

## Low Power Visible-to-UV Upconversion

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Low power visible-to-UV photon upconversion is demonstrated for the first time, achieved from two simple organic chromophores dissolved in benzene. Selective 442 nm excitation of the triplet sensitizer 2,3-butanedione (biacetyl) in the presence of the laser dye 2,5-diphenyloxazole (PPO) results in the observation of singlet fluorescence from the latter in the UV centered at 360 nm, anti-Stokes shifted by a record 0.64 eV with respect to the excitation. All of the experimental data are consistent with the upconverted singlet PPO fluorescence being produced as a result of biacetyl-sensitized triplet–triplet annihilation (TTA) of triplet excited PPO chromophores. Nanosecond laser flash photolysis performed under pseudo-first-order conditions revealed the bimolecular rate constant of triplet–triplet energy transfer between the biacetyl sensitizer and PPO acceptor,  $k_q = 9.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ . The TTA process was confirmed by the quadratic dependence of the upconverted integrated PPO emission intensity measured with respect to incident 442 nm light power density. The maximum quantum yield of the upconverted emission ( $0.0058 \pm 0.0002$ ) was determined relative to 1,8-diphenyl-1,3,5,7-octatetraene, both measured with  $0.389 \text{ W/cm}^2$  incident power density. The PPO triplet–triplet annihilation rate constant ( $k_{\text{TT}}$ ) was determined from transient absorption decays monitored at the peak of its characteristic triplet-to-triplet excited-state absorption (500 nm) as a function of incident pulsed laser fluence; this process attains the diffusion limit in benzene at room temperature,  $k_{\text{TT}} = 1.1 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

### Introduction

The efficient generation of ultraviolet (UV) and blue light in molecular systems continues to emerge as a challenge in terms of first principles in addition to device technologies such as organic-light emitting diodes (OLEDs).<sup>1</sup> The production of short wavelength photons from low energy and low power sources ultimately requires new molecules, concepts, and methodologies. One possible strategy for the generation of UV light from long wavelength sources comes from harnessing sensitized triplet–triplet annihilation (TTA) photochemistry. This is a process wherein higher energy photons are generated 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 are combined to produce a higher energy singlet state and a corresponding ground-state species.<sup>2,3</sup> This phenomenon was first introduced by Parker and Hatchard in the 1960s,<sup>4</sup> utilizing organic chromophores as the triplet sensitizers which exhibited low intersystem crossing efficiencies, thereby limiting upconversion. Notably, a UV-based upconverting system utilizing a combination of benzophenone, a high triplet yield organic sensitizer, and naphthalene acceptors has been successfully developed.<sup>5</sup> More recently this system was employed in dendritic architectures at 77 K, producing annihilation products from pulsed laser excitation.<sup>6</sup> Our group<sup>7–15</sup> and others<sup>16–22</sup> have applied similar concepts for wavelength conversion incorporating various metal-organic chromophores to increase upconversion yields resulting from the unity efficiency with which the metalated sensitizer triplet can be populated upon photoexci-

tion. We have reported numerous examples of noncoherent low power upconversion in a variety of solution and solid state media.<sup>7–15</sup> One of our earliest examples demonstrated that the combination of  $[\text{Ru}(\text{dmb})_3]^{2+}$  (dmb = 4,4'-dimethyl-2,2'-bipyridine) and 9,10-diphenylanthracene (DPA) produces green-to-blue upconversion that is readily discernible to the naked eye when a conventional 532 nm laser pointer is used as the excitation source.<sup>9</sup> An important recent contribution successfully translated green-to-blue noncoherent upconversion into solid polymer films.<sup>11</sup>

To date we have reported photon upconversion phenomena spanning a majority of the visible spectrum including the use of the first phthalocyanine incorporated into an upconverting scheme affording red-to-yellow conversion,<sup>12</sup> as well as a composition demonstrating the largest energy anti-Stokes energy difference reported to date (0.58 eV) resulting from sensitized TTA.<sup>15</sup> We have also disseminated a photochemical upconversion approach to producing white light from monochromatic excitation<sup>13</sup> in addition to the first examples of nonaromatic hydrocarbon acceptor/annihilator molecules.<sup>14</sup>

Inspired by the need to further expand the anti-Stokes energy shifts obtainable from sensitized TTA, we identified a composition that would achieve this goal while simultaneously affording visible-to-UV photon upconversion. Selective 442 nm excitation of the triplet sensitizer 2,3-butanedione (biacetyl) in the presence of the laser dye 2,5-diphenyloxazole (PPO) in deaerated benzene results in the observation of singlet fluorescence from the latter in the UV centered at 360 nm, anti-Stokes shifted by a record 0.64 eV with respect to the excitation. All of the experimental data presented below are consistent with the upconverted singlet PPO fluorescence being produced as a result of biacetyl-sensitized triplet–triplet annihilation (TTA) of triplet excited PPO chromophores.

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## Experimental Section

**General Data.** 2,5-diphenyl oxazole (PPO), 1,8-diphenyl-1,3,5,7-octatetraene (DPO) and spectroscopic grade benzene were purchased from Aldrich Chemical Co. and 2,3-butanedione (biacetyl) was purchased from Fluka. Biacetyl was vacuum distilled prior to use. All remaining reagents and solvents were used as received.

**Spectroscopic Measurements.** Static absorption spectra were measured with a Cary 50 Bio UV–vis spectrophotometer from Varian. Steady-state photoluminescence spectra were acquired with a PTI single photon counting spectrofluorimeter. Monochromatic continuous wave 442 nm excitation was achieved by a HeCd laser (Series 74-45-MRM-803-120) purchased from Melles Griot. Incident laser power was varied using a series of neutral density filters placed in front of the sample. The HeCd incident laser power was measured using a Molectron Power Max 5200 power meter. The phosphorescence lifetime of biacetyl in benzene was measured on a nitrogen-pumped broadband dye laser from PTI (model GL-3300 N<sub>2</sub> laser and model GL-301 dye laser) using an apparatus that has previously been described using coumarin 450 as the laser dye.<sup>23</sup> All luminescence samples were prepared either in a 1 cm<sup>2</sup> quartz cell purchased from Starna Cells or in a specially designed 1 cm<sup>2</sup> optical cell bearing a side arm round-bottom 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. All attempts to measure the 77 K phosphorescence of PPO in 2-methyl-THF failed even with the addition of 10% v/v ethyl iodide.

**Quantum Yield Measurements.** Prompt sensitized upconverted fluorescence quantum yield measurements of PPO were measured relative to DPO in benzene using monochromatic 442 nm excitation in the optically dilute technique, eq 1,<sup>24</sup> where  $\Phi_{unk}$ ,  $A_{unk}$ ,  $I_{unk}$ , and  $\eta_{unk}$  represent the quantum yield, absorbance, integrated photoluminescence intensity, and refractive index of the sample. The corresponding terms for the subscript *std* are for the reference quantum counter, DPO, whose quantum yield under these conditions is  $\Phi_{std} = 0.088$  at this excitation wavelength and *unk* is for the sample.<sup>25</sup> Since the quantum yield for the reference counter was previously reported in benzene,

$$\Phi_{unk} = \Phi_{std} \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{I_{unk}}{I_{std}} \right) \left( \frac{\eta_{unk}}{\eta_{std}} \right)^2 \quad (1)$$

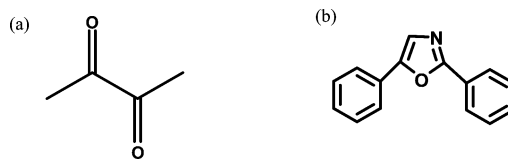
the solvent in which the upconversion quantum yield was determined, no refractive index correction is necessary and eq 2 was used for the calculation.

$$\Phi_{unk} = \Phi_{std} \left( \frac{A_{std}}{A_{unk}} \right) \left( \frac{I_{unk}}{I_{std}} \right) \quad (2)$$

The integrated intensity of the upconverted fluorescence was analyzed in the region 300–450 nm while that of DPO was analyzed in the wavelength range between 300–750 nm. All measurements were collected under identical experimental conditions and optically matched solutions at the excitation wavelength were used for both the standard and the sample. Quantum yield values reported are an average of at least two independent measurements. Even though the emission profile of the standard sample does not overlap the upconverted photoluminescence at shorter wavelengths, the experimentally determined quantum yields were reproducible using this relative actinometric method.

**Laser Flash Photolysis.** Nanosecond transient absorption measurements were collected on a Proteus spectrometer (Ul-

## CHART 1: Chemical Structures of (a) Biacetyl and (b) PPO



trafast Systems LLC) equipped with a 150 W Xe-arc lamp (Newport), a Chromix monochromator (Bruker Optics) 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 Oportek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an absorbance of  $\sim 0.40$  at the excitation wavelength. A 425 nm long pass filter was placed between the OPO and the sample to filter out the residual Nd:YAG third harmonics. Single wavelength kinetic data were processed separately in Origin 8.0. The triplet–triplet annihilation rate constant (TTA) was calculated by fitting the transient absorption decay of the PPO triplet at 500 nm as a function of the incident laser fluence according to eq 3.

$$\frac{d[{}^3M^*]}{dt} = -k_T[{}^3M^*] - k_{TT}[{}^3M^*]^2 \quad (3)$$

Here  $[{}^3M^*]$  is the concentration of the triplet excited-state of PPO,  $k_{TT}$  is the triplet–triplet annihilation rate constant and  $k_T$  is the first-order triplet decay rate constant. Integration of eq 3 produces eq 4 which readily translates into a convenient three-parameter expression (eq 5) that was used to fit the experimental data, minimized by nonlinear least-squares in Origin 8.0.

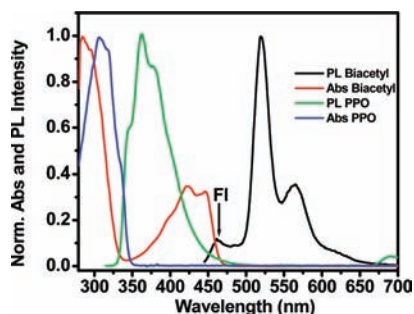
$$[{}^3M^*] = \frac{[{}^3M^*]_0 e^{-k_T t}}{1 + [{}^3M^*]_0 \frac{k_{TT}}{k_T} (1 - e^{-k_T t})} \quad (4)$$

$$y = \frac{p_1}{1 + \left( \frac{p_1 \times p_2}{p_3} \right) \exp(p_3 \times x) - \left( \frac{p_1 \times p_2}{p_3} \right)} \quad (5)$$

The terms of eq 5 are defined as  $y = [{}^3M^*]$ ,  $x = t$  (time),  $p_1 = [{}^3M^*]_0$ ,  $p_2 = k_{TT}$ , and  $p_3 = -k_T$ . It should be noted that the measured decay curve for  $[{}^3M^*]$  is in absorbance units, hence to convert this to molar concentration, the established triplet excited-state extinction coefficient of PPO was employed at 500 nm,  $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>26</sup>

## Results and Discussion

The chemical structures of the compounds investigated in this current study are shown in Chart 1. The normalized ground-state absorption and emission spectra of both biacetyl (triplet sensitizer) and PPO (acceptor/annihilator) in benzene are shown in Figure 1. Biacetyl absorbs in the blue region of the spectrum over the range 370–460 nm while PPO displays a singlet absorption maximum centered at  $\sim 306$  nm. The steady state emission spectrum of a degassed solution of biacetyl in benzene exhibits a strong phosphorescence peak at 520 nm and a shoulder at 560 nm. The high energy shoulder in the biacetyl emission profile is singlet fluorescence. PPO shows strong fluorescence in benzene (optically dilute) with a maximum near



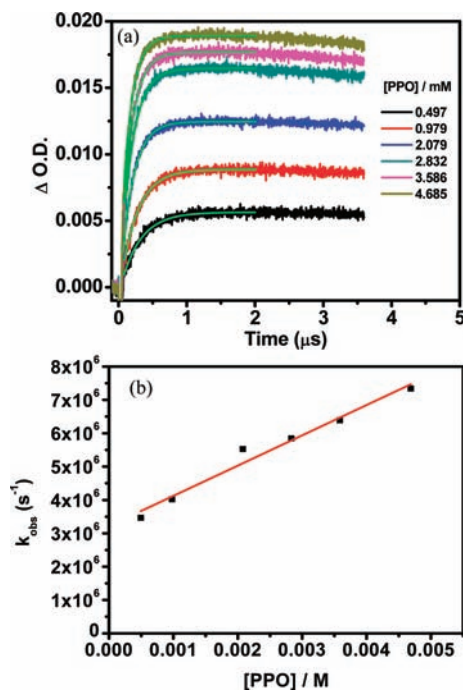
**Figure 1.** Absorbance and emission spectra of biacetyl and PPO in aerated and deaerated benzene, respectively, at room temperature, all normalized to an arbitrary maximum of 1.0. FI indicates the singlet fluorescence emanating from biacetyl.

350 nm which tails into the visible region of the spectrum. Both compounds are known to exhibit high phosphorescence and fluorescence quantum yields of  $\sim 1.0$  and  $0.85$  for biacetyl and PPO, respectively,<sup>27</sup> the latter being important for the observation of upconverted emission. Unfortunately, the phosphorescence emission intensity decay of vacuum distilled biacetyl was complex, even in the absence of PPO, adequately fit to a sum of two single exponential functions under concentrations in benzene necessary to achieve the desired upconversion phenomenon. A longer-lived component of  $43 \mu\text{s}$  and a shorter-lived component of  $11 \mu\text{s}$  were obtained with relative amplitudes of  $0.30$  and  $0.70$ , respectively. This lifetime heterogeneity in homogeneous benzene solution precluded the quantitative application of the Stern–Volmer equation,  $I_0/I = \tau_0/\tau = 1 + k_q\tau_0[Q]$ , to obtain the bimolecular energy transfer rate constant between biacetyl and PPO. We note that using the steady-state photoluminescence intensity quenching data produces a linear Stern–Volmer plot with  $K_{sv} = k_q\tau_0 = 155 \text{ M}^{-1}$ .

Although photoluminescence lifetimes cannot be used to quantitatively determine the triplet–triplet energy transfer rate constant, we confirmed that biacetyl is indeed dynamically quenched by PPO *via* triplet energy transfer using laser flash photolysis experiments. In accord with eq 6, pseudo-first-order quenching of triplet excited biacetyl ( $^3\text{Biacetyl}^*$ ) with PPO produces  $^3\text{PPO}^*$ , which is conveniently monitored by its characteristic triplet-to-triplet absorbance at  $500 \text{ nm}$ . By measuring the rate of formation of  $^3\text{PPO}^*$  as a function of PPO concentration, the bimolecular energy transfer rate constant is readily obtained, Figure 2. As the concentration of PPO is increased from  $0.497$  to  $4.685 \text{ mM}$ , the first-order rate ( $k_{\text{obs}}$ ) linearly increases from  $3.46 \times 10^6$  to  $7.34 \times 10^6 \text{ s}^{-1}$ , Figure 2b. The slope of the fitted straight line readily provides the bimolecular quenching constant,  $k_q = 9.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .



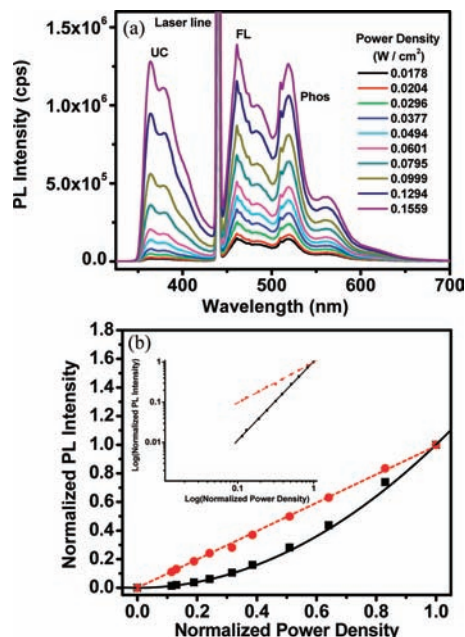
Selective excitation of biacetyl in a freeze–pump–thaw degassed benzene solution containing PPO, using the  $442 \text{ nm}$  output from a HeCd laser resulted in clearly observable upconverted fluorescence from PPO, anti-Stokes shifted relative to the excitation wavelength, with an onset near  $350 \text{ nm}$  extending into the near visible portion of the spectrum. Figure 3a presents a typical emission intensity dependence profile of this solution measured as a function of excitation power intensity ranging from  $0.018$  to  $0.156 \text{ W/cm}^2$ . Analysis of the sensitized upconverted integrated emission intensity as a function of the incident power density is shown in Figure 3b. The solid line passing through the data points represents the best quadratic fit



**Figure 2.** (a) Single wavelength kinetic traces monitoring the formation of the triplet excited-state of PPO observed at  $500 \text{ nm}$  which resulted from the triplet energy transfer from biacetyl ( $2 \text{ mM}$ ) upon  $442 \text{ nm}$  excitation at  $1.0 \text{ mJ/pulse}$  in deaerated benzene. The superimposed green line represents the first-order fit to each data set. (b) Plot generated from the pseudo-first-order fit of the formation of triplet PPO shown in part a as a function of increasing PPO concentration.

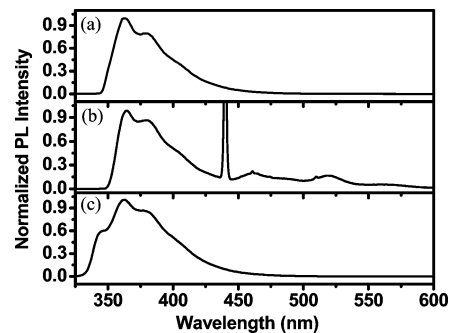
( $x^2$ ) to the data illustrating the nonlinear photochemistry driving these processes. The double logarithm plot shown in the inset of Figure 3b yields a straight line with a slope of  $1.96$ , thereby confirming the quadratic dependence of the sensitized annihilation process. These results demonstrate that the delayed fluorescence intensity is proportional to the square of the incident laser power at  $442 \text{ nm}$  and hence to the square of the triplet concentration of PPO. For comparison, the integrated emission intensity for the unquenched biacetyl emission (both fluorescence and phosphorescence) was also quantified in the same experiment, Figure 3. The presence of unquenched biacetyl emission is completely unavoidable here (Figure 3a) given the below diffusion controlled energy transfer bimolecular rate constant. The double logarithm plot of the integrated emission data, shown in the inset in Figure 3b, is rather informative as it readily differentiates between one and two (sequential) photon excitation processes. The residual biacetyl emission under our experimental conditions exhibits a slope of  $1.0$  in the Figure 3b inset which is indeed a linear one photon excitation process whereas the upconverted PPO emission clearly obeys a quadratic incident light power dependence. The combined data support a mechanism wherein selective excitation of the biacetyl sensitizer at  $442 \text{ nm}$  leads to triplet–triplet energy transfer to the acceptor in which TTA ultimately results in the generation of singlet PPO which radiatively decays to the ground-state by singlet fluorescence. A Jablonski diagram depicting the relevant chromophore energy levels and intermolecular processes necessary to produce the upconverted fluorescence of PPO in the current experiments are summarized in Scheme 1.

Figure 4 compares the upconverted fluorescence of PPO following long wavelength triplet biacetyl sensitization at  $442 \text{ nm}$  with that of the conventional fluorescence of PPO measured with  $325 \text{ nm}$  light in samples containing  $8 \text{ mM}$  PPO. By comparing parts a and b of Figure 4, the biacetyl-sensitized

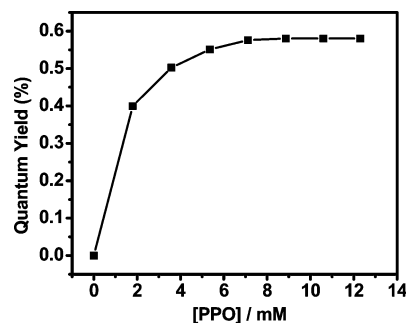


**Figure 3.** (a) Emission profile of the upconverted emission of PPO in addition to residual biacetyl fluorescence and phosphorescence in a mixture of biacetyl and PPO monitored as a function of incident light upon selective excitation of biacetyl at 442 nm in deaerated benzene. The laser line is indicated on the plot; UC is upconverted PPO fluorescence; FL and Phos indicate biacetyl fluorescence and phosphorescence, respectively. (b) Normalized integrated emission intensity of the upconverted emission between 325–425 nm and the phosphorescence of biacetyl between 445–700 nm from part a measured as a function of the normalized incident power density. The black line is the best quadratic fit ( $x^2$ ) to the normalized upconverted PPO fluorescence data (filled black squares) and the red dotted line is the best linear fit to the biacetyl emission data (filled red circles). Inset: Double logarithm plot of the normalized data; the slope of the black solid line is 1.96 and the slope of the red dotted line is 1.0.

upconverted fluorescence of PPO is completely superimposable with that measured from the control sample containing the identical concentration of PPO excited directly at 325 nm. An optically dilute PPO sample (Figure 4c) excited at 325 nm produces the more familiar PPO emission profile with all short wavelength components intact. These combined observations are consistent with an operative inner filter effect occurring in the 8 mM PPO samples which cannot be circumvented in the upconversion experiments as such concentrations are necessary to achieve the desired quenching and wavelength conversion. We conclude that the inner filter effect is responsible for the complete attenuation of the upconverted fluorescence emission



**Figure 4.** (a) Steady-state fluorescence spectrum of PPO (8 mM) in benzene excited at 325 nm illustrating the inner filter effect. (b) Upconverted fluorescence spectrum of a deaerated benzene solution containing biacetyl (2 mM) and PPO (8 mM) obtained with 442 nm excitation, scattered laser radiation results in the spike at 442 nm. (c) Steady-state fluorescence spectrum of an optically dilute solution of PPO in benzene excited at 325 nm.

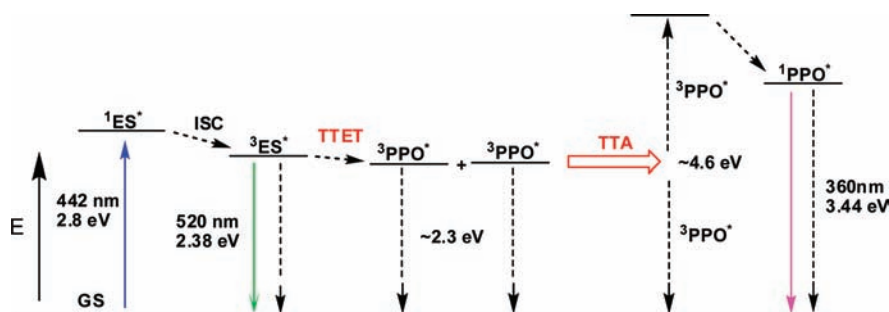


**Figure 5.** Relative percent upconversion quantum yields of biacetyl/PPO mixtures measured as a function of PPO concentration upon selective excitation of biacetyl at 442 nm at 0.389 W/cm<sup>2</sup> in deaerated benzene.

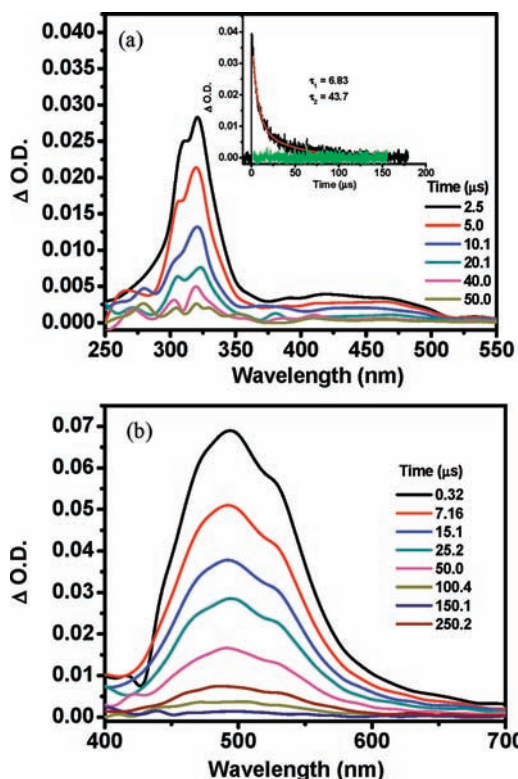
over wavelengths that spectrally overlap the singlet PPO absorption transitions, thereby producing a significantly smaller than expected anti-Stokes shift, 0.64 vs 0.74 eV.

The quantum efficiency of the upconverted PPO fluorescence was measured as a function of the PPO concentration, determined relative to DPO as the quantum counter using 442 nm excitation in deaerated benzene at 0.389 W/cm<sup>2</sup>.<sup>25</sup> These experiments measured a maximum quantum yield of  $0.0058 \pm 0.0002$ , quantified in the plateau region of Figure 5, which illustrates that the upconversion quantum efficiency increases with increasing PPO concentration up to 7.12 mM PPO at which point the effect levels off. Since the overall upconversion quantum efficiency of upconversion is the product of the efficiencies of triplet energy transfer quenching, PPO triplet–

#### SCHEME 1: Qualitative Jablonski Diagram of the Chromophores Used in the Present Study along with Their Pertinent Energy Conversion Processes<sup>a</sup>



<sup>a</sup> ISC is intersystem crossing, TTET is triplet–triplet energy transfer and TTA is triplet–triplet annihilation. Solid colored lines represent radiative transitions.

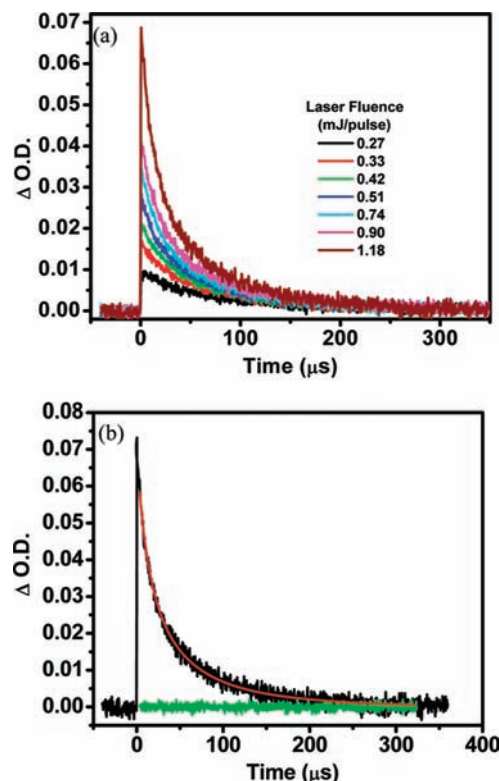


**Figure 6.** (a) Transient absorption difference spectra of biacetyl at select delay times in deaerated benzene;  $\lambda_{\text{ex}} = 442$  nm, 1.2 mJ/pulse. The inset displays the biexponential fit to the 320 nm absorption transient with fit residuals presented in green. (b) Transient absorption difference spectra of a biacetyl/PPO mixture measured in deaerated benzene as a function of delay time,  $\lambda_{\text{ex}} = 442$  nm, 1.2 mJ/pulse.

triplet annihilation, and singlet PPO fluorescence, a shortfall in one of these quantities will ultimately result in a low upconversion quantum yield.<sup>28</sup> In the present case, the data are consistent with the upconversion process being limited by a combination of the initial triplet energy transfer quenching and the fluorescence quantum yield of PPO. However, it is important to note that the energetic proximity of these two molecular triplet states still facilitates a significant anti-Stokes energy shift which was the primary inspiration for this study.

In an attempt to determine the triplet–triplet annihilation rate constant ( $k_{TT}$ ) of PPO in the present upconverting scheme, it is necessary to investigate the excited-state dynamics of biacetyl in benzene before and after the addition of PPO. Hence, to elucidate the excited-state features of biacetyl in deaerated benzene, nanosecond transient absorption (TA) measurements were collected on a 8.8 mM (an absorbance of 0.44 at 442 nm) biacetyl sample following 442 nm nanosecond pulsed laser excitation. Broad positive excited-state absorption features were observed at 320 nm with a much less intense feature near 400 nm (Figure 6a).<sup>29,30</sup> Analysis of the absorption transients at 320 and 400 nm resulted in biexponential kinetics with lifetime components similar to those recovered from the phosphorescence intensity decay analysis. The longer lifetime component measured in the TA experiments was 43.7  $\mu\text{s}$  in reasonable quantitative agreement with the photoluminescence data discussed earlier.

Nanosecond transient absorption experiments were also conducted upon the addition of 40 mM PPO to a solution of 8.8 mM biacetyl in argon purged benzene. Broad positive excited-state absorption features were observed between 400–700 nm with a wavelength maximum centered at 500 nm, Figure



**Figure 7.** (a) Transient absorption decay kinetics at 500 nm in a mixture of biacetyl and PPO in deaerated benzene measured as a function of laser pulse energy at 442 nm. (b) Representative kinetic fit at 1.2 mJ/pulse according to eq 5 (red line) and the residuals of this fit (green line).

6b. It should be noted that the high energy excited-state absorption features corresponding to biacetyl could not be observed in these experiments. This is a direct consequence of the high concentration of PPO that is needed to efficiently quench the triplet excited-state of biacetyl which limits the probe beam transmission over short wavelengths. It should also be mentioned that we could not measure the TA difference spectrum of PPO alone in deaerated benzene as our experimental apparatus cannot pump samples below 355 nm. However, the TA difference spectrum of PPO in ethanol has been previously reported<sup>31</sup> and agrees well with the difference spectra displayed in Figure 6b. Hence, we conclude that the excited-state features observed in the TA difference spectra of the biacetyl/PPO mixture exclusively results from the triplet excited-state of PPO generated *via* triplet energy transfer between biacetyl and PPO.

The kinetics of the TTA process can be readily monitored using the major sensitized transient absorption peak observed in PPO, monitored as a function of pulsed incident laser fluence at 442 nm, Figure 7a. To determine the sensitized TTA rate constant ( $k_{TT}$ ), a series of single wavelength TA traces were collected at the excited-state maximum of PPO (500 nm) upon selective excitation of biacetyl at 442 nm in a solution mixture of biacetyl/PPO in deaerated benzene (Figure 7a). When two triplet PPO molecules combine several parallel reaction pathways are possible, including the production of a quintet excited state, a triplet excited-state or a singlet excited state, the latter referred to as annihilation controlled delayed fluorescence.<sup>32</sup> The last process is the major mode of decay observed in the experiments described here. To determine the TTA rate constant the molar triplet-to-triplet extinction coefficient of PPO at 500 nm was employed which was previously determined to be  $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 500 nm.<sup>26</sup> Fitting the transient absorption

decays at 500 nm according to eq 5 recovered a  $k_{TT}$  of  $1.1 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , averaged over all of the different incident light fluences in Figure 7a. This rate constant is identical to the diffusion limit in benzene,  $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at  $20^\circ\text{C}$ ,<sup>27</sup> indicating that the TTA process is indeed diffusion controlled under the present experimental conditions.

Although limited in quantum efficiency by the initial triplet sensitization process and the fluorescence quantum yield of PPO, the combination of two simple organic chromophores successfully produced the intended visible-to-UV wavelength conversion corresponding to a record observed anti-Stokes shift based on TTA of 0.64 eV. The anticipated anti-Stokes shift of 0.74 eV was unfortunately not realized as a result of the inner filter effect mandated by the extremely large concentrations of PPO necessary to afford reasonable yields of triplet sensitization. Nevertheless, the data from the present study provides some inspiration that purely organic based triplet sensitizers can compete with heavy-metal-containing chromophores in the design of improved upconversion cocktails utilizing TTA as the wavelength conversion mechanism.

## Conclusion

Low power visible-to-UV photon upconversion was demonstrated for the first time and achieved using two simple organic chromophores dissolved in benzene. Selective excitation of biacetyl in the presence of PPO results in the observation of singlet fluorescence in the UV, anti-Stokes shifted by a record 0.64 eV relative to the excitation. All of the static and dynamic experimental data are consistent with the upconverted singlet PPO fluorescence being produced as a result of biacetyl-sensitized triplet-triplet annihilation of triplet excited PPO chromophores; the latter process attains the diffusion limit in benzene at room temperature.

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## References and Notes

- (1) *Organic Light-Emitting Devices*; Shinar, J., Ed.; Springer-Verlag: New York, 2004.
- (2) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968.
- (3) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.
- (4) Parker, C. A.; Hatchard, C. G. *Proc. R. Chem. Soc., London* **1962**, 386–387.
- (5) Parker, C. A.; Joyce, T. A. *Chem. Commun.* **1968**, 749–750.
- (6) Bergamini, G.; Ceroni, P.; Maestri, M.; Balzani, V.; Lee, S.-K.; Vogtle, F. *Photochem. Photobiol. Sci.* **2004**, 3, 898–905.
- (7) Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2004**, 2860–2861.
- (8) Islangulov, R. R.; Castellano, F. N. *Angew. Chem., Int. Ed.* **2006**, 45, 5957–5959.
- (9) Islangulov, R. R.; Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2005**, 3776–3778.
- (10) Zhao, W.; Castellano, F. N. *J. Phys. Chem. A* **2006**, 110, 11440–11445.
- (11) Islangulov, R. R.; Lott, J.; Weder, C.; Castellano, F. N. *J. Am. Chem. Soc.* **2007**, 129, 12652–12653.
- (12) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. A* **2008**, 112, 3550–3556.
- (13) Singh-Rachford, T. N.; Islangulov, R. R.; Castellano, F. N. *J. Phys. Chem. A* **2008**, 112, 3906–3910.
- (14) Singh-Rachford, T. N.; Haefele, A.; Ziessel, R.; Castellano, F. N. *J. Am. Chem. Soc.* **2008**, 130, 16164–16165.
- (15) Singh-Rachford, T. N.; Castellano, F. N. *Inorg. Chem.* **2009**, 48, 2541–2548.
- (16) Keivanidis, P. E.; Balushev, S.; Miteva, T.; Nelles, G.; Scherf, U.; Yasuda, A.; Wegner, G. *Adv. Mater.* **2003**, 15, 2095–2098.
- (17) Balushev, S.; Jacob, J.; Avlasevich, Y. S.; Keivanidis, P. E.; Miteva, T.; Yasuda, A.; Nelles, G.; Grimsdale, A. C.; Muellen, K.; Wegner, G. *ChemPhysChem* **2005**, 6, 1250–1253.
- (18) Balushev, S.; Keivanidis, P. E.; Wegner, G.; Jacob, J.; Grimsdale, A. C.; Muellen, K.; Miteva, T.; Yasuda, A.; Nelles, G. *Appl. Phys. Lett.* **2005**, 86, 061904/1–061904/3.
- (19) Balushev, S.; Miteva, T.; Yakutkin, V.; Nelles, G.; Yasuda, A.; Wegner, G. *Phys. Rev. Lett.* **2006**, 97, 143903.
- (20) Balushev, S.; Yakutkin, V.; Miteva, T.; Avlasevich, Y.; Chernov, S.; Aleshchenkov, S.; Nelles, G.; Cheprakov, A.; Yasuda, A.; Muellen, K.; Wegner, G. *Angew. Chem., Int. Ed.* **2007**, 46, 7693–7696.
- (21) Balushev, S.; Yakutkin, V.; Wegner, G.; Minch, B.; Miteva, T.; Nelles, G.; Yasuda, A. *J. Appl. Phys.* **2007**, 101, 023101/1–023101/4.
- (22) Balushev, S.; Yakutkin, V.; Wegner, G.; Miteva, T.; Nelles, G.; Yasuda, A.; Chernov, S.; Aleshchenkov, S.; Cheprakov, A. *Appl. Phys. Lett.* **2007**, 90, 181103/1–181103/3.
- (23) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, 103, 10955–10960.
- (24) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, 75, 991–1024.
- (25) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, 104, 4507–4514.
- (26) Takahashi, T.; Kikuchi, K.; Kokubun, H. *J. Photochem.* **1980**, 14, 67–76.
- (27) Montalti, M.; Credi, A.; Prodi, A.; Gandolfi, M. T. *Handbook of Photochemistry*; 3rd ed.; CRC Press: 2005.
- (28) Monguzzi, A.; Mezyk, J.; Scotognella, F.; Tubino, R.; Meinardi, F. *Phys. Rev. B* **2008**, 78, 195112/1–195112/5.
- (29) Dorfman, L. M.; Taub, I. A.; Buhler, R. E. *J. Chem. Phys.* **1962**, 36, 3051–3061.
- (30) Cundall, R. B.; Evans, G. B.; Griffin, A. C. *J. Phys. Chem.* **1968**, 72, 3871–3877.
- (31) Dempster, D. N.; Morrow, T.; Quinn, M. F. *J. Photochem.* **1974**, 2, 329–341.
- (32) Yekta, A.; Turro, N. J. *Mol. Photochem.* **1972**, 3, 307–322.