy transfer, detection of the weak anti-Stokes fluorescence was performed in our transient luminescence apparatus using pulsed laser excitation. Control experiments using a simple mixture of the two chromophores ($[\text{Ru}(\text{dmb})_3]^{2+}$, dmb = 4,4'-dimethyl-2,2'-bipyridine, and anthracene) at 3.5×10^{-5} M in CH_3CN showed an approximate 2.9-fold integrated upconversion intensity enhancement over the covalent system, likely resulting from suppression of singlet–singlet transfer subsequent to triplet annihilation. The pertinent bimolecular triplet quenching (eqn. (1)) and triplet–triplet annihilation (eqn. (2)) reactions following low energy light excitation are given below (An = anthracene):



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A key feature of this sequence is the requirement to efficiently produce two sensitized triplets in order to observe upconverted light emission from the anthracene singlet state. The utilization of the inorganic triplet sensitizer ensures quantitative production of triplet anthracene creating favorable conditions for annihilation (eqn. (2)).

The upconverted anthracene fluorescence spectrum is easily observed in our single photon counting fluorimeter under low power cw Ar^+ -laser irradiation ($\lambda_{\text{ex}} = 514.5$ nm), Fig. 1a. We note that the experimental conditions in Fig. 1 were selected to permit quantitative analysis of the anti-Stokes steady-state photoluminescence spectra. Therefore, the anthracene concentration is purposely maintained low (1.3×10^{-4} M) and these specific experiments do not exploit the full potential of the initial triplet quenching (eqn. (1)) or the annihilation process (eqn. (2)). The identical experiment using 488.0 nm excitation yields similar results and is provided as ESI.† In both cases, the upconverted fluorescence spectrum resulting from triplet annihilation was in quantitative agreement with the singlet fluorescence spectrum resulting from direct excitation ($\lambda_{\text{ex}} = 376 \pm 2$ nm). The quadratic light power dependence of the upconversion intensity is illustrative of triplet–triplet annihilation of anthracene sensitized through the selective excitation of two $[\text{Ru}(\text{dmb})_3]^{2+}$ molecules at 514.5 nm, Fig. 1b. Control experiments performed at 488.0 and 514.5 nm revealed that the upconverted fluorescence was only observed in mixtures of $[\text{Ru}(\text{dmb})_3]^{2+}$ and anthracene whereas no anti-Stokes signal could be recorded during irradiation of the independently dissolved molecules.

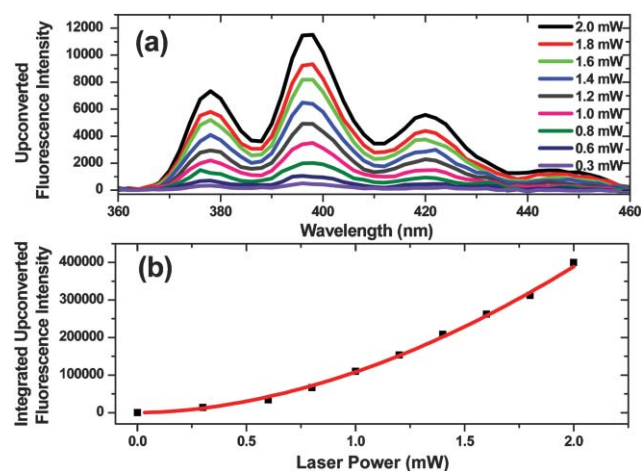


Fig. 1 (a) Upconverted fluorescence intensity profile of a deaerated CH_3CN solution of anthracene (1.3×10^{-4} M) + $[\text{Ru}(\text{dmb})_3]^{2+}$ (2.9×10^{-5} M) as a function of 514.5 nm incident laser power. (b) Integrated emission intensity data from part (a) represented as black squares. The solid red line is the best quadratic fit to the integrated emission data.

Interested in improving the relative upconversion yield, we substituted 9,10-diphenylanthracene (DPA) for anthracene in these experiments. The assumption was that DPA's increased singlet fluorescence quantum yield ($\Phi = 0.95$) relative to anthracene ($\Phi = 0.27$)⁷ would afford a modest change in upconversion efficiency. Under our experimental conditions, the substitution of DPA for anthracene in these experiments leads to an approximate 24.4 ± 6.1 enhancement of green-to-blue light upconversion enabling direct visualization of the process at low excitation power. Fig. 2a presents a direct comparison between the relative efficiency of the upconversion process ($\lambda_{\text{ex}} = 514.5$ nm, 24 mW incident power) using the $[\text{Ru}(\text{dmb})_3]^{2+}$ sensitizer and anthracene or DPA. The data clearly illustrate the enhancement gained in efficiency by using DPA as the triplet acceptor. We note that this enhancement does not result from the initial quenching of the MLCT excited state as lifetime quenching data for the MLCT emission in both cases yielded Stern–Volmer (and bimolecular quenching) constants of similar magnitude. In fact a larger quenching constant was

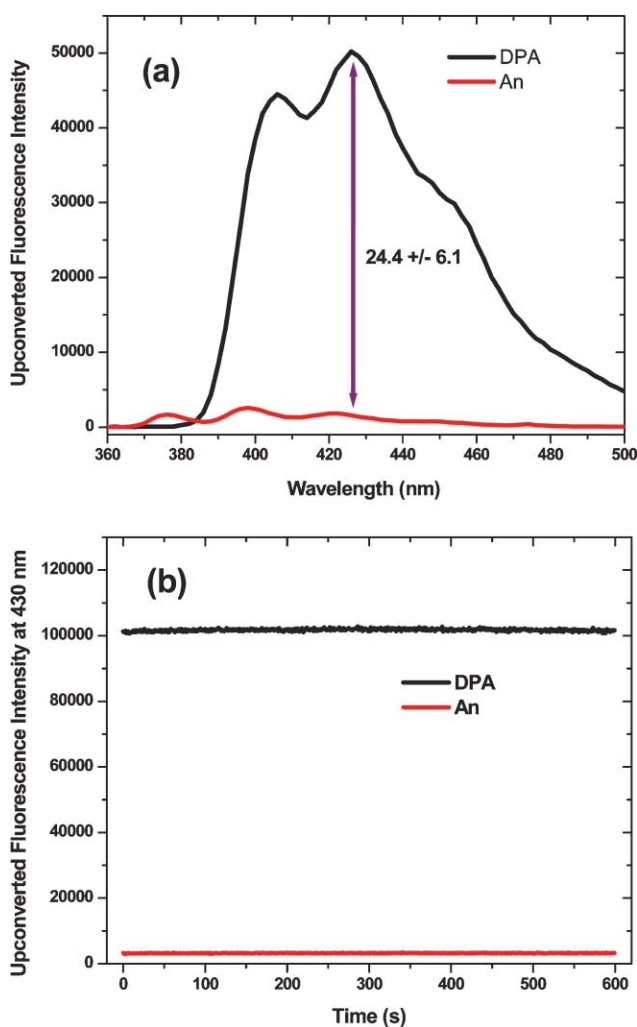


Fig. 2 (a) Comparison of upconverted emission intensity of deaerated CH_3CN solutions of: $[\text{Ru}(\text{dmb})_3]^{2+}$ (3.0×10^{-5} M) + DPA (1.3×10^{-4} M) (black line) and $[\text{Ru}(\text{dmb})_3]^{2+}$ (3.0×10^{-5} M) + anthracene (1.3×10^{-4} M) (red line). (b) Continuous kinetic scan using the samples from (a) monitoring optical output at 430 nm. Experimental conditions: $\lambda_{\text{ex}} = 514.5$ nm, laser power = 24 mW.

measured in the case of anthracene ($K_{\text{SV}} = 4492 \text{ M}^{-1}$; $k_{\text{q}} = 5.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) relative to DPA ($K_{\text{SV}} = 3465 \text{ M}^{-1}$; $k_{\text{q}} = 4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). In essence the number of initially sensitized triplets can be considered similar, albeit slightly favoring anthracene. Fig. 2b demonstrates the stability of the upconverted optical signals at 430 nm as a function of time during the course of steady-state laser photolysis of the respective chromophore mixtures. Over 10 minutes there were no obvious signs of anti-Stokes emission signal degradation in either sample, suggesting future device applications may be feasible. Similar to the anthracene system, the intensity of the upconverted fluorescence signal from DPA also follows a quadratic excitation power dependence ($\lambda_{\text{ex}} = 514.5$ nm) under a variety of experimental conditions (see ESI†). Please note that all control experiments performed with DPA alone failed to yield any measurable anti-Stokes optical output. The emission spectrum of the sensitized anti-Stokes DPA fluorescence completely superimposes the singlet fluorescence spectrum generated through direct excitation of the DPA chromophore (see ESI†).

Since the green-to-blue photon upconversion can be easily visualized in the $[\text{Ru}(\text{dmb})_3]^{2+}$ -DPA system, we decided to record digital photographs of the process. Fig. 3 shows one such image where a commercial (pulsed) green laser pointer ($\lambda_{\text{ex}} = 532$ nm, peak power < 5 mW) was used to selectively excite $[\text{Ru}(\text{dmb})_3]^{2+}$ in the mixture. The laser beam traverses the sample from bottom to top where visualization of the blue light generated through the sensitized annihilation process is easily discerned by the naked eye. This sample utilizes higher concentrations of both chromophores to enhance initial light absorption, triplet quenching, and thereby annihilation as described in eqns. (1) and (2). The “naked eye” image illustrates that low power green-to-blue upconversion is



Fig. 3 Digital photograph of upconverted fluorescence produced in 4 : 1 toluene- CH_3CN solutions of $[\text{Ru}(\text{dmb})_3]^{2+}$ (1.4×10^{-4} M) and DPA (filtered saturated solution). Excitation by a commercial green laser pointer ($\lambda_{\text{ex}} = 532$ nm, <5 mW peak power).

indeed realized in these chromophore mixtures. The blue color appearance of the anti-Stokes fluorescence in Fig. 3 corresponds to the emission spectrum presented in Fig. 2a, $\lambda_{\text{max}} \sim 430$ nm. At the present time we cannot completely account for the substantial enhancement of the anti-Stokes emission efficiency in the DPA system relative to that originally expected based on differences in singlet fluorescence quantum yield. There is no question that the anthracene ground state absorption spectrum diminishes in intensity over long term photolysis while the $[\text{Ru}(\text{dmb})_3]^{2+}$ MLCT band remains intact. Since the annihilation product yields singlet anthracene in close proximity to a ground state species, anthracene dimerization provides a pathway in competition with singlet fluorescence. Anthracene dimerization is consistent with the ground state absorption data described above and is known to be quite efficient.⁸ However, to the best of our knowledge there have not been any studies that detail anthracene dimerization processes subsequent to triplet annihilation. Importantly, this “photochemical” pathway is not available in the case of DPA since the steric bulk provided by the phenyl groups in the 9- and 10-positions prohibits the geometry required for dimerization. We believe it is this difference in dimerization reactivity that is responsible for the disparity in the anti-Stokes emission intensity over that expected based upon the variations in the singlet fluorescence quantum yields.

The current observations suggest the viability of harnessing MLCT sensitized triplet annihilation in device applications requiring the efficient production of high energy photons and/or excited states using low energy and low power light sources. As Ru(II) MLCT complexes are well known to exhibit

electroluminescence,^{9,10} we believe that a strategy similar to that presented here could be utilized to electrochemically sensitize the production of blue and UV-light using low voltages for display and lighting applications.

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