Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Photochemical & Photobiological Sciences

An international journal
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Journal Name

ARTICLE

Photochemical Upconversion and Triplet Annihilation Limit from a Boron Dipyrromethene Emitter

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Non-coherent sensitized red-to-green upconversion has been achieved utilizing platinum(II) tetraphenyltetrabenzoporphyrin (PtTPTBP) as the triplet sensitizer and a nearly quantitatively fluorescent *meso*-(2,6-dichloropyridyl)-substituted boron dipyrromethene (Cl$_2$PyBODIPY) chromophore (Φ = 0.99 in toluene) as the energy acceptor/annihilator in deoxygenated toluene. Dynamic Stern-Volmer analysis revealed that PtTPTBP phosphorescence as quenched by Cl$_2$PyBODIPY occurs with a K$_{SV}$ of 108,000 M^{-1}, yielding a triplet-triplet energy transfer rate constant of 2.3 $\times$ 10^9 M^{-1}s^{-1}. Using a non-coherent red light-emitting diode excitation source centered at 626 nm, the incident power dependence responsible for generating singlet BODIPY fluorescence in the green was shown to traverse quadratic to linear regimes, the latter being achieved near 60 mW/cm^2. These data were consistent with a photochemical upconversion mechanism being responsible for generating singlet fluorescence from the Cl$_2$PyBODIPY chromophores through sensitized triplet-triplet annihilation (TTA). Integrated delayed fluorescence transients were utilized to reveal the TTA efficiency for the Cl$_2$PyBODIPY chromophore and saturated near 46%, representing the lower limit for the TTA process. Kinetic modelling of the delayed fluorescence transient produced from 1.5 mJ laser pulses (λ_{ex} = 615 nm) revealed a maximum limiting TTA efficiency of 64% for this upconverting composition, implying that this is indeed an extremely relevant acceptor/annihilator composition for photochemical upconversion.

Introduction

Photochemical upconversion based on sensitized triplet-triplet annihilation (TTA) represents an emerging technology poised to harness lower energy photons for a variety of applications.[1-4] In this regard, progress has already been made in areas as diverse as broadening photovoltaic spectral response curves,[5-9] photoelectrosynthetic transformations,[10] cycloaddition photochemistry,[11] upconversion imaging,[12] and wastewater disinfection.[13] Similarly, significant fundamental progress has also been achieved in the selection of sensitizer and acceptor compositions,[14-33] the measurement science to best quantify this phenomenon,[34-38] as well as host materials that support photochemical upconversion in a variety of nonpolar and aqueous environments.[39-57] The primacy of reaction kinetics has also been recently highlighted along with suggestions on how to further improve upon upconversion quantum yields.[58]

In 2008, we successfully demonstrated that boron dipyrromethene (BODIPY) dyes possessed suitable singlet-triplet energy gaps enabling the use of the red-absorbing Pt(II) tetraphenyltetrabenzoporphyrin (PtTPTBP) triplet sensitizer affording high efficiency red-to-green and red-to-yellow upconversion in solution.[16] At that time, this work represented a

departure from the exclusive use of aromatic hydrocarbons as emitters in solution-based upconversion compositions. As BODIPY dyes are photochemically and thermally stable with respect to most aromatic hydrocarbons yet have similar singlet-triplet gaps, they are particularly well suited for broader incorporation in upconversion schemes. It was later shown that the Cu(I) metal-to-ligand charge transfer chromophore [Cu(dpp)$_2$]$^+$, dpp = 2,9-diphenyl-1,10-phenanthroline, could also be used as an effective sensitizer for red-to-green upconversion using the BODIPY-based laser dye pyrromethene-546.[27] Recent work from the Zhao group at Dalian has shown that select BODIPY dyes can also be used as triplet sensitizers in upconversion schemes,[59] further expanding the inventory of purely organic-based compositions.[60-64] Given the growing importance of BODIPY dyes in upconversion schemes, we decided to evaluate non-coherent upconversion in a recently synthesized green BODIPY emitter (Cl$_2$PyBODIPY) using PtTPTBP as the triplet sensitizer while determining the TTA limit that can be achieved in this donor-acceptor pair using pulsed laser excitation. Incorporation of chloro substituents *ortho* to the BODIPY substituent of the pyridine in Cl$_2$PyBODIPY and related derivatives has been correlated with

an increased fluorescence quantum yield, a valuable attribute for an upconversion emitter.[65] A Jablonski diagram for these chromophores is presented as Scheme 1 and illustrates the relevant energetics leading to sensitized TTA. Selective Q-band excitation of PtTPTBP (λ_{max} = 614 nm) at 626 ± 25 nm (fwhm) using a red light-emitting diode (LED) produces singlet BODIPY fluorescence in the green in a facile manner, centered near 536 nm in toluene. Under these benign LED excitation conditions, the incident light power dependence traversed the quadratic to linear regimes, consistent with the sensitized TTA mechanism. In pulsed laser experiments at higher sensitizer concentrations, the TTA quantum yield for $Cl_2PyBODIPY$ annihilation was determined to saturate at 46%. Since this BODIPY dye is insensitive to self-quenching, likely a result of the pyridyl *meso*-substitution, concentrations as large as 91 μM possess near quantitative fluorescence quantum efficiency in toluene (Φ_f = 0.99). Therefore, the resultant calculated upconversion efficiency for the composition under pulsed laser excitation at saturation was an impressive 41%, implying that upconversion efficacy is largely a function of the TTA efficiency. Kinetic modelling of the delayed fluorescence transient under the strongest pulsed excitation conditions (1.5 mJ @ 615 nm) revealed a maximum limiting TTA efficiency of 64% for this composition.
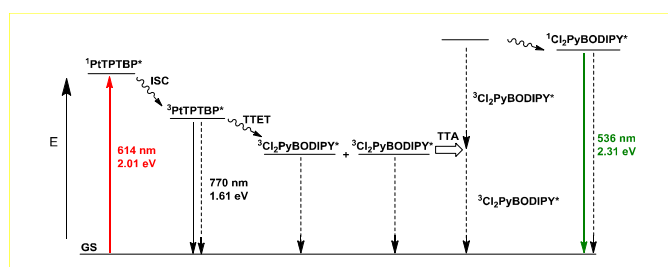
Scheme 1. Qualitative Jablonski diagram illustrating sensitized TTA-based upconversion occurring between PtTPTBP and $Cl_2PyBODIPY$.

Experimental

General Information

Platinum(II) tetraphenyltetrabenzoporphyrin (PtTPTBP) was purchased from Frontier Scientific. Rhodamine B (99+%) was obtained from Acros and used as received. The *meso*-pyridyl substituted boron dipyrromethene dye $Cl_2PyBODIPY$ was synthesized according to the published procedure.[65] Spectroscopic grade toluene were purchased from Aldrich Chemical Company and used as received.

Static UV-Vis and Photoluminescence Measurements

Absorption spectra were measured with an Agilent 8453 diode array spectrophotometer. Steady-state photoluminescence spectra were recorded using a FS920 spectrometer from Edinburgh Instruments equipped with a 450 W Xe arc lamp and a Peltier-cooled single-photon counting photomultiplier detection system (R2658P). All luminescence samples were prepared in a specially designed 1 cm² optical cell bearing a

sidearm round bottom flask and were subjected to a minimum of three freeze-pump-thaw degas cycles prior to measurement. In some cases, non-coherent excitation was achieved using a high power red LED (626 ± 25 nm fwhm, VAOL-SO1XAX-SA) purchased from VCC, which was equipped with a focus lens. The incident LED excitation power density was varied using a series of neutral density filters placed directly in front of the sample whose output was measured using an Ophir Nova II/PD300-UV power meter. The fluorescence quantum yield of $Cl_2PyBODIPY$ in toluene in optically dense solutions (91 μM) was determined relative to rhodamine B in ethanol (Φ = 0.49)[66] using a triangular cuvette providing front face detection of both sample and standard.

Time-Resolved Photoluminescence Measurements

Single wavelength emission decay kinetics spectra were collected using an LP 920 laser flash photolysis system from Edinburgh Instruments equipped with a PMT detector (R928, Hamamatsu). Excitation of the samples in these experiments was accomplished using a Nd:YAG/OPO laser system from OPOTEK (Vibrant 355 LD-UVM) operating at 1 Hz tuned to produce pulsed output at the appropriate excitation wavelength. This identical spectrometer was also equipped with an Andor iStar iCCD detector that permitted the collection of time-gated emission spectra used in the determination of sensitized TTA quantum efficiencies (Φ_{TTA}) by comparing the prompt and delayed fluorescence signals as described in detail previously.[28, 35, 36, 38] The incident laser power in these experiments was varied using a series of neutral density filters or by modifying the Q-switch delay. The delayed fluorescence was integrated over a 1 ms time window initiating from 250 ns after the 615 nm laser pulse (λ_d), capturing the delayed fluorescence in its entirety while suppressing any prompt fluorescence from $Cl_2PyBODIPY$. The prompt fluorescence, resulting from direct excitation of the $Cl_2PyBODIPY$ chromophore at 490 nm (λ_p), was integrated over a 250 ns time window starting from 50 ns before arrival of the laser pulse. The yield of delayed fluorescence (F_d) from $Cl_2PyBODIPY$ was measured after selective excitation of the PtTPTBP sensitizer at 615 nm (λ_d), which was directly compared to the prompt fluorescence (F_p) from $Cl_2PyBODIPY$ measured in the identical composite sample, observed by exciting this acceptor directly at 490 nm (λ_p). A mixture of 18 μM PtTPTBP and 91 μM $Cl_2PyBODIPY$ in toluene was contained in 1 cm² freeze-pump-thaw optical cells were used for detecting prompt and delayed fluorescence. The mixture has the same optical density (OD = 2) at their respective excitation wavelengths of 490 nm and 615 nm. Therefore 100% of the excitation photons are absorbed in each instance and they generate excited singlets with similar depth profiles in both the prompt and delayed fluorescence experiments. In both instances the $Cl_2PyBODIPY$ fluorescence is produced in identical environments and the TTA yield is readily calculated using Eq. 1.[35, 36]

$$\Phi_{TTA} = \left(\frac{2F_d E_p \lambda_d}{F_p E_d \lambda_p} \right) / \Phi_q \qquad (1)$$

Here E_d and E_p are the respective laser pulse energies and the factor of 2 scales the annihilation yield to unity, as two excited triplets are necessary to produce one fusion product. Φ_q is the quenching efficiency at the specified Cl$_2$PyBODIPY concentration, extrapolated from Stern-Volmer analysis.

Results and Discussion

The chemical structures of the PtTPTBP sensitizer and Cl$_2$PyBODIPY acceptor/annihilator used in this study along with their normalized ground state absorption and emission spectra in toluene are presented in Figure 1.
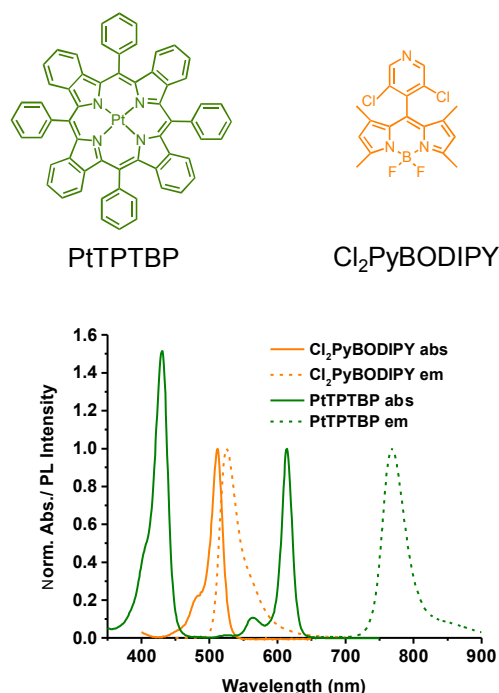

Figure 1. Normalized absorption and emission spectra of PtTPTBP and BODIPY measured in toluene.

PtTPTBP, whose phosphorescence is centered at 767 nm in deaerated toluene, displays strong absorptions at 430 nm (Soret) along with two Q-bands at 563 nm and 614 nm. These Q-bands are separated from the absorption and emission bands of Cl$_2$PyBODIPY at 512 nm and 526 nm, respectively, yielding a reasonably sized spectral window circumventing re-absorption of the upconverted photoluminescence being generated. The phosphorescence intensity decay of the PtTPTBP chromophore was efficiently quenched by the addition of Cl$_2$PyBODIPY, which was readily quantified by the Stern-Volmer relation (τ_o/τ

$= 1 + K_{SV}$[Cl$_2$PyBODIPY]. Here, τ_0 is the lifetime in the absence of the quencher and τ is the lifetime in the presence of Cl$_2$PyBODIPY; [Cl$_2$PyBODIPY] is the molar concentration of the quencher and K_{SV} is the Stern-Volmer quenching constant ($K_{SV} = k_q\tau_0$). The dynamic Stern-Volmer plot generated from these phosphorescence lifetime measurements revealed a K_{SV} of 108,000 M^{-1} with $k_q = 2.3 \times 10^9$ M^{-1}s^{-1} as presented in Figure 2. This bimolecular triplet-triplet energy transfer rate constant falls slightly below the diffusion limit in toluene,[67] indicating that the driving force for this photoreaction is not optimal.
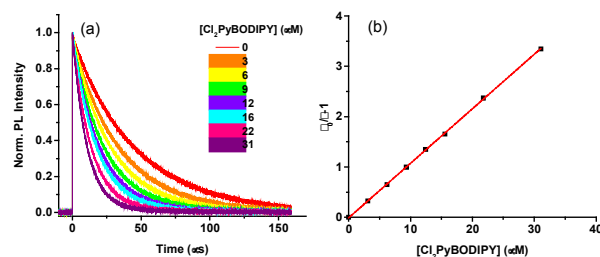

Figure 2. (a) Photoluminescence intensity decays of 1.6 µM PtTPTBP measured as a function of Cl$_2$PyBODIPY concentration in deaerated toluene. (b) Stern-Volmer plot generated from lifetime quenching of PtTPTBP with Cl$_2$PyBODIPY in dearated toluene using single exponential fits to the data from part (a).

Figure 3 shows the double logarithm plot featuring the integrated intensity of the upconverted fluorescence from Cl$_2$PyBODIPY measured as a function of red LED incident power density ($\lambda_{ex} = 626 \pm 25$ nm). Lens-focused red LED photons passed through a series of neutral density filters furnished a range of excitation power densities from 7 mW/cm^2 to 150 mW/cm^2. Under conditions where the upconverted light was easily observed by the naked eye, LED excitation below 10 mW/cm^2 clearly generated a quadratic response. Deviations from this behaviour occurred slightly above 10 mW/cm^2, continuing to attenuate in slope until linear response was achieved near 60 mW/cm^2. These are clear manifestations of the anticipated kinetic limits resulting from the photochemical upconversion process as previously demonstrated by the Monguzzi group,[34] the Schmidt group,[35, 36] and this laboratory.[37] In short, the quadratic dependence is representative of Cl$_2$PyBODIPY triplet state decay and associated pseudo-first-order quenching processes (such as quenching by dissolved O$_2$) serving as the dominant decay pathway(s), i.e. the weak annihilation limit. Linear response indicates that the second-order annihilation dominates (strong annihilation limit) and the highest possible efficiencies for upconversion from the composition have been achieved. The unique feature of the present demonstration is that non-coherent red-to-green upconversion is shown to operate at reasonably low incident power densities whilst achieving both kinetic extremes of annihilation-producing fluorescence. The ease at which the strong annihilation limit was reached in this composition exemplifies the importance of using BODIPY class of chromophores as emitters in upconversion schemes.
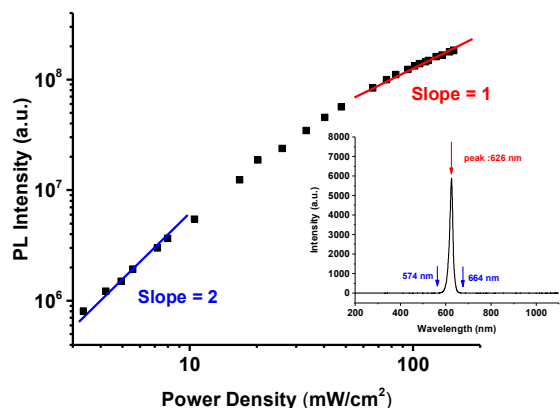
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Figure 3. Double logarithmic plots of the normalized upconversion emission intensity generated from $Cl_2PyBODIPY$ measured as a function of 626 nm incident non-coherent photons (red LED) in a mixture of 75 μM PtTPTBP and 91 μM $Cl_2PyBODIPY$ in deareated toluene. The colored lines are the linear fits with slopes of 1.0 (red, linear response) and 2.0 (blue, quadratic response) in the high and low power regimes, respectively. Inset: red LED spectral output.

Given the emerging relevance of BODIPY dyes in photochemical upconversion technology, we decided to evaluate the annihilation limit in $Cl_2PyBODIPY$ using the approach originally developed by Schmidt and coworkers.[35, 36] To the best of our knowledge the experiments described below represent the first attempts to quantify the triplet annihilation limit in a BODIPY dye. In order to evaluate the maximum possible TTA quantum efficiency from the PtTPTBP/$Cl_2PyBODIPY$ composition, optically concentrated samples were utilized, where the absorbance at $\lambda_{ex} \sim 2.0$.[38] The resultant TTA quantum yields calculated from the integrated prompt (directly excited) and delayed (sensitized) $Cl_2PyBODIPY$ transient fluorescence spectra using Eq. 1 are displayed in Figure 4. The $Cl_2PyBODIPY$ TTA quantum yield increases with increasing laser pulse energy (λ_{ex} = 615 nm) until a plateau is reached, signifying that the process has saturated, identical to that when linear incident power dependence is achieved in the related non-coherent excitation experiments presented in Figure 3. Since the numerator and denominator contained within the parentheses in Eq. 1 both scale linearly once this plateau region is reached, the efficiency for the TTA process has indeed reached its maximum. Under the current experimental conditions, the TTA efficiency (Φ_{TTA}) reaches an average saturated plateau of 46% in this composition in toluene (Figure 4b), which is within experimental error of the values previously measured for sensitized rubrene annihilation in toluene using a similar experiment.[35, 36] This is important as rubrene is generally regarded as a benchmark emitter in upconversion schemes, readily yielding some of the highest efficiencies recorded to date with red photon pumped upconversion.[4, 58] By inference, $Cl_2PyBODIPY$ clearly achieves the same annihilation efficiency as the aromatic hydrocarbon rubrene and is likely indicative of the values that can be achieved using structurally related BODIPY chromophores. It is important to note that these measured values represent the lower limit for the TTA event in $Cl_2PyBODIPY$ and the limiting efficiency at the maximum triplet concentration is significantly higher as discussed below. Since the saturation value for TTA measured in these experiments clearly exceed 40%, all quintets are regenerating their original excited triplets

and at least some of the post annihilation encounters generated T_2 excited $Cl_2PyBODIPY$ chromophores, where $T_2 > S_1$. This latter condition provides an additional intersystem crossing channel for generating fluorescent singlets derived from the annihilation event.[35, 36, 58] This gleans some insight into our work from 2008 where the upconversion efficiency from a PtTPTBP/BODIPY composition was first shown to surpass the so-called spin statistical annihilation limit of 11.1%.[16] The results found here strongly suggest that it is worthwhile to evaluate Φ_{TTA} of those original BODIPY dyes first used in photochemical upconversion. The corresponding upconversion yield (Φ_{UC}) in the PtTPTBP/$Cl_2PyBODIPY$ composition in toluene can be readily calculated from knowing the quenching efficiency (Φ_q = 0.91), the TTA efficiency, and the $Cl_2PyBODIPY$ fluorescence quantum yield (Φ_f = 0.99) as measured under the experimental conditions in Figure 4, $[\Phi_{UC} \sim \Phi_q\Phi_{TTA}\Phi_f = (0.91)(0.46)(0.99) = 0.41]$. This particular BODIPY dyes does not appear susceptible to significant self-quenching, likely due to the orthogonal pyridyl subunit projecting from the BODIPY *meso*-position preventing intermolecular π-stacking. Therefore, $Cl_2PyBODIPY$ appears to be an ideal candidate for the adaptation of upconversion technology requiring a green emitter.
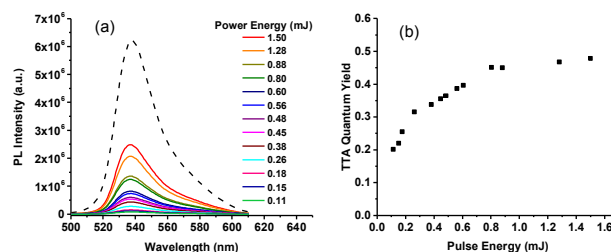

Figure 4. (a) Time gated iCCD detected delayed fluorescence spectra in 18 μM PtTPTBP and 91 μM $Cl_2PyBODIPY$ contained in deareated toluene obtained with various laser pulse energies at 615 nm (solid lines). The black dashed line is the prompt fluorescence spectrum $Cl_2PyBODIPY$ measured in the same sample obtained with a 0.63 mJ laser pulse at 490 nm. (b) Calculated TTA quantum yields as a function of incident laser pulse energy using the data from (a) and Eq 1.

As mentioned above, kinetic modelling of the delayed fluorescence transients can be used to reveal the true TTA efficiency limit occurring at the highest triplet concentration. This fitting permits access to the proportion of second order decay occurring in the initial portion of the transient and therefore the true limiting TTA efficiency.[35,36,38] A representative fluorescence intensity decay transient (sample from Figure 4 at 1.5 mJ pulse energy) along with its corresponding fit is presented in the ESI. Using the approach outlined by Schmidt and coworkers,[35,36] the limiting TTA efficiency under these conditions is 64%. This implies that the upconversion efficiency lies close to 60% under idealistic conditions. However, the experimental conditions necessary to achieve these values cannot be realized using low power continuous wave excitation such as that provided by terrestrial sunlight.

Conclusions

In summary, photochemical upconversion between PtTPTBP and Cl$_2$PyBODIPY operates quite efficiently in toluene under both low power LED and higher pulse energy laser pumping. The former experiments clearly demonstrate transitioning between the quadratic and linear incident power density regimes with a non-coherent red LED excitation source. Importantly, this upconverting composition can easily achieve high quantum efficiencies under low power excitation conditions. The pulse laser experiments permitted evaluation of the maximum annihilation efficiency that can be achieved under optical saturation conditions and was found to be 46%. Since the Cl$_2$PyBODIPY chromophore does not undergo any obvious self-quenching in toluene ($\Phi_f = 0.99$), the upconversion quantum efficiency was estimated to be 41% under the latter experimental conditions. Kinetic modelling of the delayed fluorescence transient under the strongest pulsed excitation conditions (1.5 mJ @ 615 nm) revealed the maximum limiting TTA efficiency for this composition, 64%. Therefore, the Cl$_2$PyBODIPY chromophore appears to be an ideal candidate for incorporation into upconversion schemes requiring the emission of green light and the BODIPY chromophores in general should prove viable surrogates for aromatic hydrocarbons as emitters in this wavelength shifting technology.
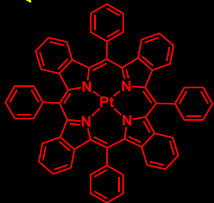
Acknowledgments

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λ_{ex} = 626 nm

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