

Exploring the IR-limit of the Triplet-Triplet Annihilation Upconversion: Tetraaryltetraanthra[2,3]porphyrin – family

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ABSTRACT

The main advantage of the techniques, using photon conversion is that conversion processes and devices can be considered and optimized independently, without affecting the particular physical properties of the operating photovoltaic material or device architectures [1].

Up to now the triplet-triplet annihilation-supported upconversion (TTA – UC) is the only upconversion process excited with moderate concentrated sunlight. Our group demonstrates UC device based on family of symmetrical tetraaryltetraanthra[2,3]porphyrins sensitizers, efficiently transforming the IR-A part of the sun spectrum into the VIS-range, operating under moderate concentrated sunlight (50 suns, AM1.5). Next important requirement is protection of UC-molecular system from the ambient oxygen. Our group demonstrates oxygen scavenging formulations, well-suited for the TTA – UC process. Compatibility between the UC device and the photovoltaic device (PV), including the subject of optical coupling is discussed.

Keywords: sunlight, photon upconversion, triplet-triplet annihilation, metallated macrocycles, solar cells.

1 INTRODUCTION

The process of TTA – UC incorporates a chain of mutually complementary processes – intersystem crossing (ISC), triplet-triplet transfer (TTT), triplet-triplet annihilation (TTA) and consequent emitter fluorescence, [2, 3, 4].

Special attention must be drawn to the fact that all molecular energy levels, involved in the process of TTA – UC are real molecular levels, thus no virtual energetic levels are involved. Consequently, no dipole forbidden processes are concerned – this fact explains partially the substantially lower excitation intensity needed for this type of UC-process. Further, the intramolecular energy relaxation happens on time-scale of several picoseconds. The characteristic time scale of the process of triplet-triplet annihilation (TTA) is predetermined by the decay time of the delayed emitter fluorescence (time scale of 100 μ s) and the diffusion controlled process of triplet-triplet energy transfer TTT (time scale of μ s). Therefore, the spontaneous processes of internal energy relaxation (i.e. thermalisation

of the electronic states of the molecules involved) and, consequently their influence on the energetic schema of the process of TTA – UC cannot be neglected.

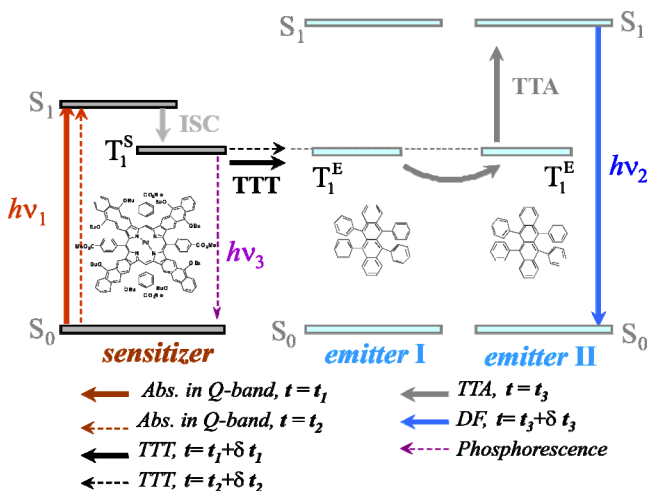


Figure 1: Simplified energetic schema of the process of TTA – UC in two-component organic system.

As a first outcome, the processes of internal energy relaxation lead to a noticeable loss of excitation photon energy, therefore the up – converted emission *a priori* has a frequency lower than the doubled frequency of the excitation light. The most important outcome of the spontaneous character of the process of internal energy relaxation is that TTA – UC is also a spontaneous process, and therefore totally non dependent on the coherence parameters of the excitation light. As shown [5, 6, 7], this process can be performed by use of sunlight, without any loss of efficiency.

Essential for the process of TTA – UC is to create high concentration of emitter molecules in excited triplet state (T_1^E , Figure 1), using single photon absorption regime. Direct photon excitation of the emitter molecule through absorption of a single photon is a spin-forbidden process. This problem is overcome by using of sensitizer molecule such as metallated macrocycles

The heavy metal atom coordinated in the sensitizer molecule, ensures efficiency of the ISC approaching unity, i.e. $\eta_{ISC} \sim 1$. The efficient ISC within the sensitizer molecules ensures a very efficient population of the

sensitizer triplet state via single photon absorption. The sensitizer triplet states with their relatively long life times serve as energy reservoir. Consequently, depopulation of the sensitizer triplet ensemble via the process of TTT becomes essential. The efficiency of the TTT is predetermined by the extent of overlap of the sensitizer and emitter triplet manifolds, $T_1^S \sim T_1^E$. Thus, significant population transfer towards emitter triplet state is observed

The quantum yield (η_{TTA-UC}) of the TTA – UC process is definitely of crucial importance, when applications in PV – devices are planned. In our study we attribute the classical term of “quantum yield” to a complex system like the TTA – UC process, using the following assumptions: the “absorption” of the UC-media is determined by the absorption of the used sensitizer species, but the “emission” is ascribed to the UC-fluorescence of the emitter species:

$$QY_{TTA-UC} = N_{\text{photons absorbed}} / N_{\text{photons emitted}} \quad (1)$$

As mentioned earlier, the studied TTA – UC process incorporates a chain of mutually complementary processes (ISC, TTT, TTA and consequent emitter fluorescence) all of them with particular efficiency (η_{ISC} , η_{TTT} , η_{TTA} and η_F , respectively).

$$QY_{TTA-UC} = \eta_{ISC} \times \eta_{TTT} \times \eta_{TTA} \times \eta_F \quad (2)$$

The main advantage of using such rigorous quantum yield definition arises from the clear and transparent evaluation of the application potential of the TTA – UC process.

2 MATERIALS AND METHODS

The aim of UCd is to enlarge the spectral brightness of the short wavelength region of the solar spectrum by using as excitation source the polychromatic sunlight from IR-A wavelength region. The absorption spectral width of the Q-band for single sensitizer ranges between $20 \div 35$ nm (the full width at half maximum (FWHM)) [3, 4]. It is clear, that by means of solitary sensitizer is not possible the harvest the sunlight energy of the entire IR-A wavelength region. It was demonstrated experimentally, that the impact of using a sensitizer ensemble on the efficiency of the TTA – UC process has an additive nature. Therefore, an appropriately structured sensitizer ensemble will allow harvesting much wider sunlight region.

In this work we report for optimized ensemble comprised by three kinds of sensitizers molecules and solitary emitter. The absorption wavelength tuning of the sensitizer ensemble is performed by decoration of the pyrrole – ring of the sensitizer molecules with electron donating group. A substantial red shift of the Q-band sensitizer absorption in order of $\Delta\lambda \sim 25$ nm is achieved.

Tetraanthroporphyrin (TAP) bearing butoxy-groups in peripheral rings (*Vic*-octabutoxy-*meso*-tetraphenyl-tetraanthro[2,3]porphyrin) was synthesized according the approach previously developed for anthra-unsubstituted *meso*-tetraphenyl-tetraanthro[2,3]porphyrin [8]. The corresponding benzyne was generated from 4,5-dibromo-

1,2-di-*n*-butoxybenzene, which was prepared by bromination of 1,2-di-*n*-butoxybenzene – the product of pirocatechin alkylation. Its adduct with furane was further introduced to the cycloaddition reaction with butadiene, generated *in situ* from sulfolene. Further steps are analogous to the synthesis of unsubstituted TAP including acid-catalyzed dehydration giving 1,4-dehydroanthracene derivative, its transformation to allylsulfone, Barton-Zard reaction and decarboxylation leading to butoxy-substituted naphthadihydroisindole. The latter was introduced to Lyndsey's condensation which however yielded PdTAP2 with decreased yield compared to those for TAP.

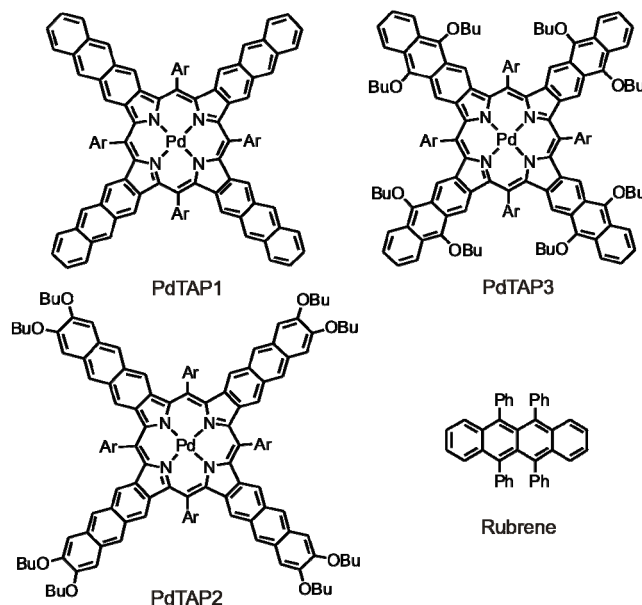


Figure 2: Structures of the used sensitizer-family: PdTAP1 – *meso*-tetraaryl-tetraanthro[2,3]porphyrin Palladium; PdTAP2 – *Vic*-octabutoxy-*meso*-tetraphenyl-tetraanthro[2,3]porphyrin Palladium; PdTAP3 – *Opp*-octabutoxy-*meso*-tetraphenyl-tetraanthro[2,3]porphyrin Palladium and the emitter molecule – Rubrene.

Tetraanthroporphyrin bearing butoxy-groups in the middle rings (*Opp*-octabutoxy-*meso*-tetraphenyl-tetraanthro[2,3]porphyrin) was performed starting from commercial 1,4-naphthoquinone which was introduced to Diels-Alder reaction with 1,3-butadiene. The adduct was further transformed to its enole form – hydroquinone compound which was then alkylated by iodobutane yielding dibutoxy-substituted 1,4-dihydroanthracene. Further steps were analogous to previously described transformation. It was found that *opp*-(BuO)₈TAP is formed in Lyndsey's condensation with much less yield compared either to TAP or *vic*-(BuO)₈TAP probably due to the steric hinderence caused by butoxy-groups.

3 RESULTS AND DISCUSSION

The absorption spectrum of the family of tetraanthro[2,3]porphyrin (TAP) sensitizers investigated in this work is shown in Figure 3, the dark red curve. The Q-band absorption of the TAP-family covers the solar bandwidth ranging between $\Delta\lambda = 760 \div 840$ nm. The terrestrial sunlight intensity (AM 1.5) in this spectral range is 7.4 mWcm^{-2} . In order to achieve excitation intensity on the level of 100 mWcm^{-2} less than 14-times concentration of the sunlight is necessary. Such sunlight concentration ratio can be realized by micro-lens arrays or by Fresnel-type focusing systems.

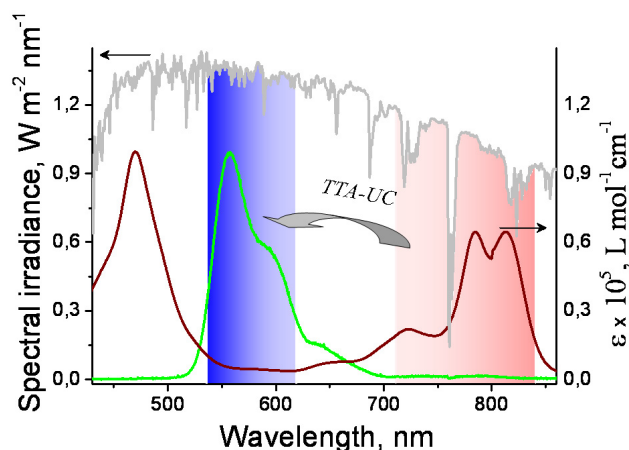


Figure 3: Molar extinction of a mixture of sensitizers, as follows: $1.25 \times 10^{-5} \text{ M}$ PdTAP1 + $0.2 \times 10^{-5} \text{ M}$ PdTAP2 + $1.55 \times 10^{-5} \text{ M}$ PdTAP3. The total molar concentration of the sensitizer-family is $3 \times 10^{-5} \text{ M}$ – dark red curve. Normalized emission spectrum of the emitter (Rubrene) – green curve.

Further, on Figure 3 is demonstrated that the chosen emitter molecule (Rubrene) has fluorescent spectrum fitting well with the transparency window of the TAP-family sensitizers: The TTA – UC process in multi-component organic systems has high complexity. Simultaneously in the UC – medium are present excited triplet states of the sensitizer and emitter molecules, as well as sensitizer molecules in ground state. All those states can absorb the generated emitter fluorescence, either through the process of excited state absorption to higher lying triplet states, or by absorption from the sensitizer ground state.

The metallated macrocycles like porphyrins and phthalocyanines have band-like absorption spectrum, with more or less two strong bands – the Soret-band and the Q-band. As seen from Figure 3 (the green line) more than 95% of the emission bands of the chosen emitter molecules are laying insight the transparency window of the selected sensitizer molecule (Figure 3, the dark red line). Thus, re-absorption of the UC-fluorescence is almost avoided.

The dependence of the integral UC – fluorescence in volatile organic solvent on the excitation intensity is shown

in Figure 4. The solid line is power law fit: $I_{UpConv} = a * I_{exc}^b$ with $b = 1.48$ for the TAP-family/Rubrene/toluene (Figure 4, the dark red line). Remarkably, the region of excitation intensities, where the UC-molecular system shows an intensity dependence that is well approximated with a sub-linear function, is more than 3 orders of magnitude broad.

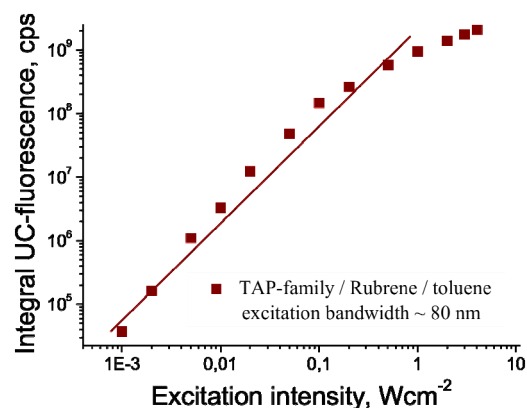


Figure 4: Dependence of the integral UC – fluorescence on the excitation intensity for the UC – systems: TAP-family/Rubrene/toluene.

The multi-component molecular process of TTA-UC in based on the presence of the long lived excited triplet state of the sensitizer molecule. Well demonstrated experimental fact is that oxygen molecules very effective quenchers of the excited triplet states of the metallated macrocycles, such as the porphyrins. This predetermines the strong dependence of the UC efficiency even upon a residual oxygen concentration in the range of ppm. Therefore, all investigated solutions were prepared from degassed and super dry toluene and sealed in a nitrogen-filled glove-box. Thus, the reported UC-QY is a specific parameter for the studied sensitizer/emitter system and valid at the given sample preparation conditions.

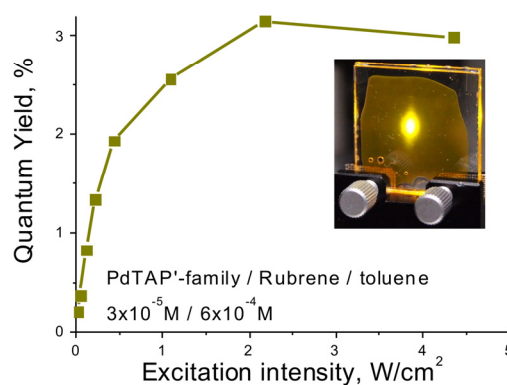


Figure 5: Dependence of the integral UC – quantum yield on the excitation intensity of the couple PdTAP's-family / Rubrene. **Inset** – photograph of a working upconversion device, no optical filter are used, day-light conditions.

Sample thickness $\sim 250\text{ }\mu\text{m}$, lateral dimensions $40\times 40\text{ mm}$, glass substrate.

4 CONCLUSION

We demonstrate validity of the experimentally stated rules [9] for achieving effective triplet-triplet annihilation photon upconversion. Strong absorption at the red-shifted sensitizer band (Q-band), together with very high ISC-rate of the sensitizer ensures dense populated sensitizer triplet ensemble. The existence of a broad transparency window between the Soret-band and Q-band of the sensitizer guarantee low degree of re-absorption and predetermines the maximal energetic shift of the up-conversion emission. The presence of strong energy overlap between the triplet bands of the sensitizer and emitter molecules, together with a large difference in the ISC-rates for the sensitizer and emitter molecules supports creation a highly populated ensemble of emitter triplets. The broad transparency window at the sensitizer absorption band ensures vanishing re-absorption of the generated UC-emission.

It was demonstrated quantum yields of the TTA -UC process for the system of TAP-family / Rubrene / toluene to be as high as 2.2% at excitation intensity of 1 Wcm^{-2} . For a broad range of excitation intensities (practically, from 1 mWcm^{-2} up to 10 Wcm^{-2}) there is sub-linear dependence of the intensity of the UC – signal. The used excitation spectrum was demonstrated extremely broad (practically, more that $\Delta\lambda \sim 80\text{ nm}$, centered at $\lambda = 800\text{ nm}$). The UCd reported here have no limitation for size scaling. The device size would be limited mainly by the size of the optical substrates, although tailoring would be fairly straightforward.

When non-volatile solvents and polymer substrates are used, the UCd can be also flexible; with the possibility to tune the total index of refraction of the device, in order to optimize photon coupling between the UCd and PV-cell.

5 ACKNOWLEDGEMENTS

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REFERENCES

- [1] T. Trupke, A. Shalav, P. Würfel, and M. A. Green, "Efficiency enhancement of solar cells by luminescent up-conversion of sunlight", *Sol. Energy Mater. Sol. Cells* **90**, pp. 3327 – 3338, 2006.
- [2] S. Balushev, V. Yakutkin, T. Miteva, G. Wegner, T. Roberts, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov, A. Cheprakov, "A General Approach for Non-coherently Excited Annihilation Up-

- Conversion: Transforming the Solar-spectrum", *New Journal of Physics*, **10**, 013007, 2008.
- [3] J. E. Auckett, Y. Y. Chen, T. Khoury, T. Clady, N. Ekins-Daukes, M. Crossley, T. Schmidt, "Efficient up-conversion by triplet-triplet annihilation", *Journal of Physics: Conference Series*, **185**, 012002, 2009.
- [4] S. Sugunan, U. Tripathy, S. Brunet, M. Paige, R. Steer, "Mechanisms of Low-Power Noncoherent Photon Upconversion in Metalloporphyrin-Organic Blue Emitter Systems in Solution", *J. Phys. Chem. A*, **113**, 8548–8556, 2009.
- [5] S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, and G. Wegner, "Up-Conversion Fluorescence: Non-coherent Excitation by Sunlight", *Physical Review Letters* **97** (14): 143903, 2006.
- [6] S. Balushev, T. Miteva, V. Yakutkin, Y. S. Avlasevich, K. Müllen, G. Nelles, S. Chernov, S. Aleshchenkov, A. Cheprakov, A. Yasuda and G. Wegner, "Blue-Green Up-Conversion: Non-coherent Excitation by NIR-light", *Angewandte Chemie-International Edition* **46**, 7693–7696, 2007.
- [7] R. R. Islangulov, J. Lott, Ch. Weder, and F. N. Castellano, "Noncoherent Low-Power Upconversion in Solid Polymer Films", *JACS*, **129** (42) 12652–12663, 2007.
- [8] M. Filatov, S. Balushev, I. Ilieva, V. Enkelmann, T. Miteva, K. Landfester, S. Aleshchenkov, and A. Cheprakov, "Tetraaryltetraanthra[2,3]porphyrins: synthesis, structure and optical properties" *J. Org. Chem.*, **77**, 11119–11131, 2012.
- [9] S. Balushev, V. Yakutkin, T. Miteva, G. Wegner, T. Roberts, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov, and A. Cheprakov, "A General Approach for Non-coherently Excited Annihilation Up-Conversion: Transforming the Solar-Spectrum", *New Journal of Physics* **10** 013007, 2008.