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Nonlinear Photochemistry Squared: Quartic Light Power Dependence Realized in Photon Upconversion

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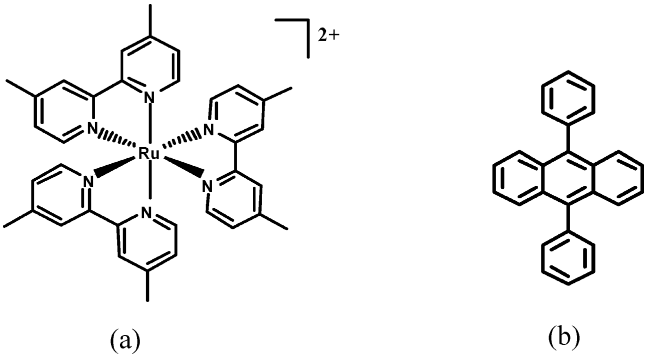
Simultaneous two-photon excitation of a solution mixture of $[Ru(dmb)_3]^{2+}$ and 9,10-diphenylanthracene (DPA) using 860 nm light pulses from a Ti:Sapphire laser resulted in triplet energy transfer followed by triplet−triplet annihilation (TTA), ultimately leading to upconverted DPA fluorescence from the sensitized DPA triplets. The photochemistry sequence was confirmed by the unprecedented quartic (x^4) incident light power dependence exhibited by this process, which incidentally generated a record anti-Stokes shift of 1.38 eV for sensitized TTA.

Introduction

Sensitized triplet−triplet annihilation (TTA) photochemistry continues to emerge as a promising wavelength-shifting technology. This process generates higher-energy photons from the absorption of lower-energy light by an efficiently quenched triplet sensitizer through sequential, highly allowed one-photon absorptions, producing TTA from the energy-transfer products. In essence, the energy stored in two sensitized triplet molecules is combined to produce a higher-energy singlet state and a corresponding ground-state species. This strategy has proven exceedingly effective when metal-based sensitizers are combined in concert with aromatic triplet acceptors/annihilators.[1,2] In terms of technological relevance, these low-power upconversion processes are readily visualized by the naked eye and have been successfully translated into a variety of solid polymeric host materials.[1e−g,i]

Simultaneous two-photon excitation (TPE) processes are generally accomplished through the use of high peak power ultrafast lasers with wavelengths ranging from the visible to the near-IR. TPE of various chromophores has led to widespread fundamental scientific progress along with notable applications in chemistry, materials science, imaging, photolithography, and micro-to-nanofabrication.[3−8] Inspired by the pursuit of new opportunities in photonics, we postulated whether the sensitized TTA process could be adapted to TPE technology. This would effectively replace the two *sequential* one-photon excitations typically associated with TTA with two independent *simultaneous* two-photon excitations, the latter exhibiting an unprecedented quartic (x^4) incident light power dependence.[9] As it is well established that Ru^{II} metal-to-ligand charge-transfer chromophores are susceptible to TPE[10] and the $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) excited state successfully promotes sensitized TTA with 9,10-diphenylanthracene (DPA),[1b] this molecular donor−acceptor pair represent a rational departure point for the present prototypical study.

CHART 1: Chemical Structures of (a) $[Ru(dmb)_3]^{2+}$ and (b) DPA



Experimental Section

General. $[Ru(dmb)_3](PF_6)_2$ was synthesized according to the published procedure.[11] 9,10-Diphenylanthracene and spectroscopic-grade acetonitrile were purchased from Aldrich and used as received.

Spectroscopic Measurements. The static absorption spectra were measured with a Cary 50 Bio UV−vis spectrophotometer from Varian. Single-wavelength emission intensity decays of $[Ru(dmb)_3]^{2+}$ in CH_3CN were acquired with a N_2-pumped dye laser (2−3 nm fwhm) from PTI (GL-3300 N_2 laser, GL-301 dye laser) using an apparatus that has been previously described.[12] Coumarin 510 was used to tune the unfocused pulsed excitation beam. Two-photon excitation measurements were accomplished with a Ti:Sapphire laser (Chameleon Ultra II, Coherent) tuned to afford 860 nm excitation at 80 MHz. The laser output was focused onto the sample cell (1 cm path length cuvette) with a planar convex lens of 65 mm focal length placed inside a time-correlated single-photon counting spectrometer (Edinburgh Instruments, LifeSpec II). The emission was collected using a microchannel plate photomultiplier tube (Hamamatsu R3809U-50) in a Peltier-cooled housing. One-photon excitation at 430 nm was accomplished by frequency doubling the

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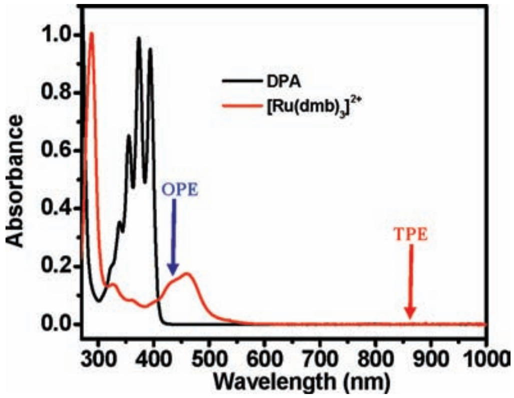

Figure 1. Normalized absorption spectra of $[Ru(dmb)_3]^{2+}$ and DPA in CH_3CN. The blue and red arrows indicate the experimental positions used for selective one- and two-photon excitation (OPE and TPE) of $[Ru(dmb)_3]^{2+}$, respectively.

860 nm excitation output from the Ti:Sapphire laser using a second-harmonic generator (Angewandte Physik & Elektronik GmbH). The power of these laser beams was measured using a Molectron Fieldmate sensor and power meter (Coherent). The optical power of the laser beam at the sample was controlled by placing a series of neutral density filters in front of the sample. All samples were deoxygenated for at least 30 min with high purity argon prior to all measurements, and a positive argon pressure was maintained throughout the experiments. All spectral data were collected and processed separately in Origin 8.0.

Stern−Volmer Quenching. The Stern−Volmer and bimolecular quenching constants were obtained according to the Stern−Volmer relation shown in eq 1

$$I_0/I = 1 + K_{SV}[Q] \tag{1}$$

where I_0 and I represent the photoluminescence intensities in the absence and 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 the DPA energy-transfer acceptor. In a typical experiment, 9.6 μM $[Ru(dmb)_3]^{2+}$ was deaerated with argon for at least 30 min, and the emission intensity was collected upon 860 and 430 nm excitation, measured as a function of DPA concentration. The determined Stern−Volmer (K_{sv}) and the bimolecular (k_q) quenching constants obtained upon one- and two-photon excitation are each the average of two independent measurements at each excitation wavelength.

Results and Discussion

The chemical structures of the two chromophores pertinent to this investigation are shown in Chart 1, and Figure 1 displays the absorption spectra of the chromophores measured in CH_3CN. The colored arrows indicate the respective wavelengths of the excitation light utilized. Ti:Sapphire laser output (Chameleon Ultra II, Coherent) at 860 nm was chosen as this wavelength provided the highest possible incident power while preserving selective TPE of the $[Ru(dmb)_3]^{2+}$ chromophore in the presence of DPA. Quenching of the $[Ru(dmb)_3]^{2+}$ photoluminescence with increasing DPA concentration was quantitatively measured following both one-photon excitation at 430 nm (10 mW @ 80 MHz) and TPE at 860 nm (1 W @ 80 MHz) in argon-degassed CH_3CN (Figure 2). Stern−Volmer analyses of the data obtained from two independent sets of experiments (<5% variation) under each excitation condition resulted in average K_{sv} values of 5121 and 5213 M^{-1}, with respective k_q's of 5.56×10^9 and 5.66×10^9 M^{-1} s^{-1} using $\tau_0 =$ 0.92 μs. The Stern−Volmer quenching data indicate that the triplet energy-transfer kinetics of the $[Ru(dmb)_3]^{2+}$/DPA donor/acceptor combination is the same regardless of the excitation pathway. Similar comparisons have been made in electron-transfer quenching of metallated porphyrins under TPE.[13] Note that the bimolecular energy-transfer rate constants obtained here are well below the diffusion limit of the solvent, 1.9×10^{10} M^{-1} s^{-1} at 25 °C.[14] In any case, these triplet-state quenching kinetics are more than adequate to support TTA photochemistry.[1]

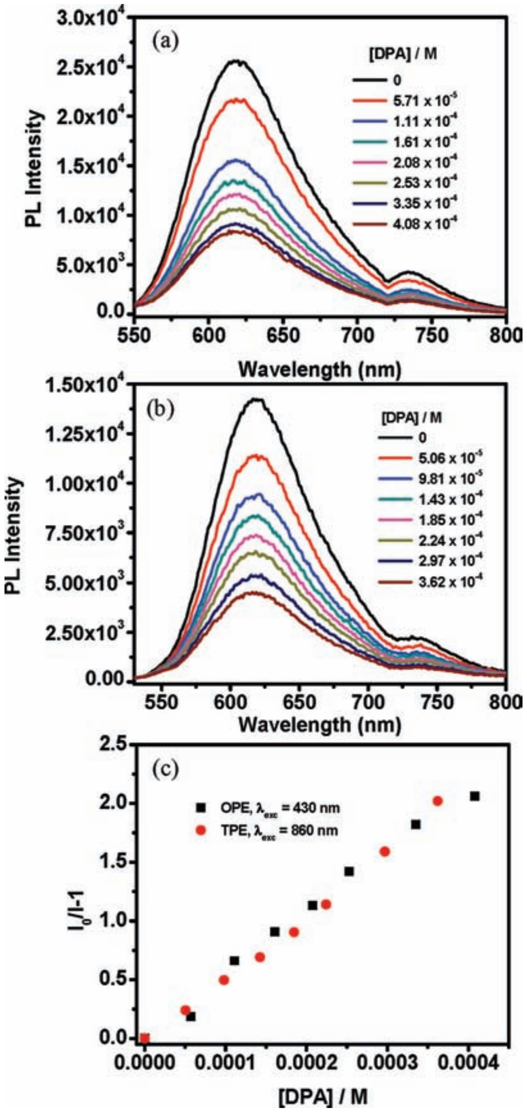

Figure 2. (a) Select photoluminescence emission spectra of 9.6 μM $[Ru(dmb)_3]^{2+}$ measured as a function of DPA concentration in deaerated CH_3CN upon (a) 430 nm excitation at 8 mW and (b) 860 nm excitation at 1.05 W, while (c) shows the Stern−Volmer plot generated from the integrated data from (a) and (b). The feature at long wavelengths is an artifact of the detection system.

Now that it is clearly established that the TPA process produces sensitized DPA triplets in an analogous fashion to OPE, we questioned whether the subsequent TTA reaction would take place. As TTA produces singlet DPA fluorescence, the incident 860 nm near-IR excitation would be readily upconverted to blue photons, leading to an unprecedented anti-Stokes shift for photochemical-induced upconversion, $\Delta E =$ 1.38 eV. As the TPE-promoted TTA process would be initiated from two-sequential simultaneous two-photon excitations, the sensitized upconverted singlet fluorescence emanating from DPA

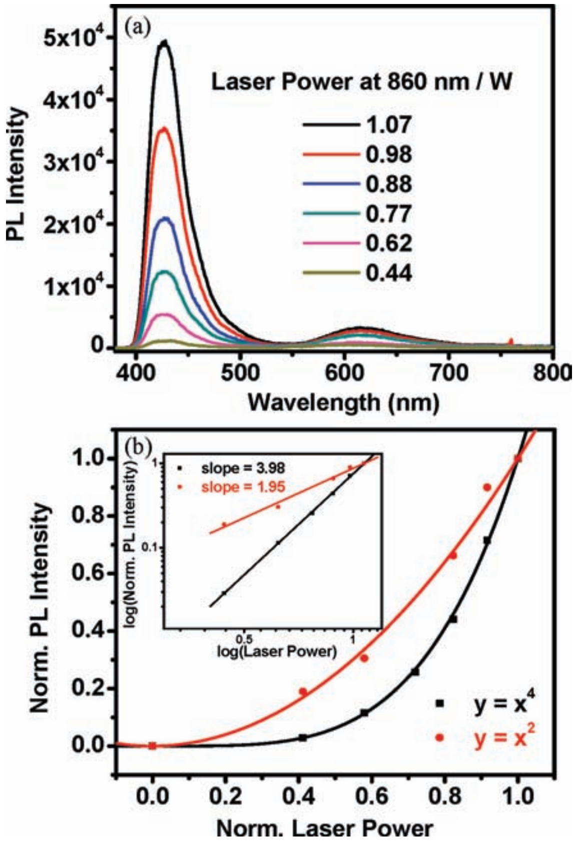

Figure 3. (a) Emission intensity profile of upconverted DPA and residual photoluminescence of [Ru(dmb)$_3$]$^{2+}$ following selective excitation of [Ru(dmb)$_3$]$^{2+}$ at 860 nm in a deaerated CH$_3$CN mixture of 9.6 μM [Ru(dmb)$_3$]$^{2+}$/2.48 × 10^{-4} M DPA, measured as a function of incident optical power. The pulse repetition rate was 80 MHz. (b) Normalized integrated emission intensity from panel (a) plotted as a function of the normalized incident light power. The solid black and red lines represent the best quartic (x^4) and quadratic (x^2) fits to the data points, respectively. Inset: Double logarithm plot of the data points in (b).

should display an extraordinary quartic (x^4) incident light power dependence. This is indeed the case when a solution mixture containing 9.6 μM [Ru(dmb)$_3$]$^{2+}$ and 2.48 × 10^{-4} M DPA in deaerated CH$_3$CN is excited at 860 nm, Figure 3. Analysis of the integrated upconverted DPA emission intensity (high-energy emission band) measured as a function of the incident laser power (Figure 3a) resulted in the anticipated quartic power dependence, as illustrated by the solid black squares and fit line (x^4) displayed in Figure 3b. The residual unquenched photoluminescence intensity of [Ru(dmb)$_3$]$^{2+}$ was also measured as a function of the incident 860 nm laser power in the same experiment (Figure 3a, low-energy emission band), resulting in the expected quadratic (x^2) dependence, as illustrated by the solid red circles and fit line presented in Figure 3b. The inset in Figure 3b presents double logarithm plots of the data in order to better differentiate between the two- and four- ($x^2 \times x^2$) photon excitation processes. Indeed, the slopes of the solid red and black lines in the inset are 1.95 and 3.98, respectively, indicating that the photochemistry that drives the observed residual photoluminescence of [Ru(dmb)$_3$]$^{2+}$ and the upconverted DPA fluorescence in the solution mixture upon 860 nm excitation is certainly two- and four-photon processes, respectively. Independent control experiments performed with 860 nm excitation (1 W) on a deaerated CH$_3$CN solution of [Ru(dmb)$_3$]$^{2+}$ (9.6 μM) or DPA (2.48 × 10^{-4} M) did not result in any measurable anti-Stokes emission emanating from DPA. Only when the two chromophores were combined were we able to observe upconverted DPA emission centered at 440 nm under the 860 nm two-photon excitation conditions.

Conclusion

The current experimental results illustrate the successful application of two-photon light activation applied to bimolecular triplet energy transfer. Triplet−triplet annihilation of the energy-transfer products yields upconverted blue fluorescence with a record anti-Stokes shift of 1.38 eV for the TTA process with respect to the 860 nm excitation light. Given the widespread application of TPE processes in materials chemistry, we postulate that the concepts presented here can potentially be translated into new experimental designs, fabrication schemes, sensory materials, and light-promoted chemical transformations.

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