Inorg. Chem. **2009**, *48*, 2541−2548

Inorganic Chemistry

Article

Supra-Nanosecond Dynamics of a Red-to-Blue Photon Upconversion System

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Received November 4, 2008

Blue-green upconverted emission from 2-chloro-*bis*-phenylethynylanthracene (2CBPEA) sensitized by the red-absorbing platinum(II)tetraphenyltetrabenzoporphyrin (PtTPBP) has been investigated in *N,N*-dimethylformamide (DMF). The upconverted singlet fluorescence of 2CBPEA resulting from its sensitized triplet−triplet annihilation (TTA) is observed following selective excitation of PtTPBP at 635 ± 5 nm. Stern−Volmer analysis of the photoluminescence quenching of PtTPBP by 2CBPEA yields a bimolecular quenching constant of 1.62×10^9 M^{-1} s^{-1}, slightly below the diffusion limit in DMF at room temperature. The TTA process was confirmed by the quadratic dependence of the integrated upconverted singlet fluorescence emission profile of 2CBPEA measured as a function of 635 nm incident laser power. Time-resolved emission spectra following 630 nm nanosecond laser pulses illustrate the prompt nature of porphyrin phosphorescence quenching and the delayed nature of the upconverted singlet fluorescence from 2CBPEA. Transient absorption decays monitored at the peak of the characteristic 2CBPEA triplet−triplet excited-state absorption (490 nm) measured as a function of incident nanosecond 630 nm pump laser fluence recovered the rate constant for the sensitized TTA process, $k_{TT} = 5.64 \pm 0.08 \times 10^9$ M^{-1} s^{-1}. To calculate this rate constant, we determined the triplet−triplet extinction coefficient of 2CBPEA (12,500 M^{-1} cm^{-1} at 490 nm) utilizing triplet energy transfer from donors with known excited-state extinction coefficients, namely $[Ru(bpy)_3]^{2+}$ and 2-acetonaphthone and averaged these values. The current work, to the best of our knowledge, represents the first example of red-to-blue upconversion thus demonstrating another viable sensitized TTA process, as well as providing the first measurements of k_{TT} in a photon upconverting scheme. As 2CBPEA is stable under ambient conditions, this chromophore represents an almost ideal candidate for light-producing sensitized TTA in aerated polymeric materials, and we demonstrate successful translation of the present donor−acceptor/annihilator system into a low T_g polyurethane.

Introduction

Photon upconversion, a phenomenon based on sensitized triplet−triplet annihilation (TTA) in the present contribution, continues to emerge as a promising wavelength-shifting technology. The sensitized TTA mechanism allows nonlinear upconversion to become linked to sequentially highly allowed one photon absorptions, thereby permitting the use of low power non-coherent continuous-wave excitation sources. This process was first introduced by Parker and Hatchard in non-covalent organic systems whose triplet sensitizers exhibited low intersystem crossing yields, thus limiting the upconversion efficiency.[1,2] Since then, tremendous advancement has been made in this area by our group and others by utilizing various heavy metal-containing sensitizers ranging from those that exhibit metal-to-ligand charge transfer as in the case of Ru(II)[3,4] and Ir(III),[5] as well as those that exhibit low energy π-π^* transitions as is the case for the wide range of metalloporphyrins that have been investigated to date.[6−12] Our group has recently reported the first example of non-

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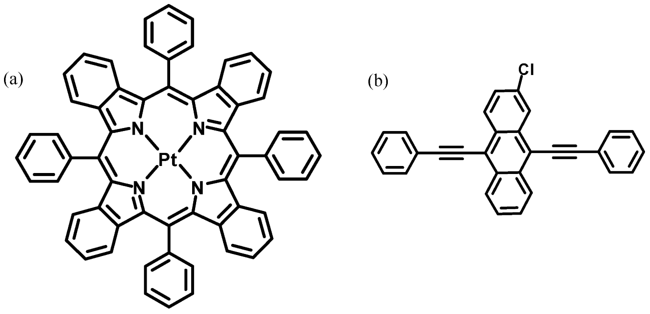
Chart 1. Chemical Structures of (a) PtTPBP and (b) 2CBPEA



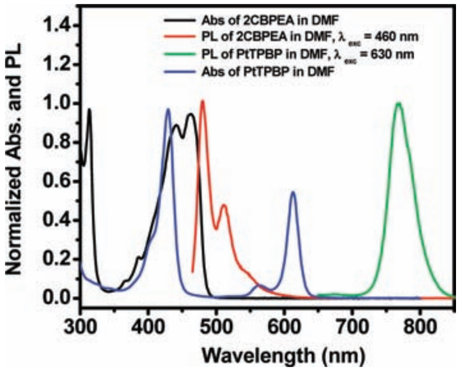


Figure 1. Absorbance and emission spectra of PtTBBP and 2CBPEA in degassed DMF at room temperature, all normalized to an arbitrary maximum of 1.0.

coherent low-power upconversion in solid polymer films and have shown that selective green excitation of palladium(II) octaethylporphyrin leads to triplet sensitization of 9,10-diphenylanthracene (DPA) eventually producing blue singlet DPA fluorescence in these films.[6] This process was clearly visible with the naked eye in an illuminated laboratory using a low power non-coherent excitation source.[6] These results demonstrate the potential utility of these systems for real world applications in photonics.

More recently we have reported a photochemical upconversion approach to produce white light upon selective excitation of $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) in the presence of 9,10-dimethylanthracene,[13] as well as the first example of photon upconversion using a phthalocyanine triplet sensitizer to observe yellow upconverted emission from rubrene.[14] We have also incorporated the latter system into the solid state and demonstrated that despite the photooxidation of rubrene in aerated solution resulting in the formation of the endoperoxide, the upconversion process is stable for days in air-equilibrated thin polymer films.[14] The instability of rubrene as the acceptor/annihilator in solution partially inspired the present work where we sought out an air-stable solution based acceptor that could be employed in an upconverting scheme as the acceptor/annihilator while shifting the excitation energy toward the red region of the spectrum with retention of a large anti-Stokes energy shift.

The upconverting scheme described in this manuscript utilizes platinum(II) tetraphenyltetrabenzoporphyrin (PtTPBP) as the triplet sensitizer and 2-chloro-*bis*-phenylethynylanthracene (2CBPEA) as the acceptor/annihilator. 2CBPEA is one of the most efficient fluorescent compounds known and is widely used as the emitting chromophore in chemiluminescent formulations such as the popular glow stick Cyalume.[15,16] Because of its remarkable high emission efficiency in the visible region of the spectrum, good solubility in a variety of solvents, chemical and thermal stability, and inertness toward dioxygen,[17] we propose this compound to be a viable acceptor/annihilator for use in upconversion schemes. The present contribution focuses on the static and supra-nanosecond excited-state absorption and emission dynamics of the upconverting system PtTPBP/2CBPEA in *N*,*N*-dimethylformamide (DMF); the former enabled the sensitized TTA rate constant (k_{TT}) of ^{3}2CBPEA* to be determined. We also present preliminary studies where these two chromophores are incorporated into a low T_g polyurethane matrix, producing upconverted photons within this solid material.

Experimental Section

General Information. 2-Chloro-*bis*-phenylethynylanthracene (2CBPEA), 2′-acetonaphthone (2-AcN), and DMF were purchased from Aldrich. Pt(II) meso-tetraphenyltetrabenzoporphyrin (PtTPBP) was purchased from Frontier Scientific and used without further purification. Spectroscopic grade toluene was purchased from Fisher Chemicals. Commercially available $[Ru(bpy)_3]Cl_2.6H_2O$, bpy = 2,2′,-bipyridine, was purchased from Aldrich and converted into the PF_6 salt by metathesis with NH_4PF_6 (Aldrich) in water. The polyurethane, Tecoflex EG-80A, was purchased from Lubrizol.

Spectroscopic Measurements. The static absorption spectra were measured with a Cary 50 Bio UV−vis spectrophotometer from Varian. Steady-state luminescence spectra were obtained with a PTI SPC spectrofluorimeter. Excitation was achieved by a 635 ± 10 nm diode laser (LHR635-100EC) purchased from Lasermate. In some cases a 635 ± 10 nm notch filter (Semrock) was placed in the emission path between the sample and the monochromator to remove scattered laser light from the emission profile. Incident laser power was varied using a series of neutral density filters. Emission lifetimes were measured on a nitrogen-pumped broadband dye laser (2−3 nm fwhm) from PTI (model GL-3300 N2 laser and model GL-301 dye laser) using an apparatus that has previously been

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described.[18] All luminescence samples were prepared either in a 1 cm^2 quartz cell purchased from Starna cells or in a specially designed 1 cm^2 optical cell bearing a sidearm roundbotton flask and were degassed for 30 min with high purity argon or subjected to a minimum of three freeze−pump−thaw degas cycles prior to all measurements The laser power was measured using a Molectron Power Max 5200 power meter. All attempts to measure the 77 K phosphorescence of 2CBPEA in 2-methyl-THF failed even upon the addition of 10% v/v ethyliodide since the quantum yield for this process is undoubtedly low.

Laser Flash Photolysis. Nanosecond transient absorption measurements were collected on a Proteus spectrometer (Ultrafast Systems LLC) equipped with a 150 W Xe-arc lamp (Newport), a Bruker Optics monochromator equipped with two diffraction gratings for visible and near-IR dispersion, respectively, with Si or InGaAs photodiode detectors (DET 10A and DET 10C, Thorlabs) optically coupled to the exit slit of the monochromator. Excitation of the samples was achieved from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant LD 355 II) operating at 10 Hz which was directed to the sample with an absorbance of ∼0.40 at the excitation wavelength. A 600 nm long pass filter was placed between the OPO and the sample to filter out residual second and third YAG harmonics. The data consisting of an average of 132 shots were collected from the Andor software and processed separately in Origin 8.0. The TTA rate constant was calculated by fitting the transient absorption decay observed at 490 nm as a function of the laser power to eq 1.

$$\frac{\mathrm{d}[^3\mathrm{M}^*]}{\mathrm{d}t} = -k_{\mathrm{T}}[^3\mathrm{M}^*] - k_{\mathrm{TT}}[^3\mathrm{M}^*]^2 \tag{1}$$

Here [^{3}M*] is the concentration of the triplet excited state of 2CBPEA, k_{TT} is the TTA rate constant, and k_{T} is the triplet decay rate constant. This kinetic scheme was first introduced by Birks in studies of triplet−triplet interactions in concentrated fluid solutions.[19] Integration of eq 1 produces eq 2 which readily translates into a convenient 3-parameter expression (eq 3) that was used to fit the experimental data, minimized by nonlinear least-squares in Origin 8.0.

$$[^3\mathrm{M}^*] = \frac{[^3\mathrm{M}^*]_0 \mathrm{e}^{-k_{\mathrm{T}}t}}{1 + [^3\mathrm{M}^*]_0 \dfrac{k_{\mathrm{TT}}}{k_{\mathrm{T}}}(1 - \mathrm{e}^{-k_{\mathrm{T}}t})} \tag{2}$$

$$y = \frac{p1}{1 + \left(\dfrac{p1 \times p2}{p3}\right)\exp(p3 \times x) - \left(\dfrac{p1 \times p2}{p3}\right)} \tag{3}$$

The terms of eq 3 are defined as y = [^{3}M*], x = t (time), $p1$ = [^{3}M*]$_0$, $p2$ = k_{TT}, and $p3$ = $-k_{\mathrm{T}}$. It should be noted that the measured decay curve for [^{3}M*] is in absorbance units; hence to convert this to molar concentration, the triplet−triplet extinction coefficient of 2CBPEA was employed, 1.25×10^4 M^{-1} cm^{-1}. This latter value was also acquired in the present study, and its measurement is described below.

The molar extinction coefficient of the triplet excited state of 2CBPEA was determined using the energy transfer method as previously described.[20,21] Using laser flash photolysis, this method involves the use of a donor with a known triplet extinction coefficient in the presence of the acceptor in a concentration sufficient enough to quench all the donor triplets. The transient absorption difference spectrum of the donor (prompt signal) and the sensitized acceptor (peak value following energy transfer) are measured at their respective (well separated) wavelength maxima and compared using eq 4. Equation 4 correlates the two molar extinction coefficients where$^3\varepsilon$(D), and$^3\varepsilon$(A) are the triplet molar extinction coefficients of the donor (known) and acceptor (unknown), respectively, and Δ*A* (D) is the maximum optical density of the donor triplet in the absence of the acceptor and Δ*A* (A) is the maximum optical density of the acceptor triplet when both donor and acceptor are present.

$$\frac{^3\varepsilon(\mathrm{A})}{^3\varepsilon(\mathrm{D})} = \frac{\Delta A(\mathrm{A})}{\Delta A(\mathrm{D})} \tag{4}$$

In the current experiments two donor molecules were independently used (2-AcN and [Ru(bpy)$_3$]$^{2+}$) to transfer their triplet excited-state energy to 2CBPEA. The donor molecule 2-AcN (ε_{T}(430 nm) = 10 500 M^{-1} cm^{-1})[21] was excited at 355 nm whereas [Ru(bpy)$_3$]$^{2+}$ (ε_{T}(364 nm) = 25 400 M^{-1} cm^{-1})[22] was excited at 510 nm, well outside the ground-state absorbance regions of 2CBPEA. The average triplet excited-state extinction coefficient of 2CBPEA was calculated from these two donors (ε_{T}(490 nm) = 12,500 M^{-1} cm^{-1}) and used to determine the k_{TT} value reported herein.

Results and Discussion

Most of the efficiently functioning upconverting systems based on sensitized TTA generally possess energy gaps on the order of ∼0.5 eV between the excitation light and the maximum singlet fluorescence emission band exhibited by the acceptor/annihilator. The present experimental system offers one of the largest energy differences to date (0.58 eV) that places both the absorption of the donor (red) and the upconverted fluorescence of the acceptor/annihilator (blue-green) in the visible region of the electromagnetic spectrum. The chemical structures of the compounds used in the present study, PtTPBP and 2CBPEA, are given in Chart 1.The ground-state absorption spectra of PtTPBP and 2CBPEA were measured at room temperature in DMF, Figure 1. PtTPBP displays strong transitions for the Soret band at 430 nm and Q-band at 611 nm which tails to ∼650 nm whereas 2CBPEA shows strong absorptions at 441 and 461 nm with extinction coefficients of 3.5×10^4 M^{-1} cm^{-1} and 3.6×10^4 M^{-1} cm^{-1} respectively, Supporting Information, Figure S1. The emission spectra of degassed solutions of PtTPBP in DMF displayed in Figure 1 shows phosphorescence at 770 nm with a long-lived excited-state lifetime of 37.5 μs at room temperature while that of a dilute solution of 2CBPEA (1.3 μM) shows intense fluorescence at 480 nm with a shoulder at 510 nm. Both compounds exhibit high

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phosphorescence and fluorescence quantum yields of 0.70[23] and 0.85[24] for PtTPBP and 2CBPEA, respectively. We were unable to accurately determine the triplet excited-state energy of 2CBPEA but it is estimated to be between 1.27−1.61 eV since it is later shown to efficiently quench the triplet excited state of PtTPBP which occurs at 1.61 eV and is estimated to be slightly higher in energy than half that of the singlet fluorescence of 2CBPEA at 2.53 eV. All attempts to measure the 77 K phosphorescence of 2CBPEA in 2-methyl-THF failed even in the presence of 10% v/v ethyliodide indicating that the quantum yield for this process is undoubtedly low.

The triplet excited-state photoluminescence of PtTPBP is efficiently quenched by 2CBPEA by energy transfer and is readily quantified by the Stern−Volmer relation (eq 5), where I_0 and τ_0 are the

$$I_0/I = \tau_0/\tau = 1 + K_{sv}[Q] \tag{5}$$

photoluminescence intensity and lifetime in the absence of the quencher while I and τ are the intensities and lifetimes in the presence of the quencher, respectively; [Q] is the molar concentration of the quencher and K_{sv} is the Stern−Volmer quenching constant. The bimolecular quenching constant (k_q) is obtained from the slope of the Stern−Volmer plot according to the relation, $K_{sv} = k_q\tau_{0.}$ Stern−Volmer plots of $\tau_0/\tau - 1$ versus [Q] (Supporting Information, Figure S2) clearly demonstrate dynamic quenching with a K_{sv} of 69530 M^{-1} and k_q of 1.84×10^9 M^{-1} s^{-1}, approaching the diffusion limit in DMF of 8.3×10^9 M^{-1} s^{-1} at 25 ^{o}C.[25] The quenching pathway is presumed to proceed through triplet−triplet energy transfer, and the upconverted fluorescence that is observed and discussed below must result from TTA implying efficient triplet production in the porphyrin quenching step.

To investigate the stability of the acceptor/annihilator (2CBPEA) under aerated conditions in DMF, the absorbance spectra of 50 μM 2CBPEA was measured as a function of irradiation time for 2 h during continuous 460 nm excitation at 45 mW incident power, (Supporting Information, Figure S3). No changes were observed in the absorbance spectrum over this entire time period even at higher excitation energy, thereby illustrating the stability of 2CBPEA under ambient conditions. Selective excitation of 3.4 μM PtTPBP in the presence of 1 mM 2CBPEA with $\lambda_{exc} = 635 \pm 5$ nm in a freeze−pump−thaw degassed solution of DMF resulted in the observation of delayed upconverted fluorescence from 2CBPEA (Figure 2a). Deaerated conditions were required to avoid the competing energy transfer reaction of excited PtTPBP with dioxygen which substantially diminishes upconversion yields in fluid solution. The integrated upconverted delayed fluorescence measured as a function of the incident laser power was evaluated; these data were normalized to the highest integrated emission intensity as well as the highest incident power. As shown in Figure 2b, the upconverted fluorescence intensity increases in a nonlinear manner as a function of increasing incident light power from 0.0538 W cm^{-2} to 0.561 W cm^{-2}. The solid line in Figure 2b represents the best quadratic fit (x^2) to the data and definitively establishes the nonlinear photochemistry that drives the upconversion through sensitized TTA.

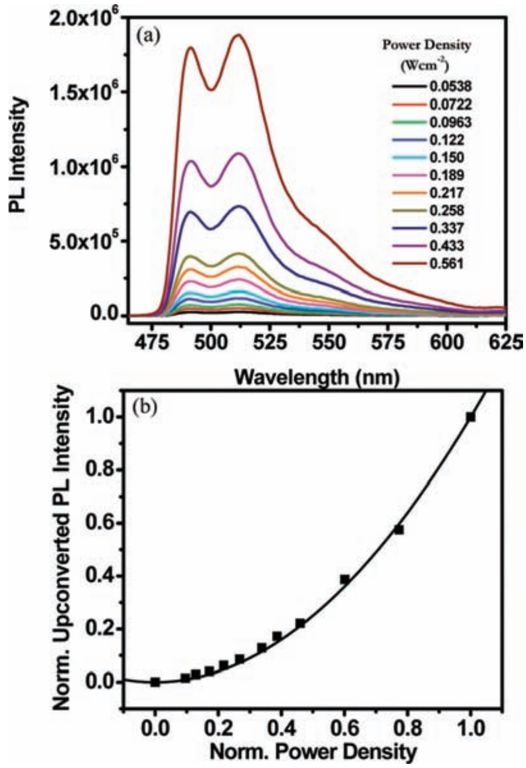

Figure 2. (a) Photoluminescence intensity profile of a freeze−pump−thaw degassed solution of PtTPBP (3.4 μM) and 2CBPEA (1 mM) measured as a function of 635 ± 5 nm incident laser power density. (b) Normalized integrated emission intensity data from panel a plotted as a function of the normalized incident power density of the laser. The solid black line is the best quadratic fit to the integrated emission data, $x^{2.0}$.

To further illustrate that photon upconversion is indeed a delayed phenomenon, the time-resolved emission spectra (λ_{ex} = 630 nm) of a solution containing 3.7 μM PtTPBP and 8.9×10^{-5} M 2CBPEA in deaerated DMF, Supporting Information, Figure S4, clearly demonstrate the delayed nature of the upconverted fluorescence from 2CBPEA. The peak corresponding to the phosphorescence of PtTPBP at 770 nm decays with respect to time while the upconverted fluorescence of 2CBPEA develops with time. The delayed fluorescence of 2CBPEA following long wavelength (630 nm) triplet sensitization is compared to the prompt fluorescence of 2CBPEA observed with 460 nm excitation in DMF (Supporting Information, Figure S5). The delayed upconverted fluorescence of 2CBPEA is anti-Stokes shifted relative to the excitation and appears to be somewhat red-shifted compared to the prompt fluorescence of 2CBPEA. This is as a result of the higher concentration of 2CBPEA that is needed to facilitate photon upconversion. The intensity of the lower energy transition in the delayed upconverted fluorescence of 2CBPEA is greater than that observed in the prompt fluorescence spectrum of this compound because of the inner filter effect at the high concentration required for upconversion, which was indeed verified by control experi-

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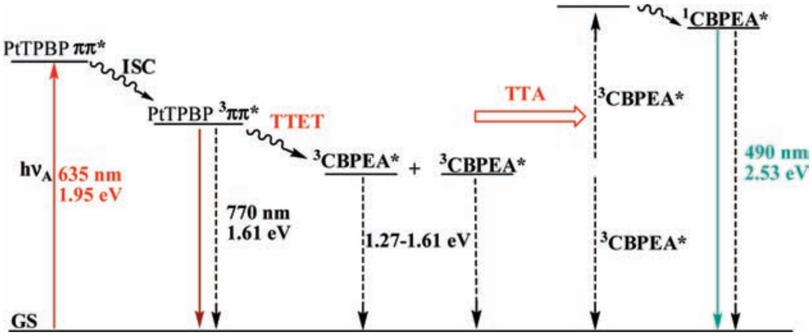
Scheme 1. Jablonski Diagram Illustrating the Sensitized TTA Upconversion Process between PtTPBP and 2CBPEA



ments at high 2CBPEA concentrations. Importantly, the emission profiles of the 2CBPEA fluorescence measured in each experiment are essentially the same, thereby illustrating that the delayed fluorescence signal emanates from singlet 2CBPEA which is produced through TTA. Scheme 1 summarizes the processes that produce the upconverted fluorescence of 2CBPEA. Selective excitation of PtTPBP leads to TTA of 2CBPEA resulting in the generation of the singlet excited 2CBPEA which radiatively decays to the ground-state by singlet fluorescence.

Nanosecond transient absorption (TA) measurements of deaerated solutions of PtTPBP (5.1 μM) and a dilute solution of 2CBPEA (13.2 μM) at room temperature in DMF were performed at 630 and 470 nm excitation, respectively, to elucidate the excited-state dynamics of these complexes. The TA-difference spectra of PtTPBP and 2CBPEA at different delay times are shown in Figure 3. Upon 630 nm excitation of PtTPBP in argon purged DMF, negative absorption signals are observed at 420 and 604 nm corresponding to ground-state bleach of the Soret and Q-bands of the porphyrin, respectively. Broad positive excited triplet state absorptions are observed between 440 to 570 nm and 630 to 800 nm, Figure 3a.[26,27] The amplitude of the TA-difference spectra in the former region is about three times that of the latter region and are similar to previously reported excited states of various metalloporphyrins.[26] Analysis of the TA-difference spectra at 500 and 660 nm resulted in an identical single exponential decay (37.4 μs) as obtained for the PtTPBP phosphorescence (37.5 μs). Also worth mentioning is at slightly higher PtTPBP concentration (7.8 μM) the TA-difference spectra of PtTPBP at 500 and 660 nm resulted in biexponential decays with components of 37.5 and 17.8 μs. The biphasic behavior observed in the transient decays of higher concentrations of PtTPBP is similar to that previously reported which has been attributed to TTA processes between excited metalloporphyrin phosphors.[28]

Nanosecond TA measurements were conducted on a 1 mM argon purged solution of 2CBPEA in DMF. Figure 3b displays the spectra obtained at different delay times following excitation of 2CBPEA at 470 nm. Positive excited-state features are observed at 480 nm with a shoulder near 506 nm. Analysis of the decay at 480 nm and at 506 nm recovered a single exponential decay with a lifetime of 123 μs. The long lifetime originating from the TA-difference spectra between 480−510 nm is attributed to the triplet−triplet excited-state absorption of 2CBPEA. The results are similar to previous reported TA studies on 9,10-*bis*-phenylethynylanthracene.[29]

Upon addition of 2CBPEA (1.0 mM) to the degassed PtTPBP (3.4 μM) DMF solution and excitation at 630 nm, a broad excited-state absorption peak relative to 2CBPEA alone was observed at a wavelength maximum near 490 nm, Figure 4. This occurs at the expense of a significant amount of the transient features associated with the triplet excited state of PtTPBP. Although a considerably large concentration of the acceptor was added to effectively quench the triplet excited state of the porphyrin, small residual transient features corresponding to that of the ^{3}PtTPBP* excited state were still observed. We believe these features combined with the limited probe beam transmission over this wavelength range contribute to the loss of the spectral resolution in the TA difference spectrum seen in the PtTPBP/2CBPEA solution mixture. Emission corrected (for 2CBPEA delayed fluorescence which substantially overlaps the 2CBPEA triplet-to-triplet absorption) TA difference spectra were also collected for this mixture and resulted in quantitatively similar spectral features to those shown in Figure 4. Clearly, the loss of spectral resolution is not a result of the sensitized delayed fluorescence being integrated into the difference spectra. It should be noted, however, that the excited-state absorption features in the solution mixture occur in essentially the same region of the spectrum on a time scale that parallels that of the independently measured solution containing only 2CBPEA. Hence, it is concluded that the excited-state absorption difference spectra observed in the PtTPBP/2CBPEA mixture is predominantly derived from the triplet excited state of the 2CBPEA acceptor from sensitized triplet energy transfer eventually leading to TTA. The kinetics of the TTA process is thus conveniently monitored using the major absorption transient of the triplet sensitized species, which in this case is 2CBPEA. When two excited triplets combine several reaction pathways can occur resulting in products such as the excited quintet ($^5A_2$*), a triplet excited state $^3A_1$*, or the

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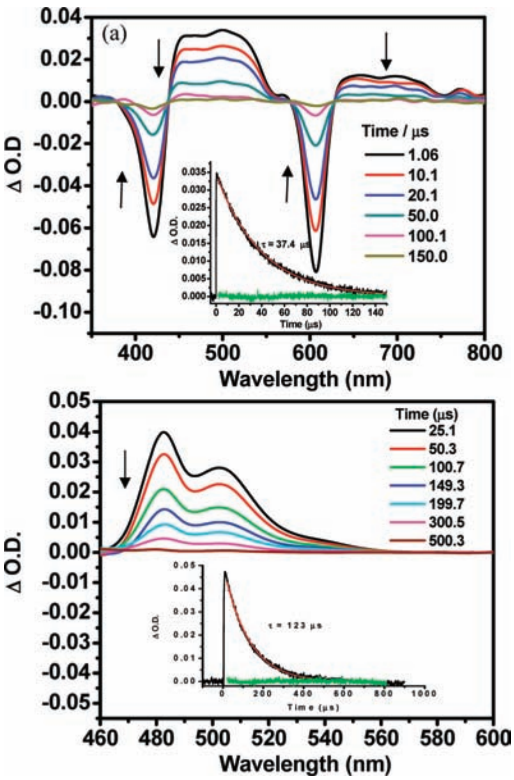

Figure 3. (a) Transient absorption difference spectrum of 5.1 μM PtTPBP measured at several delay times in deaerated DMF, 2.0 mJ/pulse, λ_{exc} = 630 nm. The inset shows the single exponential fit to the 500 nm transient with residuals presented in green. (b) Transient absorption difference spectrum of 13.2 μM 2CBPEA measured at several delay times in deaerated DMF, 2.0 mJ/pulse, λ_{exc} = 470 nm. The inset shows the single exponential fit to the 480 nm transient with residuals presented in green.

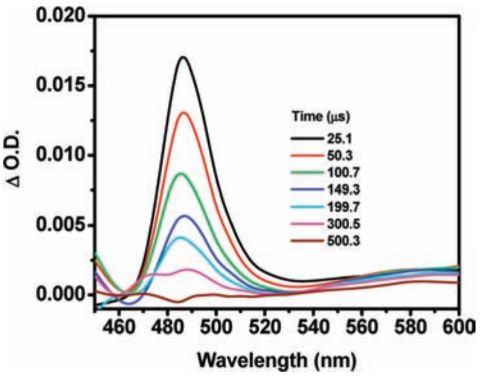

Figure 4. (a) Transient absorption difference spectrum of 3.40 μM PtTPBP and 1 mM 2CBPEA measured as a function of delay time in deaerated DMF, 2.0 mJ/pulse, λ_{exc} = 630 nm.

formation of the excited singlet (${}^1A_0{}^*$) and hence annihilation controlled delayed fluorescence.[30] These processes are outlined in eqs 6−8. However, the major mode of decay of the combining triplets in the upconverting system is TTA followed by the formation of an excited singlet, eq 8.

$${}^3A_1^* + {}^3A_1^* \rightleftharpoons {}^5(AA)_2^* \rightleftharpoons {}^5A_2^* + {}^1A_0 \tag{6}$$

$$\rightleftharpoons {}^3(AA)_1^* \rightleftharpoons {}^3A_1^* + {}^1A_0 \tag{7}$$

$$\rightleftharpoons {}^1(AA)_0^* \rightleftharpoons {}^1A_0^* + {}^1A_0 \tag{8}$$

To determine the TTA rate constant we quantitatively investigated the triplet excited-state properties of 2CBPEA with two well studied triplet donors, 2-AcN[21,31,32] and $[Ru(bpy)_3]^{2+}$ [22,33] to determine its triplet extinction coefficient at 490 nm. 2-AcN and $[Ru(bpy)_3]^{2+}$ were selectively excited at 355 and 510 nm (2 mJ/pulse), respectively, since 2CBPEA displays no significant ground-state absorption at these wavelengths. The dynamics of the triplet−triplet excited-state absorption of 2-AcN was monitored in the presence and in the absence of the acceptor, 2CBPEA, at 430 nm in argon degassed DMF solutions containing the chromophores. The triplet excited state of 2-AcN shows a monoexponential decay with a lifetime of 13.9 μs in the absence of 2CBPEA as shown in the inset in Supporting Information, Figure S6. Sufficient 2CBPEA was added to the degassed solution of 2-AcN to effectively quench the triplet excited state of the latter. Since the acceptor strongly absorbs in the region of the 2-AcN triplet−triplet absorption, it was difficult to collect the kinetic trace of 2-AcN at 430 nm upon addition of 2CBPEA since the probe beam was unable to penetrate the sample effectively. However, upon addition of 2CBPEA to the degassed DMF solution of 2-AcN, a transient absorption growth was observed with a pseudo-first-order rise time of ~1.3 μs at 490 nm. Therefore, enough 2CBPEA solid was added to the solution of 2-AcN until no further increase was observed in the 490 nm transient indicating that there is complete triplet-state energy transfer between 2-AcN and 2CBPEA. The ΔOD of 2-AcN in the absence of the acceptor and the ΔOD of the sensitized ^{3}2CBPEA* were taken from Supporting Information, Figure S6 and by using (ε_T 2-AcN at 430 nm = 10,500 M^{-1} cm^{-1}),[21] and applying these values to eq 4 resulted in a triplet extinction coefficient of 1.35 × 10^4 M^{-1} cm^{-1} for 2CBPEA. To further confirm this value, similar experiments were conducted using $[Ru(bpy)_3]^{2+}$ as the donor. Excitation of $[Ru(bpy)_3]^{2+}$ at 510 nm in the absence of the acceptor in deaerated DMF solution resulted in triplet excited-state absorption with a ΔOD of 0.0208 at 364 nm which decays with a first order rate constant of 1.06 μs. 2CBPEA was added to effectively quench the triplet excited-state absorption of $[Ru(bpy)_3]^{2+}$ which resulted in the growth of a new peak at 490 nm corresponding to the triplet excited-state absorption of 2CBPEA. Since the triplet extinction coefficient of $[Ru(bpy)_3]^{2+}$ at 364 nm is known (ε_T(364 nm) = 25,400 M^{-1} cm^{-1})[22] as well as the ΔOD of 2CBPEA at 490 nm (0.00943), the triplet extinction coefficient of 2CBPEA was calculated to be 1.15 × 10^4 M^{-1} cm^{-1}. The average of the triplet extinction coefficient of 2CBPEA calculated by triplet energy transfer of the donors 2-AcN and $[Ru(bpy)_3]^{2+}$, 1.25 × 10^4 M^{-1} cm^{-1}, were employed in all calculations involving this value and the results of the experiments above are summarized in Table 1.

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Table 1. Summary of the Experimental Data Used in the Determination of the ^{3}2CBPEA* Extinction Coefficient by Triplet Energy Transfer[a]

donor	$^3\lambda$(D)*/ nm	$^3\varepsilon$(D)* at $^3\lambda$/M^{-1} cm^{-1}	ΔOD(D)* at $^3\lambda$	ΔOD(A)* at 490 nm	$^3\varepsilon$(A)* at 490 nm/ 10^4 M^{-1} cm^{-1}
2-can	430	10500[b]	0.00866	0.0111	1.35
$[Ru(bpy)_3]^{2+}$	364	25400[c]	0.0208	0.00943	1.15

[a] D = donor; A = acceptor (2CBPEA). [b] Ref 21. [c] Ref 22.

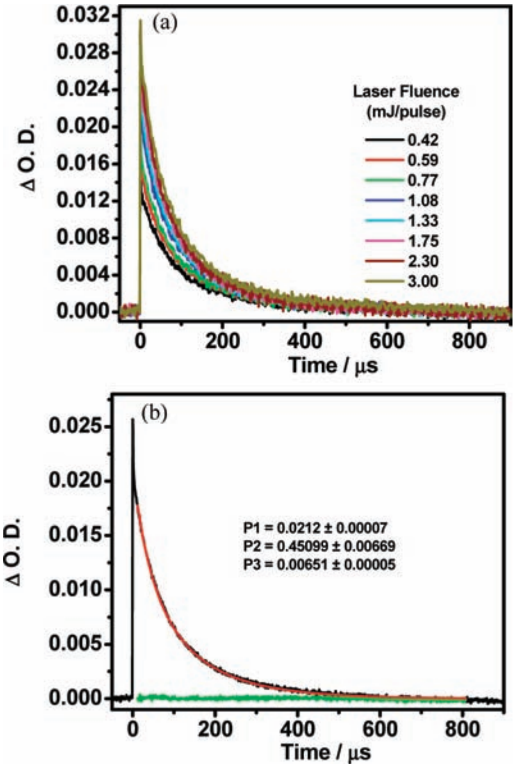

Figure 5. (a) Time resolved absorption kinetics at 490 nm of 3.40 μM PtTPTBP and 1 mM 2CBPEA in deaerated DMF measured as a function of laser pulse energy at 630 nm. (b) Representative kinetic fit (1.75 mJ/pulse data) to eq 3 (red line) and the residuals of this fit (green line).

To determine the sensitized TTA rate constant (k_{TT}) a series of kinetic transient absorption traces were collected at the triplet excited-state maximum of 2CBPEA upon selective excitation of the metalloporphyrin (630 nm) in a solution containing PtTPBP/2CBPEA (Figure 5a), measured as a function of the incident laser pulse energy. Fitting the transient absorption decays at this maximum using eq 3 recovered the value for $k_{TT} = 5.64 \pm 0.08 \times 10^9$ M^{-1} s^{-1}, Figure 5b. We note that a similar graphical-based analysis was previously employed in studies of concentration dependent TTA in biacetyl and camphorquinone in benzene and benzophenone in Freon.[30] Our present k_{TT} values approach the diffusion limit in DMF, $k_{diff} = 8.3 \times 10^9$ M^{-1} s^{-1} at 25^{o}C,[25] thereby indicating that TTA is a diffusion controlled process under the present experimental conditions.

Importantly, upon selective excitation of the metalloporphyrin sensitizer with 635 ± 5 nm light in DMF, the blue-green upconverted fluorescence is clearly discernible to the naked eye even in a well-illuminated room as shown in the digital photograph in Figure 6a. We have also demonstrated the viability of photon upconversion by incorporating the present upconverting system in a low T_g polymer for potential applications as host material in photonics and have visualized the upconversion process in this material with the aid of a bandpass filter using 635 nm excitation under ambient, air-saturated conditions. This upconverting bar is air stable and the upconversion phenomenon can be visualized for months with selective excitation of the long wavelength sensitizer. It should be noted that the polymer bar was not maintained under any special conditions and was simply stored in the ambient. These latter results demonstrate the stability of the two chromophores with respect to air in a solid host material. The combined data obtained in the present study suggests that with the proper combination of chromophores photon upconversion realized as a result of sensitized TTA is truly a generalized phenomenon as long as the proper thermodynamic and kinetic requirements are met.

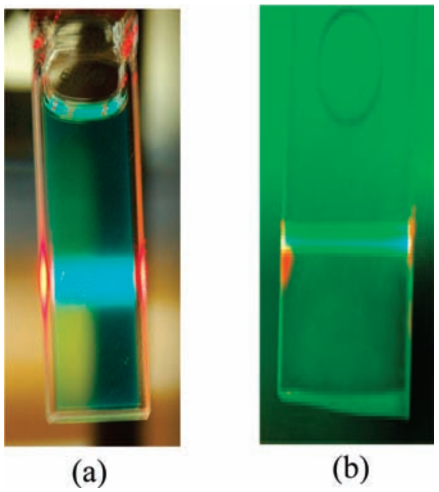

Figure 6. (a) Digital photograph of 3.40 μM PtTPBP and 1 mM 2CBPEA in deaerated DMF with laser diode excitation at 635 nm. (b) Digital photograph of the two chromphores absorbed in Tecoflex 80A following 635 ± 5 nm laser diode excitation with the emission filtered through a bandpass filter.

Conclusion

The current observations demonstrate the stability of the sensitized triplet annihilation of 2CBPEA upon 635 ± 5 nm excitation of PtTPBP thereby resulting in upconverted blue-green singlet fluorescence from 2CBPEA in deaerated DMF. The sensitized TTA process was confirmed using a variety of spectroscopic measurements including static and dynamic photoluminescence in addition to transient absorption spectrometry. Both chromophores are shown to be air stable as incorporation of the upconverting system into a low T_g polymer displays upconverted emission for months upon selective long wavelength excitation of the sensitizer. The supra-nanosecond transient absorption and photoluminescence dynamics of PtTPBP and 2CBPEA were investigated independently and in combination in DMF solutions. Excited state triplet energy transfer from $[Ru(bpy)_3]^{2+}$ and 2-AcN was used to estimate the triplet−triplet extinction coefficient of 2CBPEA in DMF which then facilitated the evaluation of k_{TT}. Analysis of the excited-state absorption decays at the peak of the characteristic 2CBPEA triplet absorption at 490 nm monitored as a function of incident pump laser fluence (selectively exciting PtTPBP) recovered the value of k_{TT}, 5.64 ± 0.08 × 10^9 M^{-1} s^{-1}. This value approaches the diffusion limit of the DMF solvent (8.3 × 10^9 M^{-1} s^{-1} at 25^{o}C), indicating that TTA is a diffusion controlled process in the present experimental system.

Acknowledgment. This research was supported by the Air Force Office of Scientific Research (FA9550-05-1-0276), the NSF (CHE-0719050), the ACS-PRF (44138-AC3), and the BGSU Research Enhancement Initative.

Supporting Information Available: Extinction coefficient determination of ^{3}2CBPEA*, Stern−Volmer quenching of PtTPBP by 2CBPEA, absorbance spectra of 2CBPEA in aerated DMF during photolysis, time-resolved spectra, prompt and delayed photoluminescence spectra of 2CBPEA. This material is available free of charge via the Internet at http://pubs.acs.org.

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