DOI: 10.1002/chem.200801305

Towards the IR Limit of the Triplet–Triplet Annihilation-Supported Up-Conversion: Tetraanthraporphyrin

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The processes by which locally (or in situ) up-converted photons are generated by NIR or IR excitation sources have been very intensively studied and have remarkable application potential in fields like up-conversion displays,^[1] biological imaging and sensing,^[2] and photodynamic therapy of cancer.^[3] The blue-shifted emission generated in the known and long-time studied up-conversion processes results from either two-photon absorption (TPA) in organic molecules, quantum dots or in proximity of metallic clusters,^[1-3] or sequential energy transfer (ETU) in rare-earth ion-doped glasses.^[4] All these processes have a common characteristic: they need an excitation source with very high brightness-in the case of TPA-based processes because of the virtual energy level used, in the case of the ETU-based processes because of the finite width of the ionic energy levels used. Additionally, both these processes need moderate or strong optical pumping, normally in order of many kWcm⁻² up to $MWcm^{-2}$.

Recently, a different approach for up-conversion (UC), based on energetically conjoined triplet–triplet annihilation (TTA) was demonstrated.^[5] The fundamental advantage of the TTA-supported UC is its inherent independence on the

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801305.

coherence of the excitation light.^[6] The TTA-supported UC resolves also another demanding limitation of the above described "conventional" methods for UC (e.g., the ETU and all types of TPA)—the necessity to excite the samples with extremely bright optical sources (e.g., lasers). In contrast, for excitation of an efficient TTA–UC, optical sources with spectral power density of 125 μ Wnm⁻¹ are sufficient^[7] and, in particular, the excitation source can be the Sun.

The next advantage revealing the enormous application potential of the energetically conjoined TTA–UC is the very low intensity needed (on the order of 100 mWcm⁻²) to achieve high quantum yields, on the order of 2–4% in organic solutions.^[7,8] In a further step, the efficiency of the TTA–UC in bulk solid-state films, composed of the sensitizer and emitter molecules blended in inactive polymer matrix, has to be optimized as it is significantly lower than in solutions.^[6b,9]

The TTA-supported up-conversion devices, based on organic solutions are very efficient, but cannot be easily sealed for the long term. The solid-state devices of this kind can be sealed easily, but they are not efficient enough. This obstacle can be avoided when highly viscous matrices are used. In fact, the energetically conjoined TTA-UC in highly viscous matrices^[10] possesses all the required characteristics: high quantum yield (comparable with those in liquid organic solution of the active species), very low excitation intensity $(\approx 25 \text{ mWcm}^{-2})$, extremely low spectral power density optical sources ($\approx 200 \,\mu Wnm^{-1}$), and versatility in excitation and emission wavelengths. These devices can be also sealed easily. The combination of all these unique characteristics and possibilities make energetically conjoined TTA-UC ready for diverse applications, such as all-organic, flexible, and transparent displays,^[10] up-converter devices for increasing the efficiency of, for example, dye-sensitized solar cells and local, in situ, generator of blue-shifted photons.

To explore the above describe applications in their full, the IR limit, that is, the lowest energy photons able to serve as pumping source for the studied energetically conjoined TTA is of crucial importance. The highest excitation wave-



length reported so far is $\lambda = 700 \text{ nm} (\text{FWHM} \approx 20 \text{ nm}).^{[8]}$ In this communication we report for direct photon up-conversion of low-intensity IR light (with maximum at $\lambda = 790 \text{ nm}$, FWHM $\approx 23 \text{ nm}$) into yellow emission ($\lambda = 570 \text{ nm}$, FWHM $\approx 65 \text{ nm}$).

To access this region of the light spectrum, we need the respective sensitizer. The π -extended porphyrins used in earlier studies (Pd or Pt derivatives of tetrabenzo- and tetranaphthoporphyrins) cannot reach as far into NIR with their Q-bands, the most red-shifted of all these falling short by almost 100 nm. Thus, a further extension of the π -system by an extra layer of benzo rings is required, leading us to the so far elusive tertraanthraporphyrin (TAP) system. Reported earlier by Luk'yanets and Kobayashi et al.,^[11] the 5,10,15triarylsubstituted TAP derivative was obtained as a Zn complex by high-temperature templated condensation. Tetraaryl-TAPs have so far been unknown. To develop a reliable synthetic approach to TAP, we have employed the dihydroisoindole strategy, earlier elaborated for the synthesis of various derivatives of tetrabenzoporphyrins (TBP) and tetranaphthaloporphyrin (TNP).^[12]

The synthesis (shown on Scheme 1) started from a readily available benzynefurane adduct (1), which was transformed via compound 2 by the procedure described by Dehaen



Scheme 1. Synthesis of tetrakis-5,10,15,20-(*p*-methoxycarbonylphenyl)tetraanthra[2,3-*b*,*g*,*l*,*q*]porphyrin (PdTAP) (**8**). Reagents and conditions: a) sulfolene, NaHCO₃, py, 120 °C, 10 h (64%); b) HCl, EtOH, reflux, 24 h (79%); c) i. PhSCl, CH₂Cl₂, RT, 2 h; ii. Oxone[®], MeOH-H₂O, RT, 7 days (78%); d) DBU, CH₂Cl₂, RT, 1 h, (97%); e) CNCH₂COOEt, *t*BuOK, THF, RT, 12 h (67%); f) NaOH, ethyleneglycol, reflux, 1 h (73%); g) i. *p*-MeOOCC₆H₄CHO, BF₃·Et₂O, CH₂Cl₂, RT, 1 h; ii. DDQ, CH₂Cl₂, RT, 1 h (36%); h) Zn(OAc)₂·2H₂O, CH₂Cl₂-py, 10 min (90%); i) Pd(OAc)₂, Et₃N, dioxane, RT, 5 h (75%).

et al.^[13] into 1,4-dihydroanthracene (3). Compound 3 was then transformed by the procedure earlier used in the synthesis of TNP derivatives (see, for example, reference [12a] into allylic sulfone 4. As we have shown, allylic sulfones are perfectly useful as substrates in place of vinylic sulfones in the sulfone-modification of the Barton-Zard reaction, if a small excess of strong base is present in the reaction mixture furnishing the conditions of reversible allylic-vinylic sulfone isomerization. The obtained naphthoisoindolecarboxylate (6) was cleanly transformed into 4,11-dihydro-2H-naphtho-[2,3-f]isoindole (7), which was introduced to Lindsey's porphyrin synthesis. The intermediate porphyrin could not be isolated, as the aromatization of annelated rings takes place readily under the conditions of Lindsey's method, and the target TAP (8) was obtained in good yield. In comparison with the respective TNP,^[12a] TAP shows rather unusual properties; in spite of the huge conjugated system, which could be expected to render even higher liability to aggregation and poor solubility, the porphyrin (8) is readily soluble in common organic solvents both as a free base and the diprotonated form. Good solubility is likely to account for unprecedented ease of Pd insertion, which takes place at room temperature within a few hours, as compared to other porphyrins, which usually require prolonged reflux in high boil-

ing solvents like PhCN. On the other hand, TAP possesses a much more marked sensitivity towards photooxidation, so all manipulations with solutions should be done under inert atmosphere or in the dark.

The absorption spectra of the sensitizer investigated in this work is shown in Figure 1 (line). The absorption of the emitting compound (Rubrene; Figure 1 filled circles) is negligible at wavelengths longer than 620 nm. Consequently, no singlet emission can be observed when the emitter molecules are exposed to light of $\lambda = 785$ nm with the intensities used in the experiment described further below (around 1 Wcm⁻², cw excitation). The energy position of the triplet state of PdTAP is around 1.12 eV, with quantum yield of the phosphorescence less than 0.5% in toluene at room temperature. The energy position of the sensitizer triplet state matches well the triplet energy position of the emitter, Rubrene.^[7a]

The hypsochromic shift between the exciting and the

Chem. Eur. J. 2008, 14, 9846-9850

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Figure 1. Normalized absorption spectra of PdTAP (line) and Rubrene (filled circles) in toluene.

emitted photons is approximately $\Delta E = 0.6$ eV (Figure 2). In Figure 3, the dependence of the UC quantum yield on the relative concentration of the emitter/sensitizer is shown. The UC quantum yield of the couple Rubrene/PdTAP at concentration of 10^{-3} M/5× 10^{-5} in toluene is 1.2%, estimated accordingly to the definition given in reference [7b] Therefore, adding the anthraporphyrin-based sensitizer with Q-band absorption centered at $\lambda = 800$ nm to the family of tetraben-



Figure 2. Normalized fluorescence of Rubrene excited in up-conversion regime at room temperature in toluene, excitation intensity 250 mWcm⁻² (laser power 10 mW, collimated beam with diameter d=2 mm), $\lambda =$ 785 nm. Inset: A CCD-camera image of the up-converted fluorescence inside the 1 mm cuvette, no optical filters were used.



Figure 3. Dependence of the UC quantum yield on the relative concentrations of the emitter Rubrene, at fixed concentration of the sensitizer - PdTAP, 5×10^{-5} M.

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zo- and tetranaphthoporphyrins^[7a] will allow for up-conversion of the whole red band of the Solar irradiation with wavelengths between 620–820 nm.

As shown in Figure 4, for excitation intensities between 20 mWcm⁻² and 10 Wcm⁻² the intensity dependences can be fitted with power law equation: $P_{up-conv} = a P_{exc}^b$ in which $b = 1.65 \pm 0.05$ for the different relative molar concentrations of Rubrene/PdTAP. Please, note that the demonstrated sublinear intensity dependence of the UC signal is observed for more than three orders of magnitude change of the excitation intensity.



Figure 4. Dependence of the energetically-conjoined TTA–UC on the excitation laser intensity for three different molar concentrations of the UC emitter and fixed concentration of the sensitizer. Solid lines are power law fits. Excitation spot size is 4×10^{-4} cm².

The sublinear dependence of the UC signal on the excitation intensity is at a first glance contradictory to the classical representation of the TTA process.^[14] Actually, in the classical experiments for TTA in which emitter triplets are created through direct absorption of a UV photon in the emitter singlet state, followed by the strongly prohibited process of ISC in the emitter molecule, there is linear dependence between the created triplet states and the excitation intensity. Taking into account, that the probability for TTA depends on square of the concentration of the excited emitter triplets, the known quadratic dependence between the excitation intensity and the intensity of the TTA signal is observed. It is important to note, that in the classical TTA experiments, delayed fluorescence is observed at excitation intensities comparable with those for the other nonlinear optical processes,^[15] namely by intensities on the order of many kWcm⁻².[14]

In the energetically conjoined TTA reported herein, the concentration of the excited emitter triplet states is proportional to the concentration of the excited sensitizer triplet states. On other hand, the phosphorescence intensity of the porphyrin molecules (related to the degree of population of the sensitizer triplet states) is known to depend as the square-root of the excitation intensity.^[14] This dependence, together with the process of triplet–triplet transfer (TTT) between molecules with large differences in the ISC coefficients, is most probably the rectification mechanism, leading

to the observed sublinear intensity dependence, shown in Figure 4. Very importantly, the reported mechanism of energetically conjoined TTA is efficient at intensities more than six orders of magnitude lower than those of the "classical" TTA.^[14]

As shown in Figure 5, the rise time of the up-conversion emission decreases with the increase of the relative concentration of the emitter molecules from about $12 \,\mu s$ at $0.1 \times$



Figure 5. Streak camera images of the time-evolution of the annihilation up-conversion fluorescence of Rubrene/PdTAP at different molar concentrations: for Rubrene a) 0.1×10^{-3} M; b) 0.5×10^{-3} M; c) 2×10^{-3} M; d) 5.0×10^{-3} M and equal for all samples concentration of PdTAP 5×10^{-5} M. Excitation intensity: 100 mW cm⁻²; pulse duration: 100 µs; $\lambda = 785$ nm.

 10^{-3} M Rubrene down to approximately 8µs for 5.0×10^{-3} M. Correspondingly, the decay time of the up-conversion emission decreases from about 25µs at 0.1×10^{-3} M Rubrene down to approximately 18 µs for 5.0×10^{-3} M. The emitter concentration in these examples increases more than 50 times, which corresponds to roughly 3.6 times decrease in the intermolecular distance. The observed decrease of the decay times (less then 25%) and, hence, the increase of the strength of the up-conversion process, is much weaker than expected.^[14]

In summary, a convenient synthetic approach towards tetraanthraporphyrin using the dihydroisoindole strategy developed earlier was realized to allow us to obtain tetraaryl-TAP in good yield. The palladium complex of this TAP was used for the energetically conjoined TTA with excitation wavelength in IR region ($\lambda \approx 800$ nm) and with ultralow-excitation light intensity of 100 mWcm⁻². The hypsochromic shift between the energy of the exciting photons and the emitted photons is $\Delta E \approx 0.6$ eV. The up-conversion process has very high quantum yield of 1.2%. To the best of our knowledge we demonstrate for the first time the most redshifted photon up-conversion based on energetically conjoined TTA. The reported molecular system shows stable operation for more than 60 days.

Experimental Section

The solutions were prepared and sealed in a nitrogen-filled glove-box with de-aerated toluene as solvent. Note the crucial importance to keep the oxygen amount less than 0.1 ppm. When the preparation is done at 0.1 ppm oxygen content in the glove-box, the degradation of the samples is not observed even after 60 days. In contrast, when the samples are prepared in 5-10 ppm oxygen-containing nitrogen atmosphere, the degradation of the samples starts immediately (ms) after their exposure to the excitation light.

A single-mode cw diode laser ($\lambda = 785$ nm) was used as the pumping source for the measurement of excitation intensity dependence. The emission spectra were registered by Optical Multichannel Analyzer (Hamamatsu Inc.). The excitation laser wavelength was effectively suppressed (more than 10⁶ times) by using a notch filter designed for $\lambda =$ 785 nm (Semrock Inc.).

The time-resolved spectra were measured on a Streak-Camera, Hamamatsu C5680 in the single-pulse regime. Both, the rising and the decaying pulse slope times of the excitation laser ($\lambda = 785$ nm) were less than 200 ns.

Keywords: energy transfer • IR excitation • palladium • porphyrinoids • triplet-triplet annihilation

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Received: June 30, 2008 Published online: October 1, 2008