Up-Conversion Fluorescence: Noncoherent Excitation by Sunlight

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We demonstrate up-conversion of noncoherent sunlight realized by ultralow excitation intensity. The bimolecular up-conversion process in our systems relies on the presence of a metastable triplet excited state, and thus has dramatically different photophysical characteristics relative to the other known methods for photon up-conversion (two-photon absorption, parametric processes, second harmonic generation, sequential multiphoton absorption, etc.).

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The direct increase of the spectral brightness of the short wavelengths spectra of the Sun from the longer wavelengths is still a very considerable challenge. Here we suggest an up-conversion of the longer wavelengths of the emission of the Sun towards shorter wavelengths by up-conversion fluorescence in a two-component organic system. The already existing examples of up-conversion, i.e., the generation of photons, notably spectrally blueshifted to the wavelength of the excitation photons, by simultaneous or sequential absorption of two or more photons with lower energy, has always been associated with the use of *coherent* light sources (lasers). Another formidable limitation of these existing methods are the high light intensities (commonly, on the order of MWcm^{-2} and GWcm^{-2}) required, which cannot be reached by means of noncoherent light sources, and especially not with the Sun. The only one notable example where photon up-conversion in the spectra of the Sun could be observed after strong focusing is anti-Stokes Raman scattering [1]. To mention but one of the many possible applications of an efficient and high-energy photon up-conversion would be its use as an elegant way to increase the efficiency of various solar cells [2].

In our previous works we have reported photoluminescence up-conversion in thin films of two or more active components—metallated porphyrin macrocycles (MOEP) as sensitizers, blended in matrix of blue emitting molecules with high fluorescence quantum yield, such as polyfluorenes (PF) and polypentaphenylenes [3,4]. The bimolecular up-conversion process in these systems relies on the presence of a metastable triplet excited state, and thus has dramatically different photophysical characteristics relative to the other known methods for photon up-conversion (two-photon absorption, parametric processes, second harmonic generation, sequential multiphoton absorption, etc.).

One advantage of our MOEP-emitter systems is the relatively broad absorption spectra of the MOEP sensitizer molecules (commonly around 15 nm width), and the possibility to combine sensitizers [3] with varying absorption maxima in order to increase the total width of the excitation spectra for up-conversion.

The crucial advantage of this bimolecular up-conversion process is its *inherent* independence on the coherence of the excitation light, because the optical excitation of the system is by resonant single photon absorption [5]. Consequently, the efficiency of the up-conversion process thus depends on the materials' properties but does not in any way depend on the coherence of the excitation photons. To the best of our knowledge so far there is no reported noncoherently excited (sunlight) up-conversion luminescence.

The principles of operation of the bimolecular up-conversion process we have devised and studied are that after absorption of a photon in the singlet Q band of the MOEP molecule, due to an effective intersystem crossing (ISC) strongly enhanced by spin-orbit coupling to the metal center of MOEP, the long lived triplet state of MOEP is highly populated (Fig. 1). This triplet state can further be considered as an excited states reservoir for subsequent energy transfers. From here, two excitation pathways are possible. First, as a consequence of a triplet-triplet annihilation (TTA) process between the excited MOEP molecules themselves [4,6], one of the MOEP

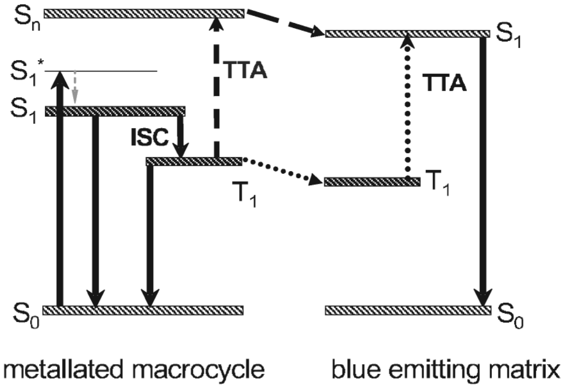

FIG. 1. Energy scheme of a TTA supported up-conversion process. The dashed pathway represents the up-conversion in system PF:MOEP [3,4], and the dotted pathway—up-conversion in system PF-co-anthracene: MOEP [3,7].

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molecules returns to the ground state and the other is excited into a higher singlet state. This is followed by an effective transfer of MOEP singlet excitation to the excited singlet state of the blue emitter [4,6] (Fig. 1, dashed pathway). Second, an additional up-conversion channel [7] comprising first of a transfer of the triplet excitation of the MOEP directly to the triplet state of the blue emitter molecules, followed again by effective TTA [this time of the blue emitter molecule triplets (Fig. 1, dotted pathway)] resulting again into the excited singlet state of the blue emitter.

Upon excitation with 532 nm, a wavelength far below the absorption of the blue emitter, the resulting luminescence spectra in these systems clearly reveals the up-converted fluorescence of the matrix molecules, together with the fluorescence and the phosphorescence of the sensitizer molecules [7,8]. An example of such luminescence spectra for a model system is shown in Fig. 2. We chose the 9,10-diphenylanthracene (DPA) molecule as a model blue emitting matrix in order to study the mechanism of the second type of up-conversion (Fig. 1, dotted pathway). It has been shown before [9] that DPA in benzene solution has high singlet fluorescence quantum yield and even though its triplet quantum yield is low upon ISC, the DPA triplet level could be populated upon benzophenone photosensitization.

The dynamic properties of the TTA supported up-conversion process in solution containing DPA sensitized with 2 wt% (2,7,8,12,13,17,18-octaethyl-porphyrinato)Pd(II) (PdOEP) are shown in Fig. 2.

The up-conversion fluorescence of the DPA molecules has a rise time of ca. 5 μs. This delay represents the time necessary for a transfer of triplet population from PdOEP-triplet to DPA-triplet level and filling of the DPA-triplet reservoir. From Fig. 2 one can observe creation of the "up-conversion channel": During the first 1 to 2 μs of the pump pulse only the PdOEP-phosphorescence (with maximum at $\lambda = 662$ nm) together with PdOEP-fluorescence (centered at $\lambda = 549$ nm) exists. Starting from the 3rd μs, a strong increase of the up-conversion fluorescence is observed, followed by an increase of the PdOEP-fluorescence, because of the reabsorption. It has to be pointed out, that this up-conversion fluorescence rise time depends strongly on the pump intensity: With increasing the pump intensity the rise time drastically decreases. The decay time of the sensitizer molecules phosphorescence, together with the decay of the annihilation up-conversion fluorescence after formation of the annihilation channel, is visible on Fig. 2—this is the emission after the termination of the pumping pulse. The PdOEP-phosphorescence decay curve shows a multiexponential character. The depopulation channels of the PdOEP-triplet state are radiative decay, transfer to the lower laying DPA-triplet state, and TTA between the porphyrin triplets. The decay of the DPA up-conversion fluorescence is much longer than the decay of the PdOEP phosphorescence. This is a clear sign that the PdOEP-triplet to DPA-triplet transfer takes place. Furthermore, two types of TTA process, responsible for the up-conversion fluorescence of DPA, should be considered: a homo-TTA process between the DPA triplets and a hetero-TTA between excited triplets of the PdOEP and DPA molecules.

Strikingly, even the linear absorption of the sensitizer PdOEP is strongly influenced (an increase of over 25%) by the presence and concentration of the up-conversion emitter DPA. Such an increase in the linear absorption of the sensitizer upon acceptor concentration (DPA in our case)

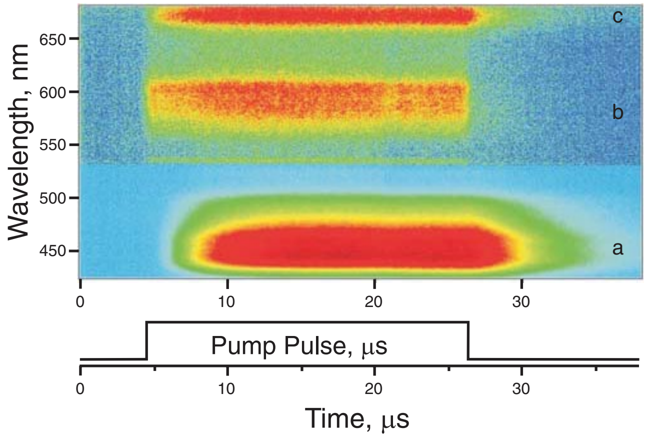

FIG. 2 (color). Time evolution of the annihilation up-conversion fluorescence of DPA (a), PdOEP fluorescence (b), and PdOEP phosphorescence (c). Pump wavelength 532 nm, intensity—80 Wcm^{-2}, excitation pulse duration 23 μs. Measured with a streak camera (Hamamatsu 5685). Note: The measured luminescence intensity at region beyond $\lambda = 530$ nm is multiplied by factor of 10 in order to represent the data on a comparable scale.

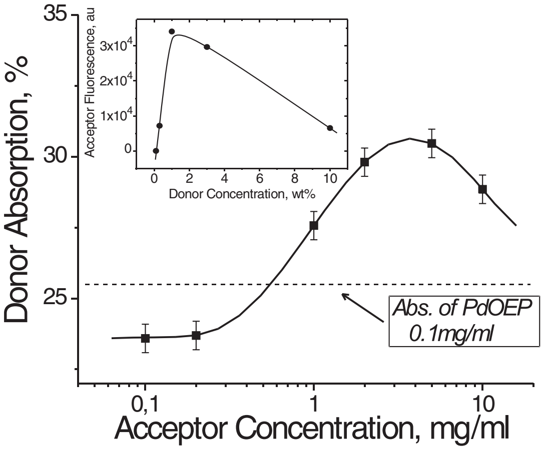

FIG. 3. Dependence of the linear absorption of 532 nm of the PdOEP molecules on the concentration of the DPA. The dashed line represents the absorption of 0.1 mg/ml PdOEP. Inset: dependence of the efficiency of DPA up-conversion fluorescence on the PdOEP concentration.

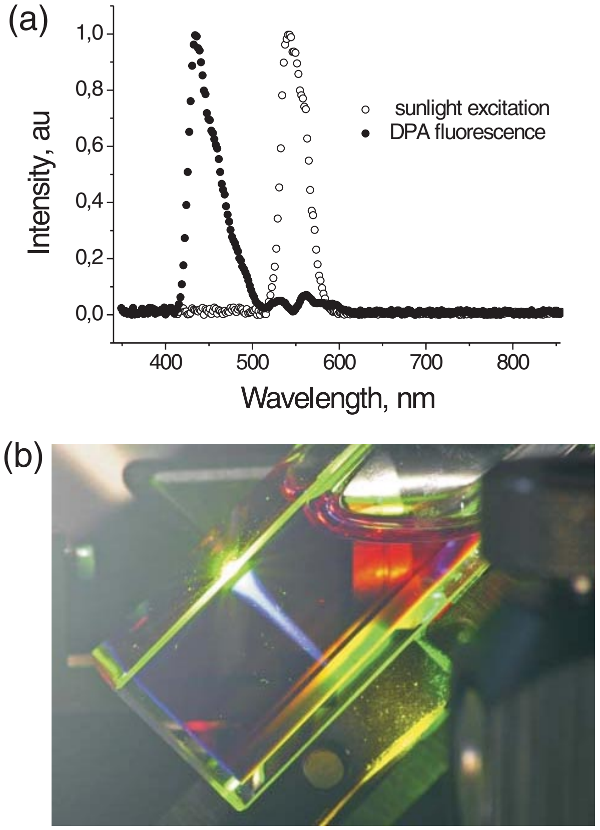

FIG. 4 (color). (a) Normalized excitation spectrum (open circles); normalized fluorescence of DPA (closed circles) excited in the up-conversion regime at room temperature, in solution, excitation intensity 10 Wcm^{-2}. (b) A CCD-camera image of the up-converted fluorescence inside the 1 cm cuvette, excited with the green part of the sun spectrum, no filters were used.

has not been reported until now. The change of the PdOEP—absorption (at concentration 0.1 mg/ml) upon increasing the DPA concentration in the solution from 0.1 to 10 mg/ml is shown in Fig. 3. Moreover, in the inset of Fig. 3 the dependence of the efficiency of the up-conversion on the sensitizer concentration is shown. The maximum increase of the sensitizer linear absorption corresponds to the highest efficiency of the up-conversion fluorescence, i.e., 2 wt% PdOEP in DPA emitter.

From a practical point of view, the external efficiency of the up-conversion process is of critical importance. In order to estimate the external up-conversion efficiency we performed cw-excitation of the DPA sample blended with the optimal concentration (described above) of 2 wt% PdOEP with two wavelengths: 407 nm (at a the singlet absorption band of DPA) and at 532 nm (the *Q*-band absorption of the sensitizer). We measured the same DPA-fluorescence signal by exciting with $\lambda = 407$ nm with intensity of 8.5 Wcm^{-2} and with $\lambda = 532$ nm with intensity of 125 Wcm^{-2}, keeping all other experimental conditions the same. We used for the quantum efficiency of the DPA in solution the value of 88% [9,10] (when excited at 360 nm) and took in to account the relative extinction coefficients of the system for 407 and 532 nm. From here we estimate an external efficiency of greater than 1% for the annihilation up-conversion fluorescence when excited by 532 nm.

Consequently, for the first time we present the achievement of up-conversion photoluminescence excited by using ultralow intensity *noncoherent* sunlight. The experimental results for a solution of DPA sensitized with 2 wt% PdOEP are shown in Fig. 4. As an excitation source we used the green part of the terrestrial solar spectrum. Through a combination of collimation lenses, long pass edge filter (RazorEdge$^{\mathrm{TM}}$, designed for $\lambda = 514.5$ nm) and broad band interference filters with central wavelength at $\lambda = 550$ nm the green part of the sun's spectrum was separated and focused to a spot of approximately 1 mm in diameter. The light intensity at the focal spot was on order of 10 Wcm^{-2}. As shown in Fig. 4(a) (open circles), the portion of the solar spectrum we thus used for excitation did not contain ultraviolet and blue bands. The observed DPA up-conversion fluorescence spectrum is also shown in Fig. 4(a) (filled circles). The blue up-converted DPA-fluorescence spectrum was observed laterally, by means of an optical fiber spectrometer, without any blocking filters. It has to be pointed out that the almost complete depopulation of the PdOEP-triplet state took place, leading to only a negligible amount of PdOEP phosphorescence. This is also visible in Fig. 4(b) where the photograph of the green sunlight excited blue DPA fluorescence is shown as a blue shaft of light appearing inside a cuvette with the sensitized solution.

In conclusion, we demonstrate for the first time, a highly efficient (more than 1% external efficiency) and high-energy photon up-conversion in a model two-component organic system in solution realized with a *noncoherent* light source (the sun) with ultralow (as low as 10 Wcm^{-2}) intensity.

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[1] C. V. Raman and K. S. Krishnan, Nature (London) **121**, 501 (1928).
[2] T. Trupke *et al.*, J. Appl. Phys. **92**, 4117 (2002); P. Würfel, *Physik der Solarzellen* (Spektrum Akademie Verlag, Leipzig, 2000).
[3] A. Yasuda *et al.*, U. S. Patent No. US2005056815 (2005).
[4] P. E. Keivanidis *et al.*, Adv. Mater. **15**, 2095 (2003).
[5] S. Carusotto *et al.*, Phys. Rev. **157**, 1207 (1967).
[6] S. Baluschev *et al.*, Chem. Phys. Chem. **6**, 1250 (2005).
[7] F. Laquai *et al.*, J. Chem. Phys. **123**, 074902 (2005).
[8] S. Baluschev *et al.*, Nano Lett. **5**, 2482 (2005).
[9] T. Suzuki *et al.*, J. Photochem. Photobiol., A **136**, 7 (2000).
[10] D. Wöhrle, M. W. Tausch, and W.-D. Stohrer, *Photochemie* (Wiley-VCH, Weinheim, 1998).