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Managing Photoexcited States in Conjugated Polymers

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Summary: Chain length dependence of the photoemission (fluorescence, phosphorescence, delayed fluorescence) and the respective life times of poly conjugated macromolecules is subject of controversy since long. An underlying question concerns coherence and extension/localization of the photoexcited states. Energy transfer within and between macromolecules as well as between sensitizers and macromolecules are relevant processes in systems to be used for displays or solar energy harvesting. In this context our recent work on photophysical characterization of pure oligo(fluorene)s and of the same oligomers containing just one fluorenone (“keto-defect”) group is reviewed. Energy transfer between poly(fluorene)s and metal porphyrins is also covered. Triplet- triplet-annihilation opens a route to efficient non-coherent energy upconversion at ultralow excitation intensity (ca 1 Wcm^{-2}). Light from the red region (635–700 nm) of terrestrial sun-light is converted into the green region with $\Delta E \geq 0.5$ eV.

Keywords: energy-upconversion; fluorescence; phosphorescence; triplet-triplet annihilation

Introduction

9,9-Disubstituted polyfluorenes have become the “fruitfly” of generic research on light emitting polymer diode materials for reasons of their potential application as blue emitters combined with thermal and oxidative stability, processability via spin-coating from common organic solvents, and thermotropic characteristics which allow alignement processes in the liquid crystalline state[1–5]. For better understanding of the structure properties relationships in polyconjugated macromolecules in general and in polyfluorenes, more specifically, it was necessary to develop methods of synthesis and study the photophysical and related properties of a series of pure oligomers with no chemical defects incorporated.[6] Such studies help to clearly identify the nature and energetics of photoexcited states as depending on molecular size and conclude on the contribution of specific defects to the photophysics of the polymers. Typical defects encountered in polyfluorenes are “keto-defects”, i.e. fluorenone groups randomly distributed in the chains because of chemical side reactions in the course of the synthesis.[7] Once the nature and lifetimes of the photoexcited states have been identified it becomes possible to identify (and optimize) their role in desired energy transfer processes involving “dopants”. Such dopants for which metallo porphyrins are a good example may serve as energy harvester and convert the initial photo energy either to photons of lower energy (e.g. via phosphorescence) or to higher energy by triplet-triplet annihilation.[8] The latter is of specific interest since it allows to convert the red part of the sunlight spectrum to the blue-green region (“up-conversion”). In the following recent work of our research group is reviewed by which we aim for better understanding of the basic processes

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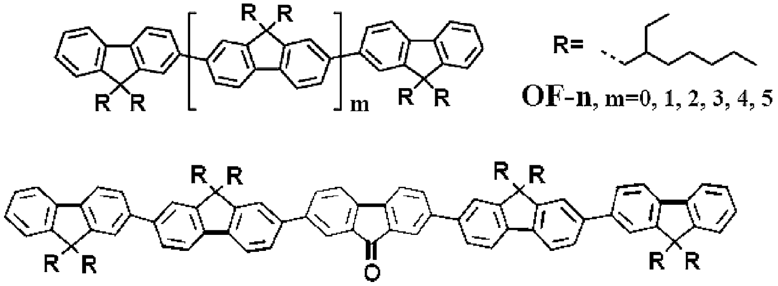

Figure 1.
structure of the oligomers.

occurring as a consequence of photoexcitation in pure and "doped" polyconjugated linear chain molecules, that is oligomers and polymers.

Oligofluorenes

9,9-bis(2-ethylhexyl)fluorene oligomers are efficiently synthesized by respective Suzuki and/or Yamamoto coupling.[6] Similarly, oligofluorenes with just one fluorenone unit in the center of the molecule have been synthesized and used as models to understand the origin of the low-energy emission ("green") band in the emission spectra of some polyfluorenes.[7] The structure of the oligomers is shown in Figure 1

As a typical result the absorption and luminescence spectra of a pure oligomer with degree of polymerization n = 5(OF5) are displayed in Figure 2. It shows the

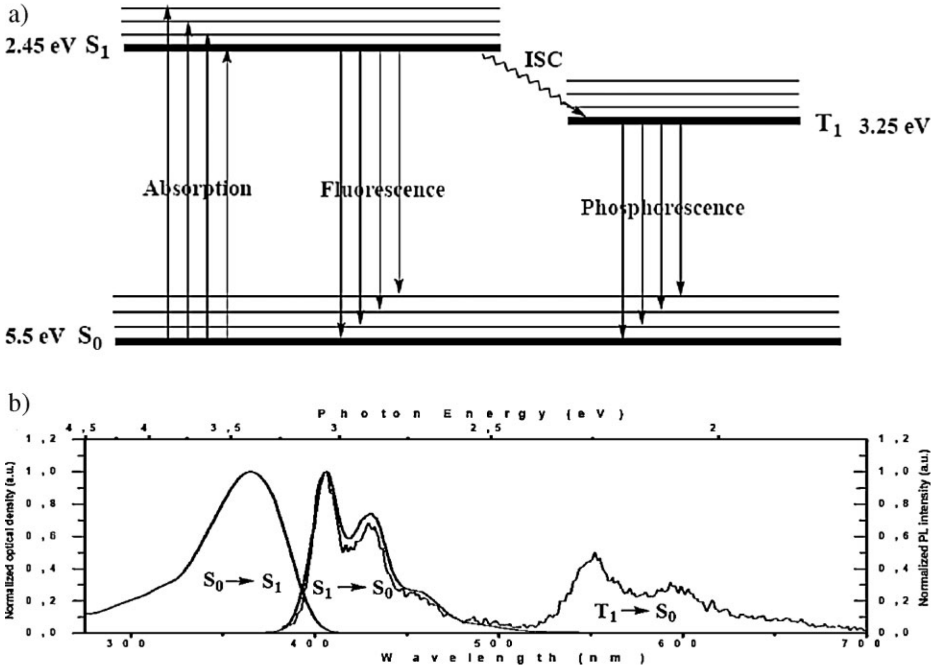

Figure 2.
a + b: Absorption, luminescence and energy level diagram for the oligomer OF5 (c.f. Figure 1).

absorption spectra ($S_o \rightarrow S_1$), the fluorescence spectra ($S_1 \rightarrow S_o$) and the phosphorescence spectra ($T_1 \rightarrow S_o$) together with a self explaining but simplified energy level diagram. The latter indicates the values of the energy levels.

The wave-length of maximum absorption λ_{max} relates to the chain length n as$\lambda_{max}^{-1} = 3.13 + 1.28\ n^{-1}$, while for the fluorescence it is found[7,9] that $\lambda_{max}^{-1} = 2.80 + 1.23\ n^{-1}$ and for the phosphorescence $\lambda_{max}^{-1} = 2.05 + 0.89\ n^{-1}$. The spectroscopic findings correlate very well with the electro-chemical properties of the same oligomers as studied by Cyclovoltametry.[10]

The oxidation potential, energy gap, ionization potential and electron affinity of the oligomers show all linear relationships with the reciprocal degree of polymerization. When a chain length of ca. 14 repeat units is reached a stable structure of the oxidized state is reached with ca. one positive charge per 3.5 repeat units distributed over the whole length of the molecule. The oxidation potentials increase by 1.35/n (V) with increase of oxidative step number for the oligomers consisting of n repeat units.[10]

A particularly interesting result comes from the study of the life-time of the fluorescence of the pure oligomers. We have found[11] a monoexponential decay for all chain lengths and the life-times follow a simple relationship with n as $\tau(\mathrm{ps}) = 386 + 808\ n^{-1}$. This is the classical case discussed by Strickler and Berg[12] many years ago. Moreover, a clean extrapolation to the experimentally found life-time of fluorescence of the pure polymer in dilute solution (397 ps) is found (all data in MTHF at 22 °C). A straightforward conclusion from these results is that the photoexcited singlet "sees" or "explores" the whole molecule along its full length in dilute solution and there is no "self-trapping" or localization observable under these conditions.

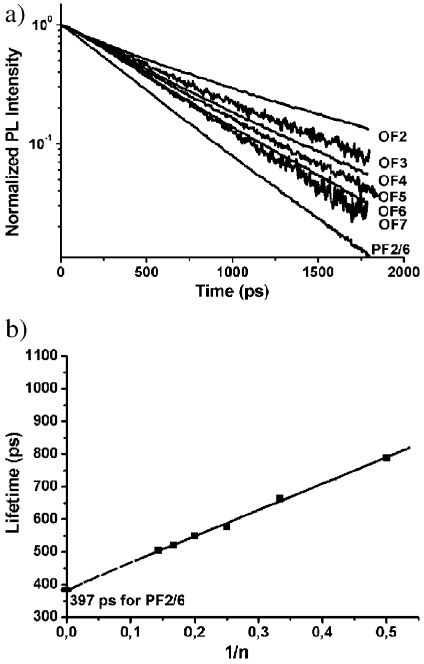

Figure 3.

a: Decay of the fluorescence of oligomers OFn (c.f. Figure 1) in MTHF at 22 °C[11]; b: life time depending on reciprocal chain length n.[11]

The oligomers having a "keto-defect" in the center of the molecule[7,9] show typical absorption and fluorescence spectra as depicted in Figure 4a. The "blue" fluorescence of the fluorene segments is completely quenched and a "green" fluorescence appears at $\lambda_{max} = 547$ nm. It is due to a n-π^* transition localized at the moiety carrying the keto-group (c.f. Figure 1). In consequence, this fluorescence peak is independent of molecular length indicating rapid intra molecular energy transfer and localization at the trap site. It is by coincidence that the "green" phosphorescence of the pure oligomers and polymers (Figure 4b) occurs in the same spectral range as the (strong) n-π^* related fluorescence of the keto group containing species. However, time resolved spectroscopy allows a clear discrimination since the life time of the n-π^* populated state is in the order of less than 10 nsec while the one of the phosphorescence of pure oligomers amounts to 3 msec.[7]

Energy transfer from photoexcited fluorene chains or segments to fluorenone

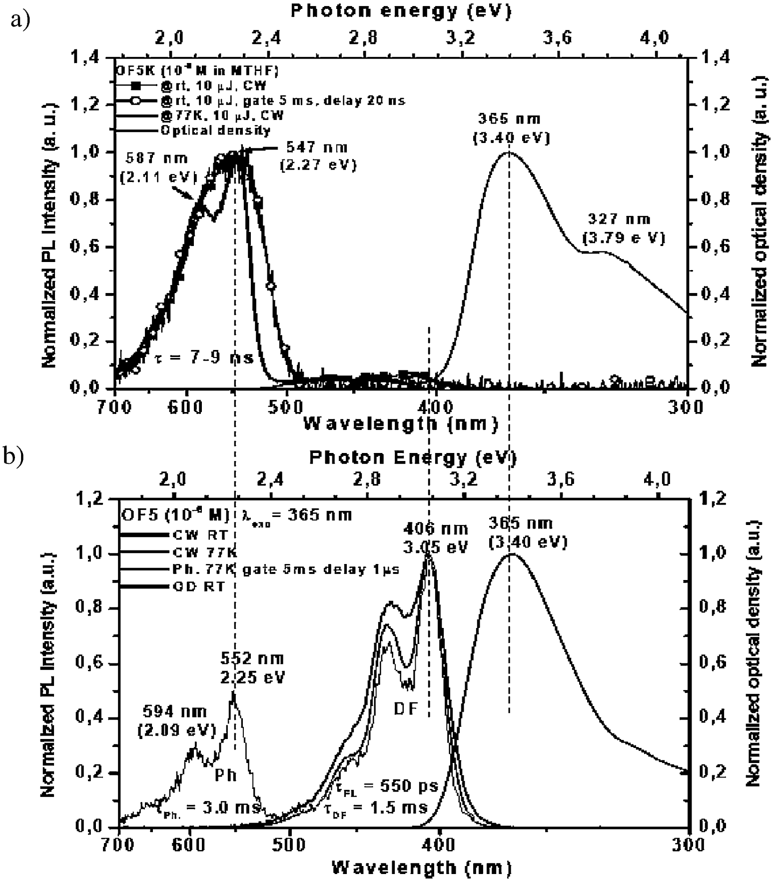

Figure 4.

a) absorption ($\lambda_{max} = 366$ nm) and fluorescence ($\lambda_{max} = 547$ nm) of a pentamer having a fluorenone group in the center (c.f. Figure 1); b) absorption ($\lambda_{max} = 365$ nm), prompt fluorescence ($\lambda_{max} = 406$ nm) and phorsphorescence ($\lambda_{max} = 552$ nm) spectra of the equivalent pure pentamer (see also Figure 2b).[7,9]

residues situated in only a few chains in a mixture of pure and keto group containing oligomers occurs very rapidly as well.[7] This is demonstrated by Figure 5. It shows the fluorescence spectra of poly(9,9-bis[2ethylhexyl]fluorene) free of keto groups with admixtures of a keto group containing trimer. The concentration of the trimer was varied between 0.1 and 10 wt percent. Note that the trimer is completely miscible with the polymer. The spectra show that the quenching capability of the keto groups is noticed at already such a small amount of admixture as 0.1 wt percent (amounting to ca. one keto group per 1000 fluorene residues. Concomitantly,

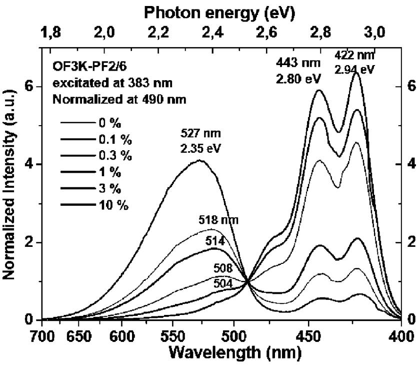

Figure 5.

Steady state fluorescence spectra of spin-coated film of polyfluorene doped with different amounts of keto group containing trimers at RT ($\lambda_{max} = 383$ nm).

the life time of the "blue" fluorescence is shortened.

We note in passing that both the pure and the keto group containing oligomers are mesogenic materials and give smectic liquid crystals which may be quenched into liquid crystal glasses.[13,14] The dielectric properties of these materials have been studied.[14] They allow to conclude that the glass transition is related to freezing of local rotational motions of the molecules with a strong intramolecular coupling. The oligomers carry a dipole moment of 0.27 D perpendicular to the backbone independent of chain length.

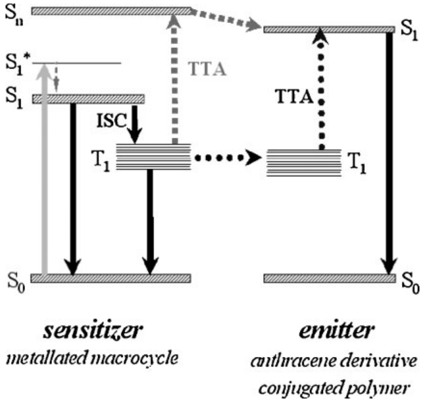

Figure 6.
Triplet-Triplet-Annihilation (TTA) supported up-conversion[19–21]).

Energy Up-Conversion by Triplet-Triplet Annihilation

Long-lived triplet states in organic and polymer systems offer the potential to observe further energy migration and transfer processes. Among these, triplet-triplet annihilation is long known. It is the source of "delayed fluorescence" that is frequently observed in systems in which back transfer of energy from triplet to singlet states occurs and where the life-time of the delayed fluorescence mirrors the lifetime of the triplet states (and diminishes the intensity of the phosphorescence).

Triplet-triplet annihilation is particularly interesting and potentially useful in binary systems composed of two types of chromophores which we like to call "sensitizers" and "emitters". In such systems the phenomenon of up-conversion may be seen. It describes the generation of photons of higher energy (spectrally "blue shifted") from the photons of lower energy which are used to excite one (the sensitizer) component of the system.[8,15–21] Figure 6 describes schematically the paths of energy migration in such systems, e.g. a dilute solution of a metallo porphyrin in a polyconjugated polymer.

Light absorption by the sensitizer followed by efficient intersystem crossing (ISC) to a long-lived triplet state would naturally lead to phosphorescence in the sensitizer subsystem. However, if the sensitizer is embedded in a second subsystem of suitable position of its own energy levels with regard to the sensitizer energy levels either of the two options exist: a) energy transfer from the sensitizer triplets to the emitter triplets followed by TTA in the emitter manifold resulting in delayed fluorescence from the emitter molecules. If the system is chosen such that the energy difference between singlet and triplet in the sensitizer is much smaller than the one in the emitter subsystem, the emitted light will be of higher energy as the exciting light. B) delayed fluorescence may also occur from TTA on the sensitizer subsystem followed by energy transfer from a higher singlet state of the sensitizer to the S_1 state of the emitter. Experimentally, both paths are observed, however, path a) is the more efficient one according to our experience. It is very important to note that the described processes do not need coherent light but are inherently multiphoton processes whose efficiency rests mainly on the absorption cross-section of the sensitizer, the efficiency of ISC and the lifetime of the T_1 states.

The described TTA based up-conversion was observed for a variety of metal complexes, mainly metallated macrocycles (e.g. Pt- and Pd-octaethylporphyrins) embedded in emitter polymers (e.g. polyfluorenes,[8,20–22] polyspirobifluorene-anthracene copolymers,[22] ladder type polyphenylenes[15,16] etc. Alternatively the

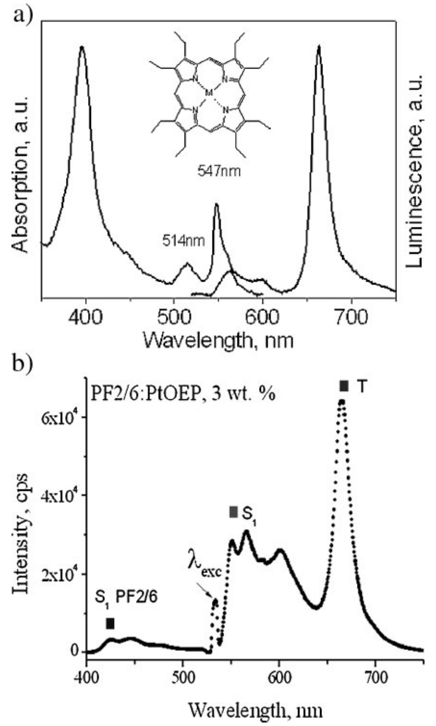

Figure 7.
a: absorption and emission spectra of platinocta ethyl porphyrin (PtOEP). b: emission spectra of a thin film of polyfluorene doped with 3 wt % of PtOEP (photo excitation at 514 nm): note the emission of the "blue" fluorescence of the polyfluorene (see also Figure 4 and 5).

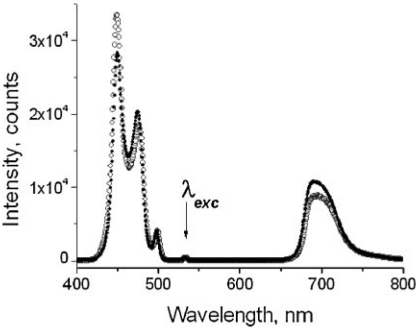

Figure 9.
Emission spectra of a physical mixture of poly(pentaphenylene) and Pd-sensitizer (full points) compared to emission of end-capped material (c.f. Figure 8) (open points); laser excitation at 532 nm, 125 kw cm^{-2}.[17]

sensitizer can be dissolved in solutions of the emitters in low molecular weight organic solvents or amorphous polymer films. An early example is demonstrated by Figure 7

The efficiency of up-conversion is much enhanced matching the triplet energy levels of the involved subsystems and optimizing molecular topologies. An example is shown by Figure 8, a system in which the sensitizer is positioned as end group in a conjugated (polypentaphenylene) subsystem.

The blue emission intensity of the pentaphenylene subsystem with $\lambda_{max} = 445$ nm ($\lambda_{exc} = 530$ nm) is much enhanced in the case of the end capped molecular system compared with a physical blend of the Pd-tetraphenylporphyrin in the pure polymer of the same structure as the linker chain in the molecule depicted in Figure 8. This is shown in Figure 9

The difference between paths a and b mentioned above namely TTA on the sensitizer subsystem vs. TTA on the emitter subsystem is exemplified by Figure 10. Here, we compare up-conversion efficiency using the identical metallated porphyrin (PtPtOEP) in case a (Figure 10, a) doped

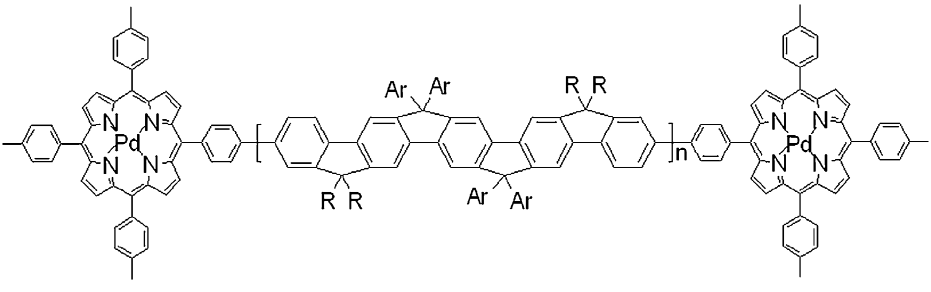

Figure 8.
Pd-porphyrin end-capped poly(pentaphenylene); R = n-octyl Ar = 4-octylphenyl.[17]

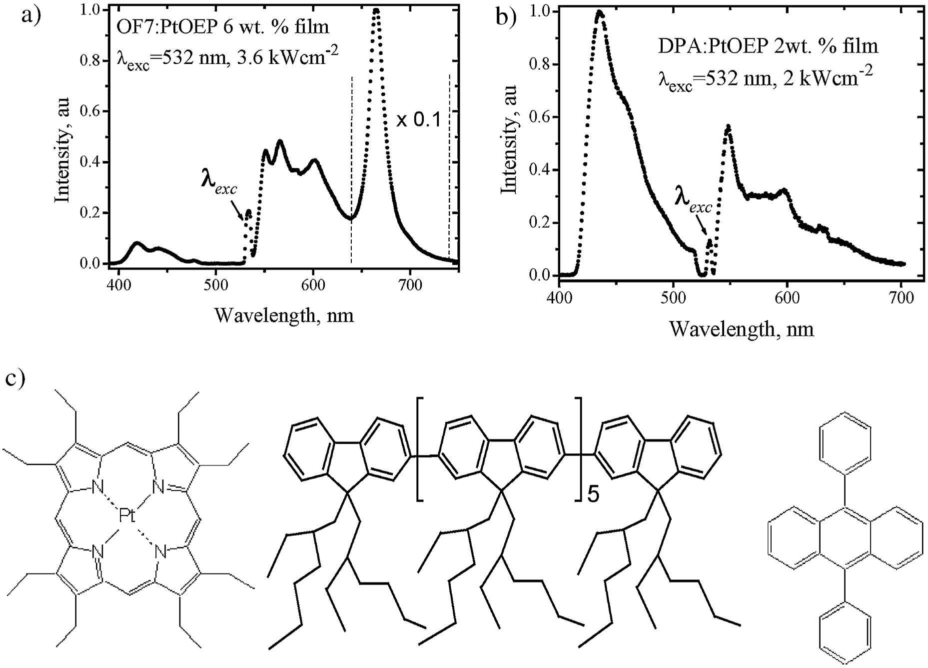

Figure 10.
b: comparison of photon up-conversion via TTA on the sensitizer subsystem (a) and emitter subsystem (b). c: Structure of the materials used for experiments in 10a,b.

into a thin film of the oligofluorene (OF7) (c.f. Figure 1) of n = 7, and in case b doped into a thin polystyrene film which contained diphenylanthracene (DPA) as the emitter. Wave length of excitation was chosen to be identical at 532 nm, but at different intensities as indicated. The case a) shows the blue (up-converted) emission from the oligofluorene, however, accompanied by strong emission of both fluorescence and phosphorescence of the sensitizer. The case b) shows very efficient quenching of the sensitizer excitation and strong emission of DPA.

Finally, the potential which is inherent to photon up-conversion is demonstrated below. Since it is a process which does not require coherent excitation conditions (laser radiation) simply sun light can be used.[19,21]

Figure 11 shows the experiment in which the green part of the sun light was fed to a light emitting guiding fibre which was placed to the wall of a cuvette containing a solution of PdOEP and DPA in toluene.

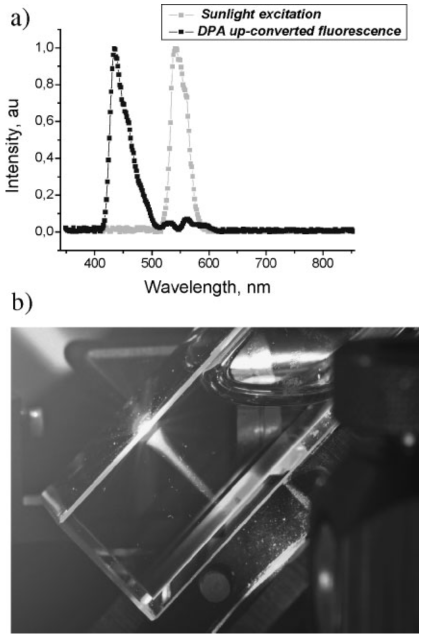

Figure 11.
a: up-conversion of the green part of sunlight (550 nm to blue radiation (420 nm). b: experimental set-up (see text).[19]

As the green beam emerging from the fibre penetrates into the cuvette it is converted into blue light. The corresponding excitation and emission spectra are shown at the right of Figure 11 which also allows to estimate the energy difference between exciting and up-converted light. Our experiments have indicated that a ΔE of up to 0.6 eV is possible over the whole range of the sun-spectrum; thus, even the far red end of the sun spectrum can be up-converted with photon-quantum-efficiencies of up to 3.2 percent.

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