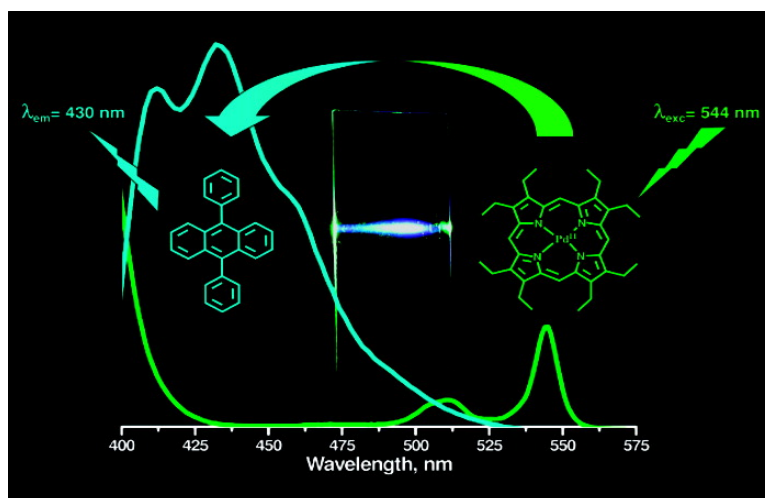


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Noncoherent Low-Power Upconversion in Solid Polymer Films

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Upconversion, that is, the generation of higher energy photons with respect to incident light, is a nonlinear process and therefore usually requires high excitation intensities. A possible route to lowering the optical power requirements for upconversion lies in harnessing energy through triplet–triplet annihilation (TTA).^{1–3} In a sensitized TTA scheme, the upconversion of (noncoherent) light 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. 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 upconversion.¹ The combination of benzophenone, a high triplet yield organic sensitizer, and naphthalene has been successful in mediating UV-based upconversion,² even in dendritic architectures at 77 K.³ In recent developments, our group⁴ and others⁵ have demonstrated that the incorporation of metal-organic chromophores can markedly enhance upconversion yields since the sensitizer triplet state can be populated with high efficiency upon light absorption. This strategy has proven exceedingly effective. For example, in solutions comprising the metal-to-ligand charge-transfer sensitizer [Ru(dmb)₃]²⁺ (dmb = 4,4'-dimethyl-2,2'-bipyridine) and 9,10-diphenylanthracene (DPA), green-to-blue upconversion is readily possible when a conventional 532 nm laser pointer is used as the light source; the blue emission thus generated is clearly detectable by the unassisted eye, even in a well-illuminated room.^{4b} Another important advance includes the observation of incoherent-light-driven upconversion in solutions comprising Pd(II)octaethylporphyrin [PdOEP] (**1**) in concert with DPA (**2**).^{5d} To our best knowledge, noncoherent upconversion using TTA has hitherto only be observed in solution. In order to fully exploit the approach, it would be attractive if solid materials could be developed that were capable of displaying the effect. This advance would, for example, permit the utilization of wavelength-shifting thin films in combination with solid-state lasers,^{4,5} or in photovoltaics,⁶ enabling more complete harnessing of the solar spectrum, particularly valuable for making better use of the near-IR region in real devices. With the notion that some exciton diffusion is required to allow for triplet–triplet annihilation, we surmised that noncoherent low-power upconversion could be achieved in solid polymer films, by blending high concentrations of the previously employed sensitizer **1** and emitter **2** with a rubbery host polymer—an ethyleneoxide/epichlorohydrin copolymer P(EO/EP) was found to display suitable properties (good transparency, low crystallinity and glass transition temperature, high dye solubility, and adequate mechanical properties).⁷

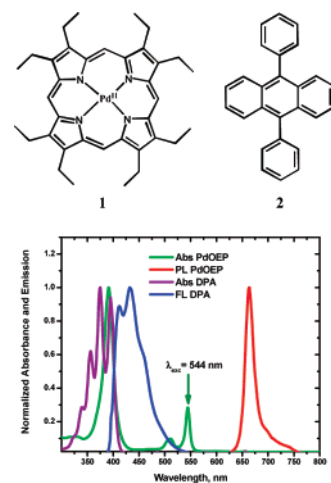


Figure 1. Absorbance and photoluminescence spectra of PdOEP and DPA in DMF. The center excitation wavelength used in this study to generate upconverted DPA emission (400–525 nm) is indicated (544 ± 18 nm). Intensities are normalized to arbitrary maxima of 1.

Figure 1 presents the normalized absorption and emission spectra of commercially available **1** and **2** measured in dimethylformamide (DMF), the solvent used for the dissolution of all thin film components. Selective excitation of the PdOEP Q-band at 544 nm produces long-lived triplet phosphorescence at 663 nm, which sensitizes DPA triplet formation through diffusive energy transfer, eventually leading to TTA of ³DPA* molecules.^{5d} The TTA process generates the same singlet fluorescence as observed upon direct excitation of DPA, depicted in Figure 1. We note that the upconversion process is significantly enhanced when PdOEP is used instead of [Ru(dmb)₃]²⁺ as the sensitizer under identical experimental conditions. This enhancement exclusively results from initial triplet energy transfer quenching by DPA and has its origin in the relative excited-state lifetime differences of the sensitizer. A comprehensive study related to the optimization of solution-based upconversion processes utilizing DPA will be presented elsewhere.⁸ Thin films containing **1** and **2** were prepared as follows: 2.0 g of 50:50 P(EO/EP) [Epichlomer C, Daiso, Co., Ltd.] (5% in DMF) was mixed with 1 mL of a solution of **1** (0.28 mM) and 0.5 mL of a solution of **2** (19 mM) in DMF. The mixture was cast onto a glass microscopy slide. The slide was placed in a conventional oven at 90 °C for 5 min then cooled to room temperature. Two additional coatings were applied in the same manner, and the final samples were stored at room temperature in the dark for at least 1 week to yield dry films with a typical thickness of 100 μm. Portions of the films show clear signs of DPA phase separation resulting from the high concentrations used in this study; however, this did not adversely influence the photonics.

Figure 2a presents the emission spectra of a typical static experiment performed in a conventional single photon counting

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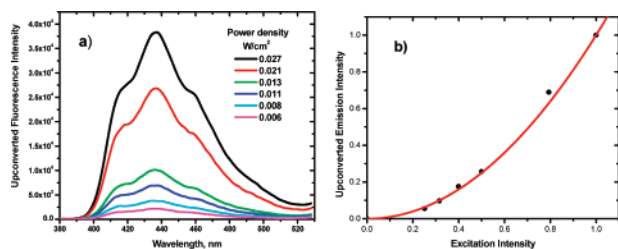


Figure 2. (a) Upconverted emission intensity profile of a thin PdOEP/DPA/P(EO/EP) blend film as a function of 544 ± 18 nm incident power density. (b) Normalized integrated emission intensity data from part (a) plotted as a function of incident power. The solid red line is the best quadratic fit (x^2) to the emission data, normalized to the highest incident intensity (27 mW/cm^2).

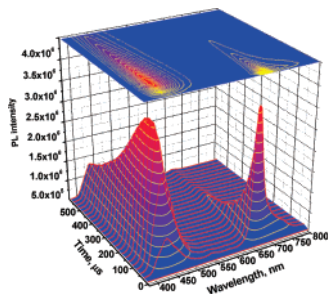


Figure 3. Time-resolved emission spectra of a thin PdOEP/DPA/P(EO/EP) blend film measured following 7 ns , $544 \pm 2 \text{ nm}$ laser pulses from a Nd:YAG/OPO laser system.

fluorimeter. The PdOEP in the blend film was selectively excited with incoherent light from a Xe lamp/monochromator ($\lambda_{\text{ex}} = 544 \pm 18 \text{ nm}$) in conjunction with a 515 nm long pass filter at various incident power densities ranging from 6 to 27 mW/cm^2 . The upconverted DPA fluorescence is clearly observed anti-Stokes to the excitation. It closely resembles the features of neat DPA in solution, and the shape of the emission profile is clearly independent of the excitation power. It is important to state that the data presented in Figure 2a were acquired under ambient conditions and stem from a blend film that was processed under ambient atmospheric conditions. This is of utmost importance for real-world applicability.

Analysis of the incident light intensity dependence on the sensitized upconversion emission signal of the new PdOEP/DPA/P(EO/EP) blend is provided in Figure 2b. Individual data points represent the integrated emission spectra from Figure 2a plotted against incident power density, both normalized with respect to the highest emission intensity and incident power density. The solid line represents the best quadratic fit to the data and definitively establishes that nonlinear photochemistry drives the photon upconversion through sensitized TTA, that is, the emission signal is proportional to the square of the incident power and hence to the square of the DPA triplet concentration.^{1–5} We also observe identical power dependence for upconverted emission in mixtures of **1** and **2** in DMF solution. In related work, other investigators have noted that solid-state upconversion required high-intensity laser irradiation and generated an unusual power dependence, halfway between linear and quadratic (i.e., $x^{1.5}$).^{5b} We do not observe such phenomena in the current work, likely a result of the low incident power necessary to generate the effect. Time-resolved emission spectra of the blend film recorded after 7 ns , $544 \pm 2 \text{ nm}$ laser pulses are displayed in Figure 3. These data clearly demonstrate that PdOEP phosphorescence at long wavelengths decays while the upconverted DPA fluorescence is produced as a function of time.

This is analogous to the solution-based process leading to the conclusion that anti-Stokes delayed DPA fluorescence is indeed sensitized through triplet state quenching of PdOEP in the film. Upconversion processes in solution are a complex function of incident power as well as sensitizer and quencher/annihilator concentration;⁸ therefore, a detailed discussion of the kinetic processes occurring in the sample represented by Figure 3 would be misleading. Detailed experiments along these lines will be the subject of future studies. Qualitatively, we note that, while the solution process is kinetically faster, the solid polymer host successfully enables consecutive bimolecular reactions implying that relatively fluidic microenvironments exist in this material.⁷ This statement is further supported by the fact that upconversion is completely suppressed in the same film at 77 K , well below the glass transition temperature of the P(EO/EP). Presumably, diffusion is largely or completely inhibited under such conditions, retarding the necessary bimolecular chemistry steps required for sensitizer quenching and TTA. It is therefore the proper combination of host and chromophore dopants that have led to the first realization of noncoherent upconversion in solid polymer films.

The current work represents the first example of noncoherent low-power upconversion in solid polymer films. The quadratic incident power dependence as well as the static and time-resolved emission data supports the sensitized TTA-based mechanism where selective excitation of PdOEP leads to triplet sensitization of DPA which eventually annihilates with a second triplet-sensitized DPA chromophore, producing delayed singlet DPA fluorescence. The experimental evidence is quite compelling that sequential triplet excited-state bimolecular processes are operative in the P(EO/EP) matrix under ambient, air-saturated conditions. This suggests further use of such host materials in photonics applications employing triplet state photochemistry and photophysics.

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