

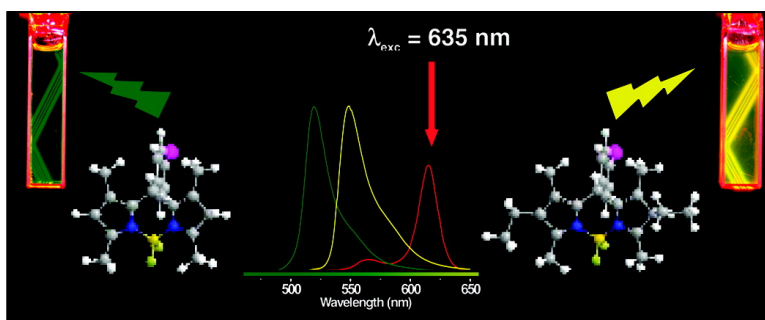
Communication

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Boron Dipyrromethene Chromophores: Next Generation Triplet Acceptors/Annihilators for Low Power Upconversion Schemes

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Photon upconversion based on sensitized triplet–triplet annihilation (TTA) continues to emerge as a promising wavelength-shifting technology. The sensitized TTA mechanism permits nonlinear upconversion phenomena to become linked to sequential highly allowed one-photon absorptions, thereby permitting the use of low-power noncoherent continuous-wave excitation sources. This strategy has proven exceedingly effective when late transition metal-based sensitizers are combined in concert with aromatic hydrocarbon-based triplet acceptors/annihilators.^{1,2} In many recent examples, the sensitized TTA upconversion process is readily visualized by the naked eye in a lighted room.^{1c–g} In addition to these technologically relevant light-producing reactions, we recently succeeded in the realization of “photochemical” upconversion to promote the [4 + 4] dimerization of anthracene, a photochemical reaction traditionally requiring ultraviolet light excitation.^{1d} What should be immediately recognized is the fact that in every single example of upconversion via sensitized TTA, the acceptor/annihilator molecules have been exclusively limited to aromatic hydrocarbons, largely based on anthracene derivatives.^{1,2} This represents a strategic choice since aromatic hydrocarbons conveniently possess large splitting in their singlet–triplet energy gaps, permitting the relevant sensitizer levels to be sandwiched between, facilitating the necessary thermodynamics. This limiting experimental reality has severely restricted both fundamental research and the broader applicability of low-power upconversion phenomena.

Fortunately, recent efforts have revealed the presence of large singlet–triplet energy gaps in the boron dipyrromethene (BODIPY) class of fluorophores, $E_T \approx 1.6$ eV.³ BODIPY chromophores are popular molecular probes exhibiting high fluorescence quantum yields and are strongly resistant to photobleaching thereby making them suitable candidates for incorporation into upconversion schemes.^{4–6} In the present study, the red-light absorbing platinum(II) tetraphenyltetraabenzoporphyrin (PtTPBP) was used as the triplet sensitizer ($\Phi_p = 0.7$,⁷ $\tau = 40.6$ μ s in benzene) in conjunction with two distinct iodophenyl-bearing BODIPY derivatives **BD-1**⁸ ($\Phi_F = 0.69$) and **BD-2**⁹ ($\Phi_F = 0.78$), producing highly efficient, stable green ($\Phi_{UC} = 0.0313 \pm 0.0005$) and yellow ($\Phi_{UC} = 0.0753 \pm 0.0036$) upconverted emissions in benzene, respectively. Notably, the nature of the current photochemical systems afforded highly reproducible upconversion quantum efficiency determinations, which to the best of our knowledge are the first time such quantitative measurements have been reported.

The two BODIPY chromophores were synthesized using standard procedures^{4,5,8,9} and the associated characterization data are consistent with their respective structures, see Supporting Information for details. Figure 1 presents the normalized absorption and

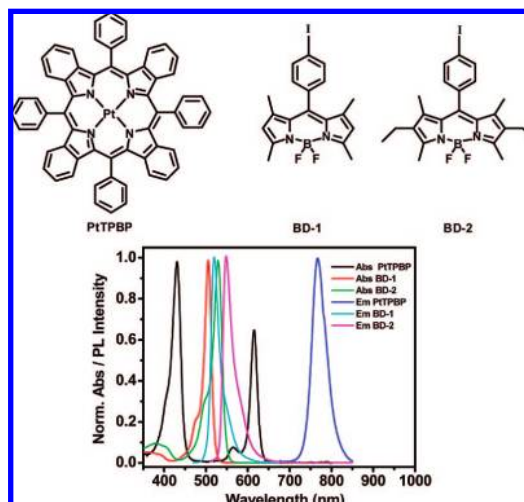


Figure 1. Normalized absorption and emission spectra of PtTPBP, **BD-1**, and **BD-2** in benzene.

emission spectra of the three chromophores used in the present study measured in benzene, the solvent utilized for all measurements herein. PtTPBP exhibits prominent visible absorptions with a Q-band maximum at 614 nm which tails to ~ 650 nm. **BD-1** and **BD-2** have similar absorption band shapes with maxima at 505 and 518 nm, respectively. The fluorescence spectra of **BD-1** and **BD-2** exhibit an almost mirror-image symmetry with their corresponding absorption spectra, $\lambda_{max} = 527$ and 548 nm, respectively. Selective excitation of PtTPBP at 635 ± 5 nm leads to the generation of long-lived phosphorescence at 766 nm, which has the ability to sensitize triplet state formation in either **BD-1** or **BD-2** through diffusive energy transfer, eventually leading to TTA of the ³BODIPY* chromophores. Triplet energy transfer rate constants from the PtTPBP sensitizer were established using dynamic Stern–Volmer analysis (Figures S3 and S4), yielding bimolecular quenching constants of 4.18×10^8 and 1.06×10^9 $M^{-1} s^{-1}$ for **BD-1** and **BD-2**, respectively. The attenuated quenching constant in the former is attributed to the smaller driving force for triplet energy transfer from the PtTPBP sensitizer.

Displayed in Figure 2a,b is the typical emission intensity power dependence of a solution containing PtTPBP and **BD-1** or **BD-2** upon 635 ± 5 nm excitation using a 635 ± 10 nm notch filter in the emission path. The sensitized anti-Stokes upconverted fluorescence of **BD-1** or **BD-2** is clearly visible and quantitatively reproduces the features of the singlet fluorescence spectra resulting from direct excitation of **BD-1** or **BD-2** in benzene. Analysis of the sensitized upconverted integrated emission intensity of **BD-1** or **BD-2** as a function of the incident light intensity is shown in Figure 2 panels c and d, respectively. The solid lines represent the

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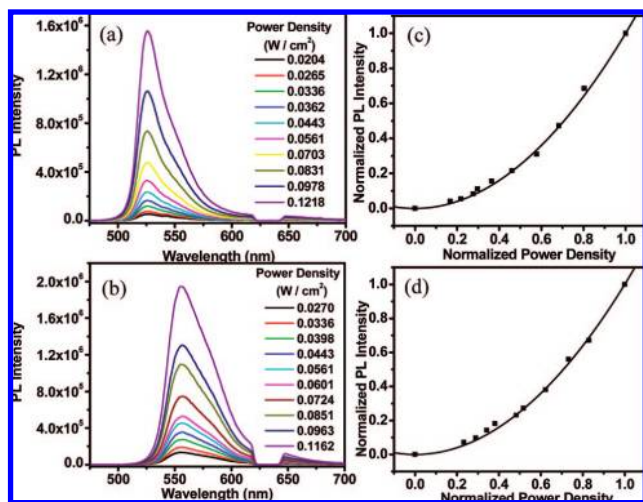


Figure 2. (a, b) Normalized upconverted emission intensity profile of **BD-1** and **BD-2**, respectively, following selective excitation of PtTPBP ($\lambda_{\text{ex}} = 635 \pm 5$ nm) measured as a function of incident power density with a notch filter in the emission path; (c, d) normalized integrated emission intensity from panels a and b, respectively, plotted as a function of the normalized incident light power. The black line in panels c and d represents the best quadratic fit to the data, x^2 .

best quadratic fits (x^2) to the data, illustrative of the nonlinear photochemistry driving these processes. Clearly, the upconverted fluorescence intensity is proportional to the square of the incident light power at 635 nm and hence to the square of the triplet BODIPY concentration.

The percent quantum efficiency of upconverted fluorescence was measured as a function of the concentration of both **BD-1** and **BD-2**, determined relative to a methylene blue quantum counter ($\Phi_{\text{f}} = 0.03$)¹⁰ with excitation at 635 ± 5 nm,¹¹ Figures S1 and S2. Although the emission profile of methylene blue does not effectively overlap that of **BD-1** or **BD-2**, highly reproducible quantum yield data were obtained in both instances over many independent measurements in our conventional single photon counting fluorimeter (see Supporting Information for details). Figure 3a displays the increase in the observed upconverted fluorescence of **BD-1** with increasing its concentration. A plateau in quantum efficiency is observed beyond 3.65×10^{-4} M **BD-1** and similar results were obtained across the **BD-2** concentration profile. With measured upconversion quantum efficiencies in hand and dynamic Stern–Volmer quenching established, the TTA quantum efficiency with a theoretical maximum of 11.1%,¹² can be calculated from these data. If we assume that $\Phi_{\text{UC}} = \Phi_{\text{q}}\Phi_{\text{TTA}}\Phi_{\text{f}}$, where the upconversion quantum efficiency is the product of the quantum efficiencies of PtTPBP triplet quenching, BODIPY triplet–triplet annihilation, and singlet BODIPY fluorescence, respectively, then Φ_{TTA} is readily calculated from the remaining three experimentally determined quantities, yielding $\Phi_{\text{TTA}} = 0.049$ and 0.099 for **BD-1** and **BD-2**, respectively. Since these values are below the theoretical maximum, it stands to reason that our experimentally measured Φ_{UC} quantities are quite reasonable.

To the best of our knowledge the current observations represent the first examples of the use of the boron dipyrromethene (BODIPY) acceptors/annihilators in upconverting schemes, completely eliminating the need for aromatic hydrocarbons. This advance is significant as it truly generalizes the phenomenon of low power photon upconversion and promotes the practical possibilities of this technology. In terms of the latter, we note that the present PtTPBP/BODIPY systems are readily incorporated into low T_{g} polymeric

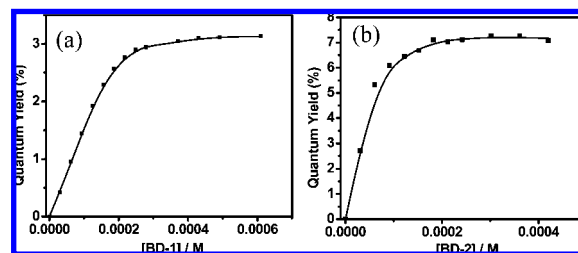


Figure 3. Relative upconverted fluorescence quantum yield of (a) **BD-1** and (b) **BD-2** as a function of increasing concentration of the dyes under selective excitation of PtTPBP (635 ± 5 nm) in deaerated benzene.

solid-state materials^{1c} and successfully upconvert red photons. The solution-based properties of the current donor–acceptor/annihilator pairs permitted highly reproducible red-to-green and red-to-yellow upconversion quantum yields to be experimentally determined. The observed upconversion processes in both instances were extremely stable as a function of irradiation time. In concert with dynamic Stern–Volmer data, TTA quantum efficiencies are reliably estimated from upconverted fluorescence data and can approach theoretical limits. We hope that the present work inspires researchers to identify other viable donor–acceptor/annihilator chromophore compositions for utilization in upconversion-based wavelength-shifting ventures.

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Supporting Information Available: Additional experimental and synthetic details, NMR spectra, Stern–Volmer analyses, and upconversion quantum yield determinations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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