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Pd(II) Phthalocyanine-Sensitized Triplet−Triplet Annihilation from Rubrene

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Upconverted yellow singlet fluorescence from rubrene (5,6,11,12-tetraphenylnapthacene) was generated from selective excitation (λ_{ex} = 725 nm) of the red light absorbing triplet sensitizer palladium(II) octabutoxyphthalocyanine, PdPc(OBu)$_8$, in vacuum degassed toluene solutions using a Nd:YAG/OPO laser system in concert with gated iCCD detection. The data are consistent with upconversion proceeding from triplet−triplet annihilation (TTA) of rubrene acceptor molecules. The TTA process was confirmed by the quadratic dependence of the upconverted delayed fluorescence intensity with respect to incident light, measured by integrating the corresponding kinetic traces as a function of the incident excitation power. In vacuum degassed toluene solutions, the red-to-yellow upconversion process is stable under continuous long wavelength irradiation and is readily visualized by the naked eye even at modest laser fluence (0.6 mJ/pulse). In aerated solutions, however, selective excitation of the phthalocyanine sensitizer leads to rapid decomposition of rubrene into its corresponding endoperoxide as evidenced by UV−vis (in toluene), ^{1}H NMR (in d^6-benzene), and MALDI-TOF mass spectrometry, consistent with the established reactivity of rubrene with singlet dioxygen. The upconversion process in this triplet sensitizer/acceptor-annihilator combination was preliminarily investigated in solid polymer films composed of a 50:50 mixture of an ethyleneoxide/epichlorohydrin copolymer, P(EO/EP). Films that were prepared under an argon atmosphere and maintained under this inert environment successfully achieve the anticipated quadratic incident power dependence, whereas air exposure causes the film to deviate somewhat from this dependence. To the best of our knowledge, the current study represents the first example of photon upconversion using a phthalocyanine triplet sensitizer, furthering the notion that anti-Stokes light-producing sensitized TTA appears to be a general phenomenon as long as proper energy criteria are met.

Introduction

Photon upconversion based on sensitized triplet−triplet annihilation (TTA) is a nonlinear process involving multiple diffusion controlled energy transfer steps, ultimately resulting in the generation of delayed singlet fluorescence that is of higher energy than the incident light.[1−5] In the sensitized TTA scheme, photon upconversion from low-power, continuous-wave excitation sources is facilitated by the use of chromophores that efficiently absorb incident radiation through an allowed one-photon process, undergo intersystem crossing, and subsequently transfer this energy to the species capable of TTA.[1−6] The original exploration of this approach by Parker and Hatchard utilized solutions of organic chromophores as triplet sensitizers which exhibited low intersystem crossing efficiencies and, thus, limited the observed upconversion.[1] Most notably, the combination of benzophenone, a high triplet yield organic sensitizer, and naphthalene have been successful in mediating UV-based upconversion,[2] more recently in dendritic architectures at 77 K.[3] Over the past few years, various aromatic organic chromophores have been successfully employed in upconversion schemes employing Ru(II) and Ir(III) metal-to-ligand charge transfer (MLCT) complexes in addition to heavy metal porphyrin triplet sensitizers.[4,5] In the latter cases, upconversion can be efficiently engineered to the point that the process is readily discernible with the naked eye in the illuminated laboratory. An exciting recent development from our group in this area includes the observation of low power noncoherent upconversion in solid polymer films utilizing 9,10-diphenylanthracene (DPA) and the sensitizer Pd(II) octaethylporphyrin (PdOEP).[6] This latter result is a prerequisite for real-world applications of wavelength shifting materials pumped by terrestrial solar radiation.

In an attempt to further generalize the range of chromophores applicable for upconversion, we report herein red-to-yellow upconversion utilizing rubrene (5,6,11,12-tetraphenylnapthacene) as a triplet acceptor/annihilator along with a palladium(II) 1,4,8,11,15,18,22,25-octabutoxyphthalacyanine, PdPc(OBu)$_8$, triplet sensitizer in toluene solutions as well as in solid polymer films. The current experimental work quantitatively explores the sensitized TTA process utilizing time gated iCCD detection in concert with Nd:YAG/OPO excitation at 725 nm. The resulting time-resolved emission spectra following selective excitation of the phthalocyanine are readily correlated to spectral features emanating from the excited singlet state of the rubrene chromophore. PdPc(OBu)$_8$ is a photochemically stable compound with intense absorption in the red to deep red region of the electromagnetic spectrum with a phosphorescence quantum yield of 77% and a lowest triplet energy suitable for energy transfer to the rubrene acceptor (Scheme 1).[7] Rubrene has been shown to exhibit a fluorescence quantum yield of near unity, rendering it an attractive acceptor/annihilator for upconversion.[8] Most notably, rubrene is currently used as a yellow dopant in light emitting diodes (LEDs)[9] as well as in organic photovoltaics (PVs).[10] An inherent disadvantage to rubrene lies in its

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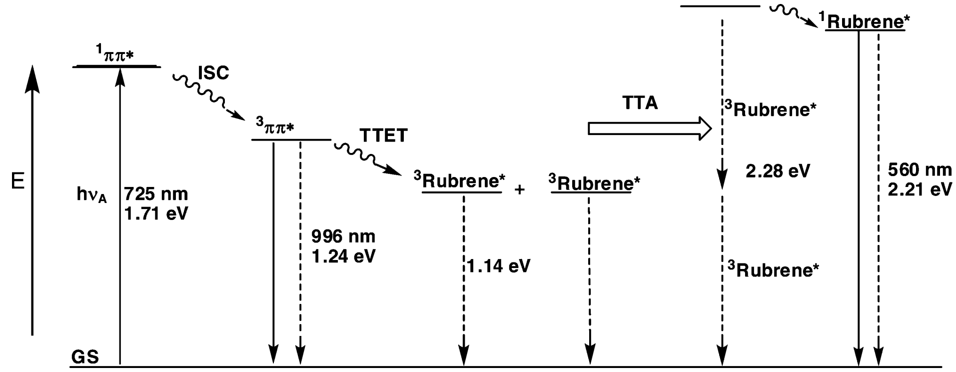
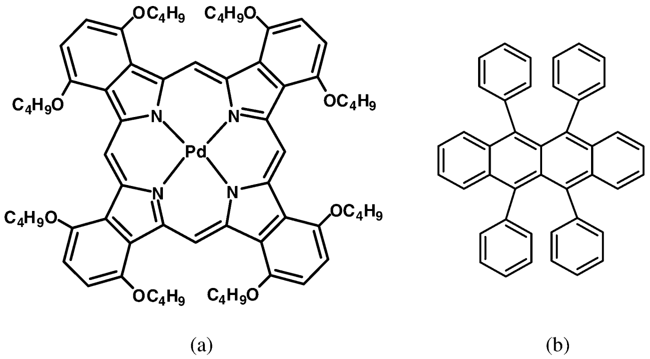
SCHEME 1: Energy Level Diagram of the Upconversion Process between $PdPc(OBu)_8$ and Rubrene



propensity to photooxidize which reduces the stability and lifetime of devices where it serves as an active component.[11,12] In the present work, all solution based photochemistry/photophysics was performed in vacuum degassed solutions (minimum of four freeze−pump−thaw−degas cycles) which completely inhibited all side reactions of rubrene with molecular oxygen. We also preliminarily explored whether the current chromophore combination would yield red-to-yellow upconverted light in the same solid polymer film material we utilized earlier this year.[6] These solid samples did produce the desired result; however, under ambient aerated conditions, the rubrene chromophore degraded steadily with time, and upconversion ceased after 4 days. Importantly, the polymer host matrix did successfully extend the operational lifetime of the upconversion process by inhibiting the rubrene chromophore obliterating side reactions with molecular oxygen.

CHART 1: Chemical Structures of (a) $PdPc(OBu)_8$ and (b) Rubrene



(a) (b)

Experimental Section

General. Palladium(II) 1,4,8,11,15,18,22,25-octabutoxypthalacyanine [$PdPc(OBu)_8$] and rubrene (5,6,11,12-tetraphenylnapthacene) were purchased from Frontier Scientific and Sigma Chemical Co., respectively, and used without further purification. All other reagents and spectroscopic grade solvents were used as received. Rubrene endoperoxide was independently synthesized by the irradiation of 0.5 g rubrene in deuterated aerated toluene for 1 h using a 300 W xenon lamp whose output was passed through a water filter in addition to a 400 nm long pass filter. The 50:50 ethyleneoxide/epichlorohydrin copolymer, P(EO/EP), was purchased from Epichlomer C, Daiso, Co. Ltd., kindly provided by Dr. Christoph Weder at Case Western Reserve University. Preparation of polymer thin films incorporating the phthalocyanine and rubrene chromophores follow our previously described method with a few modifications.[6] The initial polymer solution was degassed by the freeze−pump−thaw (three cycles) method, and the films were made inside an argon saturated oven that was maintained at 90 °C. To maintain an inert environment the film was placed inside a cuvette that was purged with argon and maintained under a positive argon atmosphere. ^1H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer in d^6-benzene. Five millimeter NMR tubes were utilized in the exploration of the photochemical products generated in aerated solutions following selective excitation of $PdPc(OBu)_8$ in the presence of rubrene. MALDI-TOF mass spectra were obtained from a Bruker OmniFlex mass spectrometer using dithranol as the matrix. Absorption spectra were measured with a Cary 50 Bio UV−vis spectrophotometer from Varian. Steady-state luminescence spectra were obtained with a single-photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). All solution based samples were prepared using spectroscopic grade toluene in a specially designed 1 cm^2 optical cell bearing a sidearm round-bottom flask and subjected to a minimum of four freeze−pump−thaw−degas cycles.

Time-Gated Upconversion Experiments. Time-resolved emission spectra were collected on an Andor iStar iCCD detector equipped with a Micro HR Horiba/JY spectrograph (300 gr/mm, 500 nm blaze grating). Unfocused excitation at 725 nm from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an optical absorbance of 0.06 at the excitation wavelength. A 715 nm long pass filter was placed between the OPO and the sample to filter out residual second and third YAG harmonics. The iCCD camera was synchronized with a DG535 digital delay generator (Stanford Research Systems) which was triggered from the laser flashlamp output. The individual transients measured at 2 μs steps after the laser pulse at each incident power was integrated over the entire upconverted fluorescence spectral profile yielding relative intensities that were each reproducible within 1% of their respective values. All data were collected from the Andor software and processed separately in Origin 7.5.

Results and Discussion

The chemical structures of the compounds used in the current experiments are shown in Chart 1. These compounds exhibit extended π systems having intense absorbance in the red and yellow regions of the spectrum.[7,13] The absorbance and fluorescence spectra of $PdPc(OBu)_8$ and rubrene in toluene are shown in Figure 1. $PdPc(OBu)_8$ displays prominent visible absorptions with Q bands at 646 and 725 nm, the more intense band at lower energy. $PdPc(OBu)_8$ exhibits fluorescence at 734 nm, while the phosphorescence has been reported at 996 nm ($\tau_T = 3.5$ μs, $\Phi_T = 0.77$).[14,15] We were unable to confirm the phosphorescence spectrum of $PdPc(OBu)_8$ because of wave-

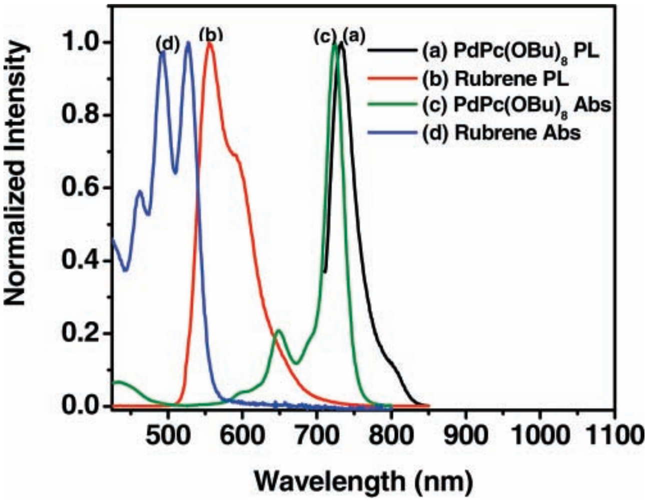


Figure 1. Absorbance and fluorescence spectra of PdPc(OBu)$_8$ and rubrene in degassed toluene at room-temperature, all normalized to an arbitrary maximum of 1.0.

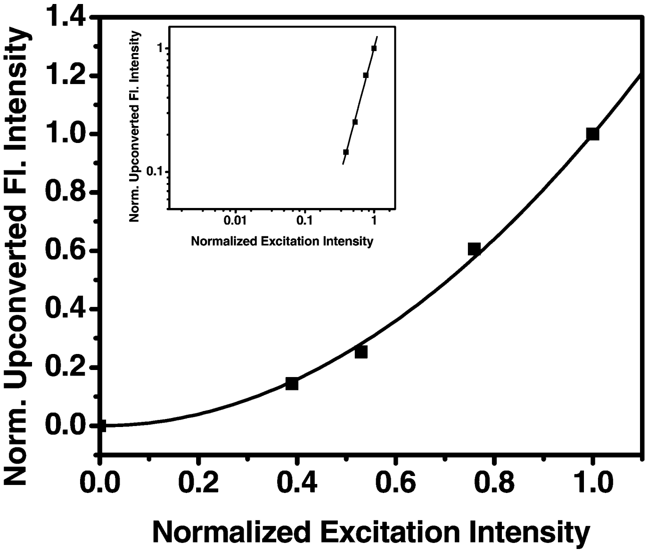


Figure 2. Normalized integrated emission intensity of the upconverted emission of rubrene in a mixture of 1.61 × 10^{-5} M PdPc(OBu)$_8$ and 5.86 × 10^{-4} M rubrene plotted as a function of the normalized power density of the laser. The black line is the best quadratic fit (x^2) to the emission data, normalized to the highest intensity of 20 mW (2 mJ/pulse at 10 Hz). Inset: Double logarithm plot of the normalized upconverted emission of rubrene; the slope of the solid line is 2.1.

length detection limitations in our experimental apparatus. Rubrene has intense absorbance bands at 493 and 527 nm with a weaker band at 462 nm. Rubrene is shown in Figure 1 to exhibit broad fluorescence from 510 nm which tails out at 761 nm with an emission maximum at 560 nm in degassed toluene.

Selective excitation of 1.61 × 10^{-5} M PdPc(OBu)$_8$ in the presence of 5.86 × 10^{-4} M rubrene in degassed toluene with $\lambda_{ex} = 725$ nm at various incident excitation powers ranging from 0.086 to 0.28 W/cm^2 resulted in the observation of delayed upconverted fluorescence from rubrene, Figure 2. We note that the upconversion signal from rubrene is completely stable for at least 2 h under continuous Nd:YAG laser irradiation at 725 nm in vacuum degassed solutions. The solid line passing through the data points represents the best quadratic fit (x^2) to the data, clearly illustrating the nonlinear nature of the anti-Stokes emission process. The double logarithm plot in the inset of Figure 2 yields a straight line with a slope of 2.1 confirming the quadratic dependence of the sensitized annihilation process; that is, the delayed fluorescence intensity is proportional to the square of the incident laser power and, hence, to the square of the triplet concentration. Since excitation is in the longer wavelength region and time-gated detection is employed, the upconverted fluorescence is completely free from potential emission artifacts. The delayed upconverted fluorescence of rubrene is anti-Stokes shifted to the excitation wavelength and resembles the profile of the prompt "normal" fluorescence measured for neat rubrene in solution, Figure 3. The vibronic features of the fluorescence of neat rubrene observed in the prompt steady-state spectrum were not observed in the time-gated experiments because of significantly lower spectral resolution in the latter instrument. However, the wavelength regions in which the fluorescence of rubrene is observed are the same in both techniques. A degassed toluene solution containing only rubrene at the same concentration described above was also excited at 725 nm and yielded no delayed fluorescence signal whatsoever. Upconverted photons can only

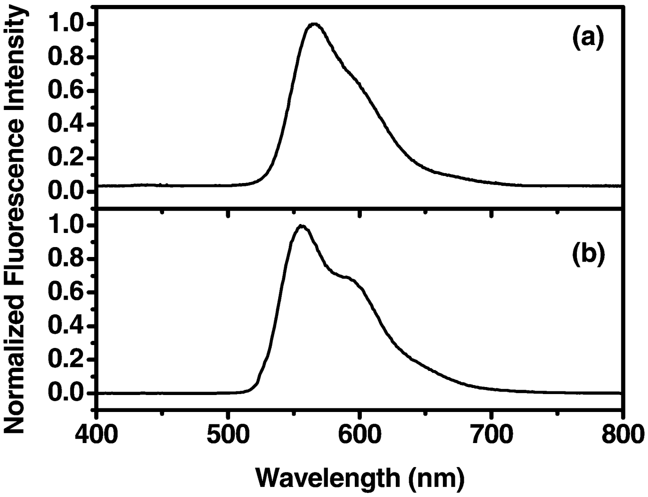


Figure 3. (a) Delayed fluorescence spectrum of a toluene solution containing 1.61 × 10^{-5} M PdPc(OBu)$_8$ and 5.86 × 10^{-4} M rubrene measured 8 μs after a 725 nm, 2 mJ/pulse at 10 Hz. (b) Prompt steady-state fluorescence spectrum of 2.0 × 10^{-4} M rubrene in toluene excited at 526 nm.

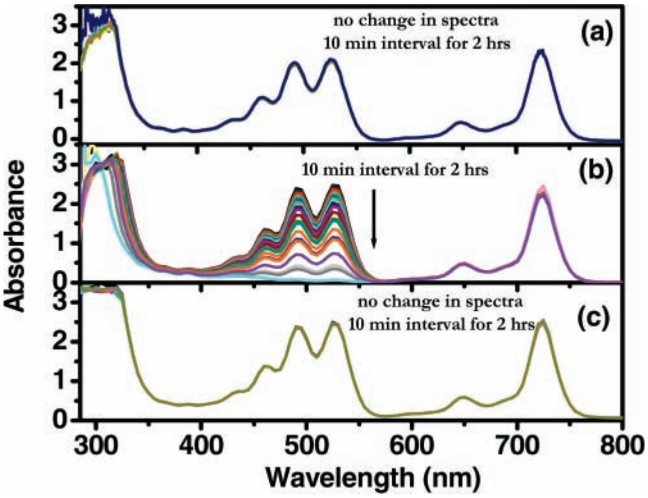


Figure 4. Absorption spectra of solutions containing 1.25 × 10^{-5} M PdPc(OBu)$_8$ and 4.96 × 10^{-4} M rubrene following 725 nm photolysis in (a) vacuum degassed toluene and (b) aerated toluene and (c) a control sample where an aerated toluene solution was maintained in the dark. The absorption spectra were monitored over a 2 h period, and spectra were taken every 10 min upon continuous 725 nm excitation (20 mW, 2 mJ/pulses at 10 Hz).

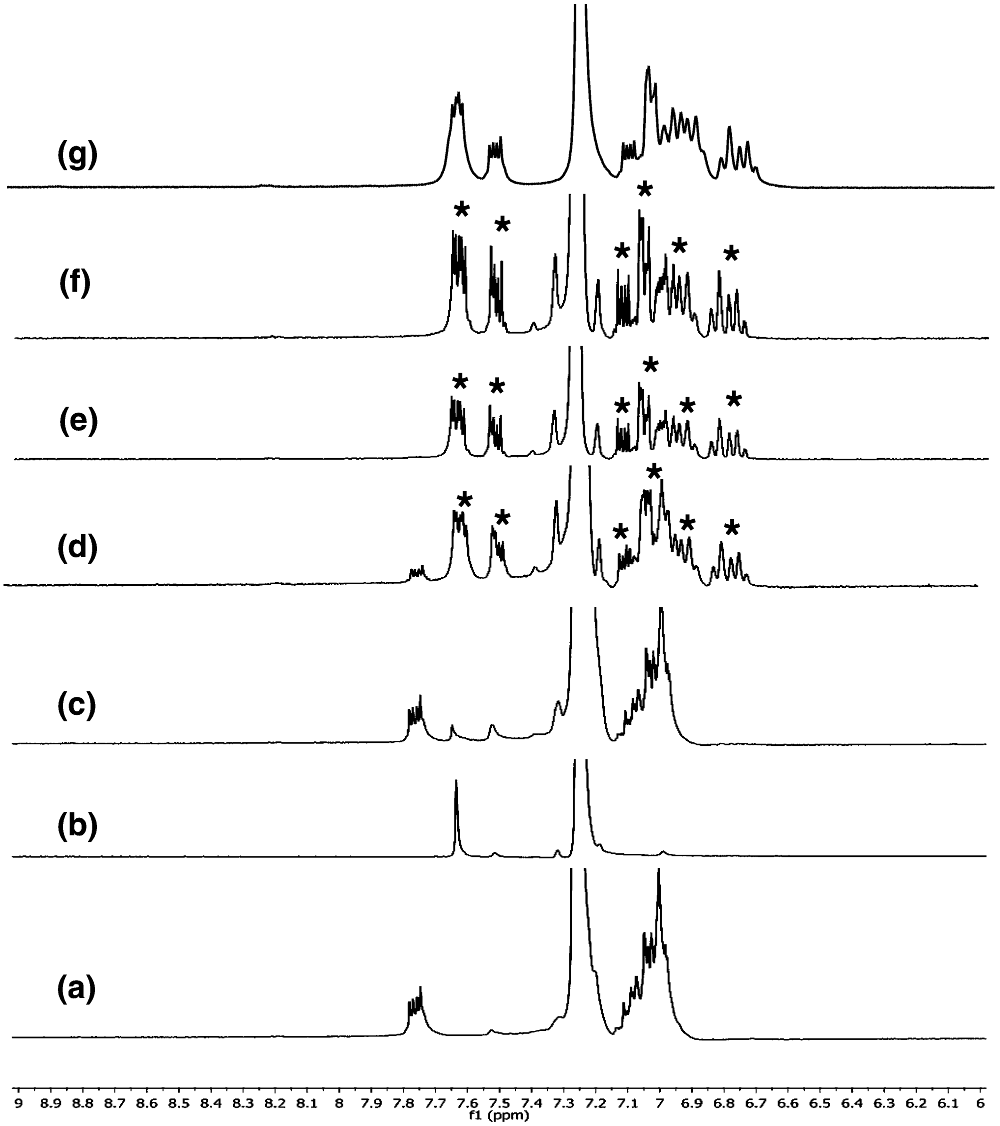


Figure 5. ^{1}H NMR spectra of (a) 3 mM rubrene and (b) 0.5 mM PdPc(OBu)$_8$; a mixture of 3 mM rubrene and 0.5 mM PdPc(OBu)$_8$ at (c) $t = 0$ min, (d) $t = 5$ min, (e) $t = 10$ min, and (f) $t = 15$ min of continuous irradiation in aerated d^6-benzene at $\lambda_{\text{exc}} = 725$ nm; * indicates the growth of new peaks during the photolysis. (g) Rubrene endoperoxide independently prepared in situ following direct visible photolysis of rubrene for 1 h in the presence of oxygen.

be produced using 725 nm excitation in the presence of both chromophores.

When aerated toluene solutions containing rubrene and PdPc(OBu)$_8$ were exposed to either room light or red laser excitation, the solution was observed to change from an orange to green color within 3 h. Therefore, significant care must be exercised in the preparation of all solution-based samples. Rubrene is well-known to react with singlet oxygen to form a colorless endoperoxide, and we postulated that selective excitation of the PdPc(OBu)$_8$ would likely lead to the same decomposition product.[16,17] To investigate the nature of the reaction of PdPc(OBu)$_8$ and rubrene in degassed toluene upon exposure to red light, the reaction of 1.25×10^{-5} M PdPc(OBu)$_8$ and 4.96×10^{-4} M rubrene was followed by UV−vis as a function of 725 nm excitation. The solution was deoxygenated by four freeze−pump−thaw cycles and exposed to 2 mJ/pulse fluence continuously for 2 h, where no change in the absorption spectra was observed over this time period, Figure 4a. However, excitation of aerated solutions of similar concentrations at 725 nm over the same time period results in UV−vis spectra corresponding to the disappearance of the rubrene-based absorption bands in the region from 400 to 560 nm, indicating that complete sensitized photodegradation of rubrene occurred (Figure 4b) under these conditions. As a control, the experiment was repeated under the same experimental conditions except the solution was not exposed to red laser excitation or room light (Figure 4c). Figure 4c shows that rubrene does not decompose in the dark as negligible changes were observed in its characteristic absorption bands over 2 h. It should also be noted that the vacuum degassed solutions maintained under inert atmosphere are stable for weeks when stored in our specially designed 1 cm^2 anaerobic optical cell.

The reaction of 0.5 mM PdPc(OBu)$_8$ and 3 mM rubrene excited at 725 nm in aerated deuterated benzene at ambient temperature was followed as a function of photolysis time by ^{1}H NMR. The aromatic region in the ^{1}H NMR spectrum of rubrene, PdPC(OBu)$_8$, and a mixture of these two solutions at the concentrations described above at $t = 0$ are displayed in Figure 5a−c, respectively. Figure 5d illustrates the degradation of rubrene after 5 min of 725 nm photolysis of the composite solution (Figure 5c). Here, it is immediately noticed that there is a generation of new features with the concomitant disappearance of resonances corresponding to rubrene. The intensity of the new peaks continues to grow over the next 10 min of

SCHEME 2: Proposed Mechanism for the Formation of Rubrene Endoperoxide Following Selective Excitation of $PdPc(OBu)_8$ Where ISC Is Intersystem Crossing, TTET Is Triplet−Triplet Energy Transfer, TTA Is Triplet−Triplet Annihilation, and RO_2^* Is Excited-State Rubrene Endoperoxide

$$\mathrm{PdPc(OBu)_8} + h\nu \longrightarrow {}^1\mathrm{PdPc(OBu)_8}$$

$${}^1\mathrm{PdPc(OBu)_8} \xrightarrow{\mathrm{ISC}} {}^3\mathrm{PdPc(OBu)_8}$$

$${}^3\mathrm{PdPc(OBu)_8} \xrightarrow{\mathrm{TTET}} {}^3\mathrm{Rubrene}$$

$${}^3\mathrm{Rubrene} + {}^3\mathrm{Rubrene} \xrightarrow{\mathrm{TTA}} {}^1\mathrm{Rubrene} + \mathrm{Rubrene}$$

$${}^1\mathrm{Rubrene} \longrightarrow \mathrm{Rubrene} + h\nu'$$

$${}^1\mathrm{Rubrene} \longrightarrow {}^3\mathrm{Rubrene}$$

$${}^3\mathrm{Rubrene} + {}^1\mathrm{O_2} \longrightarrow \mathrm{RO_2}^*$$

$$\mathrm{RO_2}^* \longrightarrow {}^3\mathrm{Rubrene} + \mathrm{O_2}$$

$$\mathrm{RO_2}^* \longrightarrow \mathrm{RO_2}$$

excitation (Figure 5e), and after an additional 5 min of continuous irradiation, the reaction is complete as is evident from the data presented in Figure 5f. The solution at this time by visual inspection has lost a significant amount of its original visible absorbance. The new NMR bands indicated by the asterisks in Figure 5e,f are consistent with the formation of a new product, displaying a more complicated (and asymmetric in nature) ^{1}H NMR (Figure 5f) spectrum than that displayed by pure rubrene (Figure 5a). From the UV−vis data presented earlier, we know that the rubrene is consumed during this photolysis, and the only colored species remaining detectable by UV−vis and fluorescence is the $PdPc(OBu)_8$ chromophore. All of these collective data are consistent with the formation of a rubrene endoperoxide photoproduct, which was further characterized by MALDI-TOF mass spectrometry where an envelope of peaks corresponding to the rubrene endoperoxide was observed at *m*/*z* 565, presented in Supporting Information. Diagnostic mass features corresponding to rubrene were also observed at *m*/*z* 532, consistent with loss of dioxygen from the parent structure. The rubrene endoperoxide was independently prepared from the irradiation of rubrene in aerated deuterated benzene solution, and the ^{1}H NMR resembles that obtained from the reaction of $PdPc(OBu)_8$ and rubrene upon selective excitation of the phthalocyanine sensitizer, Figure 5g. MALDI-TOF mass spectrometry of this product resulted in peaks at *m*/*z* 532 and *m*/*z* 564 corresponding to rubrene and rubrene endoperoxide, respectively, as observed in the sensitization experiments; see Supporting Information. These results are consistent with the established reactivity of rubrene with singlet dioxygen in a one-to-one manner,[18,19] and the data provided here gives spectroscopic structural evidence for this intermediate resulting from the triplet-based photochemistry at the heart of this study.

A possible mechanism for the formation of the rubrene endoperoxide in solution is presented in Scheme 2. Excitation of the sensitizer eventually results in the TTA of rubrene in the idealized photochemical scenario. However, the triplet excited-state of rubrene can also react with singlet oxygen, produced via triplet energy transfer, either from rubrene itself or from $PdPc(OBu)_8$, with ground state triplet molecular oxygen forming an excited endoperoxide (RO_2^*). RO_2^* can either produce the ground state endoperoxide or revert to the triplet excited-state of rubrene and molecular oxygen. Similar mechanisms have been proposed for the photooxidation of anthracene and diphenylanthracene in solution in various solvents including benzene at varying oxygen concentration,[18] and are also consistent with previous reports on rubrene photooxidation.[19] We note that subsequent reactions of the rubrene endoperoxide are indeed plausible; however, under the confines of long wavelength triplet sensitization, we believe that such reactions are unlikely in terms of energetics.

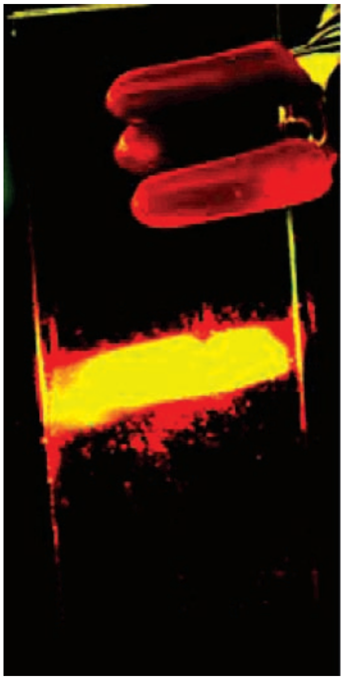


Figure 6. Digital photograph of upconverted fluorescence observed in the P(EO/EP) material containing 2.0×10^{-5} M $PdPc(OBu)_8$ and 6.0×10^{-4} M rubrene taken during an incident 725 nm, 2 mJ laser pulse.

To circumvent the issue of rubrene photooxidation in solution, we incorporated $PdPc(OBu)_8$ and rubrene in a solid polymer film. In our previous work, dioxygen did not markedly impede upconversion photochemistry between PdOEP and DPA in P(EO/EP) thin films,[6] so we hoped for reduced rubrene/O_2 reactivity in this material. A mixture of 2.0×10^{-5} M $PdPc(OBu)_8$ and 6.0×10^{-4} M rubrene was integrated into the polymer P(EO/EP), which upon excitation at 725 nm resulted in the sensitized upconversion of rubrene fluorescence under ambient aerated conditions, Figure 6. The upconversion process was easily detected without the aid of filters resulting in an intense bright yellow emission and was observed from the same film for 4 days. However, the intensity of the upconverted fluorescence slowly decreased over this time period, concomitant with the degradation of rubrene as clearly evidenced by the loss of its characteristic visible absorption bands. Similar rubrene degradation results have also been reported for thin films grown on SiO_2 where continuous visible photolysis results in rubrene photooxidation.[12] To further circumvent this problem, the polymer films were prepared in an inert argon atmosphere using freeze−pump−thawed (three cycles) polymer solutions containing the sensitizer and acceptor. The mixture was cast onto a glass slide inside an argon saturated oven at 90 °C, and the solid film was placed inside an argon saturated cuvette that was maintained under a positive argon atmosphere. Selective excitation of $PdPc(OBu)_8$ at 725 nm in the blend film at various incident power densities ranging from 0.0173 to 0.0932 W cm^{-2} resulted in the emission profile shown in Figure 7a. Integration

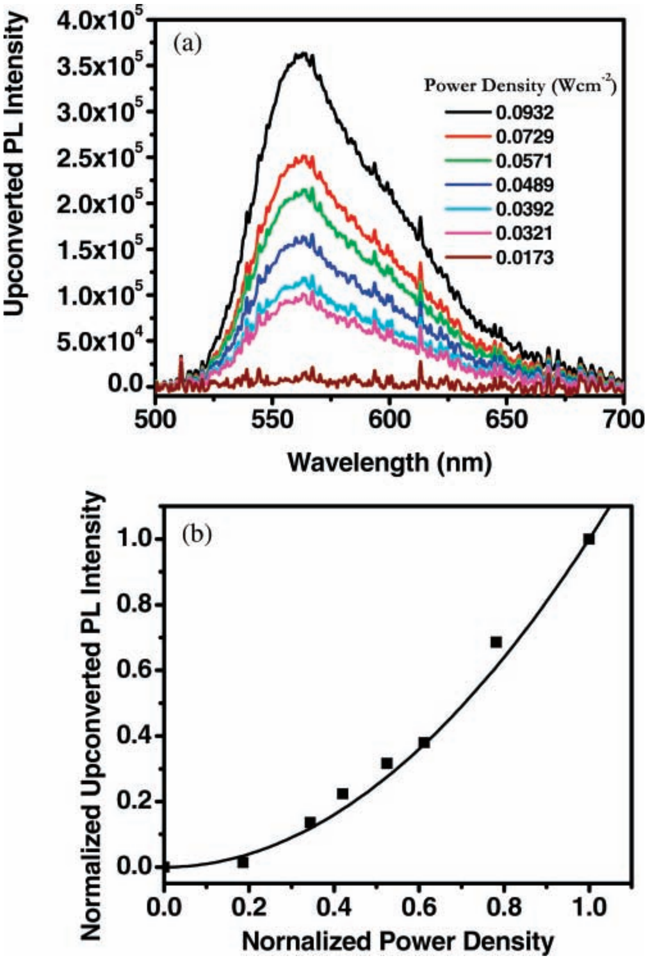


Figure 7. (a) Upconverted emission intensity profile of a thin PdPc-$(OBu)_8$/Rubrene (P/EO/EP) blend film as a function of 725 nm laser that was made under an inert atmosphere and kept under a positive argon environment. (b) Normalized integrated emission intensity in part (a) as a function of the highest incident intensity of 18.3 mW (1.8 mJ/pulse at 10 Hz) in de-aerated environment. The black line is the best quadratic fit (x^2) to the data.

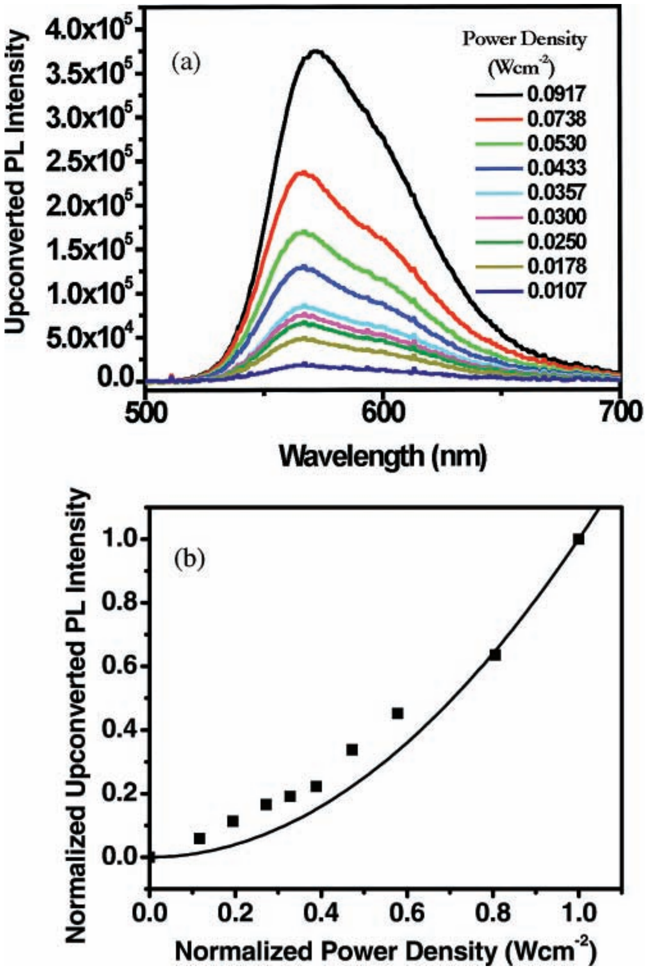


Figure 8. (a) Upconverted emission intensity profile of a thin PdPc-$(OBu)_8$/Rubrene (P/EO/EP) blend film as a function of 725 nm laser that was made under an inert atmosphere and studied under aerated conditions. (b) Normalized integrated emission intensity in part (a) as a function of the highest incident power of 18.0 mW (1.8 mJ/pulse at 10 Hz) in aerated environment. The black line is the best quadratic fit (x^2) to the data.

of the delayed fluorescence of the spectra shown in Figure 7a against the subsequent measured laser pulse normalized to the highest power density resulted in a nonlinear dependence in the inert blend film (Figure 7b). The black line in Figure 7b shows the best quadratic fit (x^2) to the data confirming the nonlinear photochemistry that drives the photon upconversion in the thin film through TTA. It should be noted that the films were made under an inert atmosphere using the best of our current experimental capabilities; however, it is inevitable that oxygen may have diffused into the system, and hence, the data obtained in the blend film that was kept under an inert atmosphere does not fall along a perfect quadratic fit (x^2) as could be obtained in vacuum degassed solutions mixtures of the two chromophores. The incident power dependence studies of blend films containing $PdPc(OBu)_8$ and rubrene that were made in an inert atmosphere were also studied under air-saturated conditions (Figure 8). This system deviates more from the anticipated sequential one-photon absorption-based nonlinear photochemistry observed in the blend films relative to those studied under argon saturated conditions. This deviation from a perfect incident intensity quadratic dependence is likely representative of oxygen diffusion into the film leading to the formation of rubrene endoperoxide which disrupts the light-producing upconversion photochemistry in the film. Therefore, we have demonstrated that with improved processing conditions (inert atmosphere) and proper handling, substantially more stable upconversion materials can be produced that incorporate rubrene. Detailed studies are underway to better understand how P(EO/EP) polymer host successfully mediates sensitized TTA while aiding in suppressing rubrene's side reactions with molecular oxygen.

Conclusions

The present work demonstrates upconverted yellow singlet emission of rubrene upon red excitation of $PdPC(OBu)_8$ at 725 nm in vacuum degassed toluene solutions using a Nd:YAG /OPO laser system equipped with a gated iCCD detector. The TTA process is confirmed by the quadratic dependence of the upconverted delayed fluorescence measured as a function of the incident light intensity. We have shown that selective excitation of the Pd^{II} phthalocyanine triplet sensitizer in aerated solutions results in the decomposition of rubrene to form its corresponding endoperoxide. Complete removal of oxygen from solutions containing the sensitizer and acceptor using freeze−pump−thaw degassing leads to a chromophore composition that is stable for periods of weeks, and the upconversion process maintains its output stability for at least 2 h during continuous 725 nm pulsed laser photolysis. The upconversion process in solid polymer films was also investigated and is shown to be stable for days in air-equilibrated samples. These ambient stored solids slowly degrade over time as is evident by the disappearance of the absorption bands of rubrene. However, blend polymer films that were made under an inert atmosphere and kept under a positive argon pressure shows a quadratic incident power dependence supporting the notion that, similar to the solution based phenomenon, nonlinear photochemistry drives the photon upconversion in these thin films through TTA. The current work demonstrates that photon upconversion realized through TTA successfully operates using a heavy metal phthalocyanine sensitizer both in solution and in solid polymer films, suggesting the widespread generalization of this phenomenon as long as proper energy criteria are met.

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Supporting Information Available: MALDI-TOF mass spectra of relevant photolysis reaction mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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