Fluorescence

DOI: 10.1002/anie.200700414

# Blue-Green Up-Conversion: Noncoherent Excitation by NIR Light**

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The phenomenon of photon up-conversion—the generation of photons, spectrally blue-shifted 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). Already well-developed methods[1] for up-conversion, such as two-photon absorption, second (or higher-order) harmonic generation, parametric processes, and sequential multiphoton absorption, all have a common serious limitation: the requirement for very high intensity light excitation (on the order of $\mathrm{MW\,cm^{-2}}$). Some requirements that are specific for those processes, like phase-matching conditions, for example,[1] are fulfilled only for a limited spectral region. Therefore, even when the necessary light intensity was lowered substantially (on the order of $\mathrm{kW\,cm^{-2}}$), the requirement of extremely high spectral power density of the excitation source could not be overcome.[2–4]

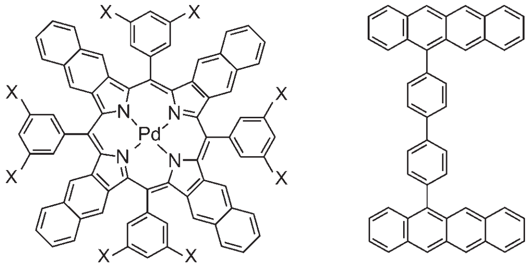
In comparison to the above-described methods, the fundamental advantage of the triplet–triplet annihilation-supported bimolecular photon up-conversion process is its *inherent* independence[5] on the coherence of the excitation light. Another principal advantage[5] of this up-conversion process is the very low intensity (as low as $1\,\mathrm{W\,cm^{-2}}$) and extremely low spectral power density (as low as $600\,\mu\mathrm{W\,nm^{-1}}$) needed from the excitation source; thus, the source can be the sun.

The process of photon up-conversion, based on triplet–triplet annihilation in multimolecular systems,[5–8] is to be considered as an inherently connected chain of three processes already studied in the past. The first process in this chain is intersystem crossing (ISC), which is strongly enhanced by the spin–orbit coupling to the metal center of metalated macrocyclic sensitizer molecules.[9] The second process in the chain is the transfer of the excitation energy of the sensitizer triplet to the emitter triplet.[10] The third process is the subsequent triplet–triplet annihilation, which in our system occurs mostly between emitter-molecule triplets.[11]

The key feature of the annihilation up-conversion process is the large population of the triplet states of the emitter molecules created in a chain of events following absorption of single photons. Therefore, the sensitizer molecules have to supply a long-lived triplet state highly populated by single-photon absorption. Moreover, the strong overlap of the triplet levels of the sensitizer and the emitter molecules is of crucial importance for this type of up-conversion.

Herein we report the direct photon up-conversion of the near-infrared part of the solar spectrum (around 700 nm) into blue-green emission (480–580 nm). The external quantum efficiency of the studied system is as high as 0.04.

Extension of the π-conjugated system in metalated porphyrins by annelated aromatic rings leads to a noticeable red shift[12] in the absorption and emission spectra. Our interest in porphyrins such as tetrabenzoporphyrins[13] arises from the ability to shift the excitation spectra for up-conversion deep into the red region of the visible spectrum. Accordingly, the triplet levels of the emitter molecules have to be tuned into the infrared region too. The structures of the materials investigated in this work are shown in Figure 1. The palladium–porphyrin complex **1** and the bis(tetracene) **2** were synthesized in our group.



**1** **2**

*Figure 1.* Structures of **1** and **2**; X = OMe.

Compound **1** was synthesized by using a recently developed general method[14] by the condensation of 4,9-dihydro-

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[**] S.C., S.A., and A.C. thank the Russian Foundation of Basic Research for the support through grants RFBR-04-03-32650-a and RFBR-07-03-01121-a.

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2*H*-benzo[*f*]isoindole with 3,5-dimethoxybenzaldehyde and subsequent in situ aromatization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 34 % yield. The introduction of 3,5-substituents in the *meso*-aryl rings, even groups as simple as MeO, helps in increasing the solubility of the π-extended porphyrins,[15] which are well-known to show enhanced aggregation and low solubility in organic solvents. The prepared porphyrin turned out to be readily soluble in common organic solvents. Palladium was inserted by heating the porphyrin with $Pd(OAc)_2$ in benzonitrile for 0.5 h, and the Pd complex was isolated by column chromatography in 60 % yield.

Compound **2** was synthesized in two steps: bromination of tetracene to 5-bromotetracene with one equivalent of *N*-bromosuccinimide, under the conditions described previously,[16] and Suzuki coupling of 5-bromotetracene with commercially available 4,4′-biphenylene diboronic acid. It was shown that Suzuki coupling of 5-bromotetracene with commercial boronic acids using $[Pd(PPh_3)_4]$ as a catalyst formed the target compounds only in low yield (ca. 10 %).[17] Varying the reaction conditions did not improve the yield. However, the Suzuki coupling of 5-bromotetracene with diboronic acid was successfully applied by using the following catalyst: a combination of $[Pd_2(dba)_3]$ with the ligand bis(2-(diphenylphosphino)phenyl)ether (DPEPhos), which has been described as an efficient catalyst for the Suzuki coupling of sterically hindered, *ortho*-disubstituted benzene derivatives.[18] The application of this catalytic system afforded 4,4′-bis(5-tetracenyl)-1,1′-biphenylene in 58 % yield. Aqueous potassium carbonate was used instead of potassium phosphate in the original procedure. Compound **2** was purified by column chromatography on silica gel and had greater than 98 % purity (TLC, MS, NMR, elemental analysis).

The absorption spectra of **1** and **2** are shown in Figure 2. The absorption of the blue-green-emitting **2** is negligible at wavelengths longer than 520 nm. Consequently, no singlet emission can be observed from **2** when the emitter molecules are exposed to light of 700 nm with intensities less than about 10 W cm$^{-2}$, as described below.

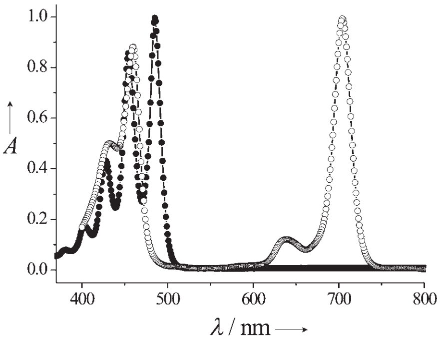

*Figure 2.* Normalized absorption spectra of **1** (○) and **2** (●) in toluene.

The steady-state luminescence spectra, generated through up-conversion for a solution of **2** in toluene blended with 5 mol % **1**, is shown in Figure 3. The spectra clearly show fluorescence of **2** (with local maxima at about 500, 533, and 573 nm), together with bands from phosphorescence (local maxima at about 916 and 942 nm) of the sensitizer **1**. The fluorescence of the sensitizer (maxima at about 720 and 790 nm) is completely suppressed by the use of edge filters. It is important to note that the phosphorescence of the sensitizer is almost completely quenched.

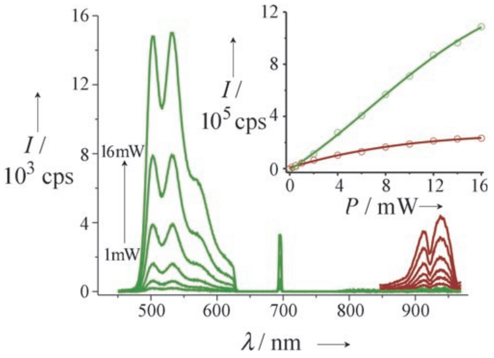

*Figure 3.* Comparison of the phosphorescence of a toluene solution containing only the sensitizer **1** ($10^{-4}$ M; red lines) and the fluorescence of a blended toluene solution of $2\times10^{-3}$ M **2** and $10^{-4}$ M **1** (green lines) at different excitation intensities. Inset: integral phosphorescence (red circles) and integral fluorescence (green circles) as a function of the excitation intensity *P*.

Figure 3 shows also the dependence on excitation intensity of the phosphorescence of the solution containing only sensitizer, compared to the up-converted fluorescence of the blended solution containing both sensitizer and emitter. The sensitizer concentration in both solutions was the same. It is important to note that the amount of the absorbed photons in both the nonsensitized and the sensitized solution was kept the same. The inset of Figure 3 shows the integral phosphorescence of the pure sensitizer solution (red circles, integration window 850 nm–960 nm) and the integral fluorescence (green circles, 480 nm–620 nm) as a function of the excitation intensity, at constant emitter and sensitizer concentration.

It is evident from Figure 3 that for the given concentration of the emitter, sensitizer, and constant excitation intensity, the total emitter fluorescence in the blended solution exceeds the total phosphorescence of the solution of pure sensitizer by a factor of more than 2–5. Taking into account that at least two triplet states of the sensitizer need to be used for the emission of one up-converted photon, the amount of nonradiative decaying triplet states is reduced much more strongly than could be estimated directly from Figure 3. These facts lead to the conclusion that adding **2** to a solution of **1** strongly reduces the number of the porphyrin triplets that decay in a nonradiative way. To the best of our knowledge, there are no previous examples for enhanced optical triplet harvesting of such deep-lying triplets by means of up-conversion fluorescence.

The potential for possible applications of the triplet–triplet annihilation-supported bimolecular process of photon up-conversion is demonstrated in the experimental results for a noncoherent excitation of a solution of $5\times10^{-4}$ M **2** sensitized with $2.5\times10^{-5}$ M **1** (Figure 4). The excitation source was the NIR part of the terrestrial solar spectrum as shown in Figure 4 (red). The observed up-conversion fluo-

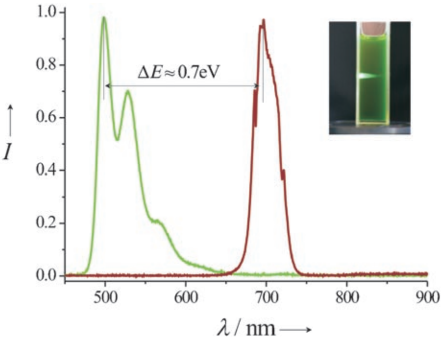

*Figure 4.* Normalized excitation part of the solar spectrum (red line); normalized fluorescence of **2** (green line) excited through up-conversion at room temperature in toluene at an excitation intensity of 1 $\mathrm{W\,cm^{-2}}$. Inset: a charge-coupled device (CCD) camera image of the up-converted fluorescence inside the 1-cm-wide cuvette; the fluorescence was excited with the near-infrared part of the solar spectrum, and no filters were used.

rescence spectrum is also shown in Figure 4 (green). The hypsochromic shift between excitation and emitted energy is estimated to be as large as $\Delta E \approx 0.7$ eV. The emission spectra were registered by an optical-fiber spectrometer in the lateral direction without using any blocking optical filter. It is important to mention that the noncoherent excitation intensity was 14 mW, collected from an excitation band with more than $\Delta\lambda \approx 20$ nm (FWHM) spectral width. The excitation spot diameter was $1/e \approx 1.8 \times 10^{-3}$ m; thus, the excitation intensity was lower than 1 $\mathrm{W\,cm^{-2}}$. The quantum yield for the up-conversion fluorescence for this experiment was estimated to be more than 0.04 (obtained by standard actinometry; Figure 5).

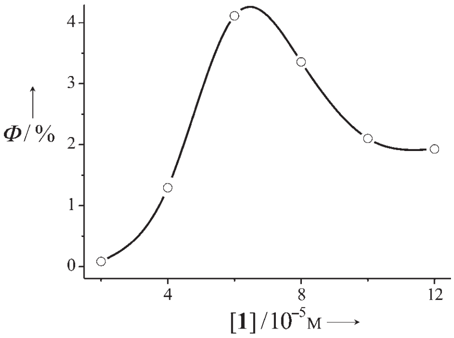

*Figure 5.* Dependence of the up-conversion quantum yield $\Phi$ on the sensitizer concentration at constant sensitizer-to-emitter molar ratio (ca. 1:10). As an actinometric standard, a solution of perylene in toluene with a quantum yield of 0.95[19] was used. The highest external up-conversion quantum yield (0.04) was observed for $6\times10^{-5}$ M **1** and $6\times10^{-4}$ M **2**.

In summary, an emitter/sensitizer couple, specially designed for the process of noncoherently excited photon up-conversion, was investigated. The hypsochromic shift between the energy of the excitation photons and the emitted photons is about 0.7 eV. The up-conversion process has a very high external quantum yield of 0.04. As the noncoherent excitation source, the NIR part of the terrestrial solar spectrum, with an intensity as low as 1 $\mathrm{W\,cm^{-2}}$ and a spectral width of $\Delta\lambda \approx 20$ nm, was used. To the best of our knowledge, the demonstrated triplet harvesting of low-energy triplet states (as low as 1.3 eV) by means of photon up-conversion has not been achieved previously.

## Experimental Section

The solutions were prepared and sealed in a glove box by using degassed toluene. A single-mode continuous-wave diode laser ($\lambda = 695$ nm) was used as the excitation source for the measurement of excitation-intensity dependence. The emission spectra were recorded on an Optical Multichannel Analyzer (Hamamatsu C7223, 16-bit analog-to-digital acquisition). The excitation laser wavelength was effectively suppressed (by a factor of more than $10^6$) by using suitable edge filters (Semrock Inc.). The emission spectra of the sensitizer and the emitter molecules in individual solutions under single-photon excitation as collected in the conditions used for the up-conversion experiments are shown in the Supporting Information, together with all known quantum yields.

A Dobsonian telescope (12″ Lightbridge, Meade Ins. Corp.) was used to collect the sunlight and couple it into a fiber (Multimode, 1000 μm, NA 0.48, Thorlabs Inc.). The infrared tail of the solar spectrum (wavelengths longer than 750 nm) was removed with a large interference filter (AHF Analysentechnik GmbH) before focusing into the fiber. The part of the solar spectrum used as an excitation source was selected using a broadband interference filter at the output of the optical fiber.

Received: January 30, 2007
Revised: May 2, 2007

**Keywords:** energy transfer · fluorescence · macrocycles · NIR solar light · triplet–triplet annihilation

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