Up-Conversion Photoluminescence in Polyfluorene Doped with Metal(II)–Octaethyl Porphyrins

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Polyfluorenes (PFs) have established themselves as functional materials in light-emitting diodes[1] and solar cells,[2] as gain media for lasers[3] and optical amplifiers,[4] and as active materials in field-effect transistors.[5] These polymers have good thermal and oxidative stability. The liquid crystal properties of some PFs additionally offer possibilities to control the chain orientation and film morphology.[6] Recently, two-photon absorption (TPA) and the associated luminescence has been observed in PFs.[7] Consequently, the very appealing idea to enhance the up-converted emission led us to the search for more efficient mechanisms and processes of low-energy photon PF excitation.

The phenomenon of up-conversion, i.e., the generation of higher-energy photons by simultaneous or sequential absorption of two or more lower-energy photons is frequently associated with the use of relatively high light intensities available from pulsed lasers. Up-conversion has been described for a large number of inorganic materials in the solid state,[8] including thin films and nanoparticles.[9] Most of the organic materials capable of up-conversion are dyes with large TPA cross-sections. They have been studied either in solution or as films, including the use of polymers as an inactive and inert matrix. A broad search for new organic dyes of greater TPA cross-section and suitable compositions based on them is noted.[10] Up-conversion fluorescence can also be produced when the higher-energy excited state is generated by a multistage absorption process (i.e., involving absorption to an intermediate state followed by absorption of another photon). Furthermore, up-conversion fluorescence can be a product of bimolecular processes, in which the mechanism of triplet–triplet annihilation plays a prominent role.[11] In some cases, up-conversion was observed as a result of hot-band excitation,[12] i.e., by population of high vibrational states of the molecules. This effect has been used for laser cooling of matter.[13]

Here, we demonstrate that using a suitable optical scheme and sample composition, it is possible to excite PF efficiently in a regime of up-conversion, using as the pump-source low-cost, commercially available solid-state or gas lasers.

The following describes quasi-continuous wave (cw) up-conversion in systems, composed of poly(9,9-bis(2-ethylhexyl)fluorene) (PF2/6) doped with (2,7,8,12,13,17,18-octaethyl-porphyrinato)M^{II} (MOEP). An intracavity frequency-doubled diode-pumped cw-Nd:YAG laser (532 nm) and the green line of a He–Ne laser (543 nm) were used as pumping sources.

The structures of the MOEP (**1**) and PF2/6 (**2**) used are shown as insets in Figure 1. It shows the absorption and fluorescence spectra of PF2/6 as a film and the absorption spectra of PdOEP, as an example for MOEP, at a concentration of 10 wt.-% in polystyrene (PS). The absorption of PF2/6 at 532 nm is negligible for the laser intensities used in the experiment described further on (from 2 kW cm^{-2} to 1.3 MW cm^{-2}). Consequently, there is no PF2/6 emission when the polymer is excited at this wavelength. The emission spectrum of PdOEP (not shown) when excited at 532 nm is very similar to the one obtained if excited at 400 nm (i.e., Soret-band absorption, shown in the book by Dolphin).[14]

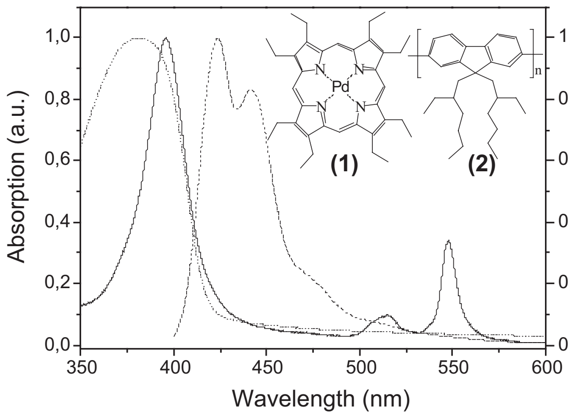

Fig. 1. Normalized absorption spectrum of the film with PdOEP 10 wt.-% in PS (solid line), PF2/6 film (dotted line). Normalized PL spectrum of PF 2/6 film (dashed line), excitation 390 nm. Inset: Molecular structure of PdOEP (**1**) and PF2/6 (**2**).

When a film of PF2/6 doped with 3 wt.-% PdOEP was excited at 532 nm (13.5 kW cm^{-2}), the characteristic blue emission of PF2/6 was observed (Fig. 2a) together with the expected phosphorescence of the PdOEP component. The absorption of the PdOEP component at 532 nm is very low, only around 1/8 of the Q-band absorption peak at 547 nm, and it increases at 543 nm by about four times. Yet, almost the same integral PL intensity of the PF2/6 was obtained using intensities of 13.5 kW cm^{-2} at 532 nm (Fig. 2a) and 2 kW cm^{-2} at 543 nm (Fig. 2b). This corresponds to more than a six-fold increase in efficiency when approaching the PdOEP Q-band absorption maximum. Considering this evidence, two channels for PF excitation are considered possible—sequential multiphoton absorption and triplet–triplet annihilation in the MOEP component, followed by energy transfer to the active matrix. Here, we cannot give a full account in favor or against one of these mechanisms; however, the following experiments suggest that a mechanism involving a sequential multiphoton absorption may be dominant.

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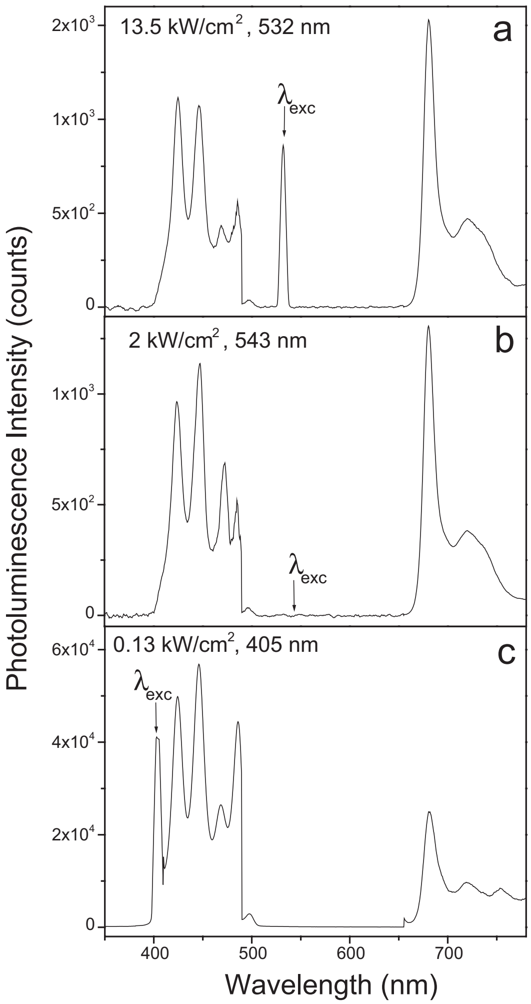

Fig. 2. Integral PL intensities at room temperature of the film of PF2/6 doped with 3 wt.-% PdOEP, laser excitation: a) 405 nm, b) 543 nm, c) 532 nm. In order to present the spectra on comparable intensity scale, multiplication factors for the spectral regions were applied as follows: 490–655 nm a–c) factor 10^{-6}; 656–800 nm a) factor 0.025, b) factor 0.0125, c) factor 1.

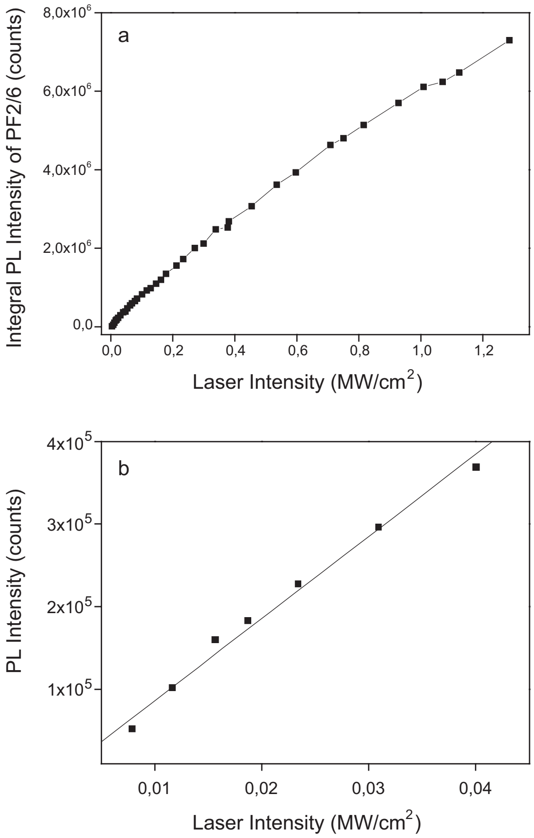

Fig. 3. a) Dependence of the integral PL intensity of the film of PF2/6 doped with 3 wt.-% PdOEP on the laser excitation intensity at room temperature. b) Magnified region of (a) at low intensities. The lines are guides to the eyes.

Increasing the excitation intensity at 532 nm up to 1.3 MW cm^{-2}, a sublinear increase in the integral PL intensity of PF2/6 was observed (Fig. 3). Figure 3b demonstrates the initial slope of the intensity dependence ($I_{\mathrm{PF2/6}} = a\, I_{532}$, with $a = 9.94$). At intensities higher than 0.07 MW cm^{-2} a slope $a = 6.4$ is observed. This experiment suggests that, even under steady-state excitation, the generated emission is far away from being saturated. This opens the possibility to reach higher up-conversion efficiencies, i.e., much higher integral PF blue emission, either by increasing the cw-pumping intensity or by using short pumping pulses.

Furthermore, considering the relatively low absorbance of the dopant at the used wavelength (the optical density of the PF2/6:PdOEP samples at 532 nm is typically 0.004), one can increase the efficiency of the up-conversion process by using a sample geometry in which the pump wavelength is coupled into a slab waveguide structure.

Having the excitation wavelength fixed at 532 nm one can select the metalloporphyrin with regard to the central metal atom such that the position of the Q-band comes more or less close to the excitation laser wavelength. In other words, the absorption of the metalloporphyrin is tuned towards the excitation wavelengths. The dependence of the integrated emission of PF2/6 on the excitation laser intensity is shown in Figure 4 for a group of different metallated porphyrins at a doping concentration of 3 wt.-%. Available spectra of the

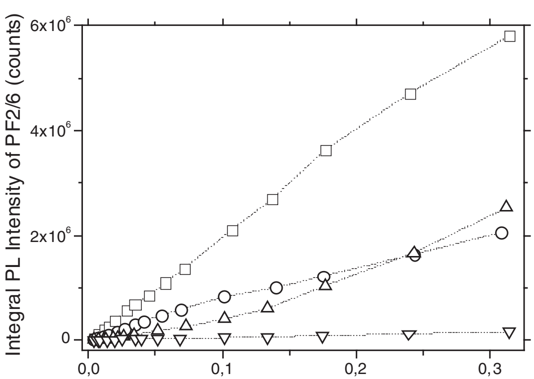

Fig. 4. Comparison between the integral PL intensity spectra of the PF 2/6 doped with 3 wt.-% different MOEP, excitation 532 nm, room temperature: (□) PtOEP, (○) PdOEP, (△) CuOEP, (▽) ZnOEP. In order to present the spectra in comparable intensity scale, the data for PF2/6:PtOEP are divided by factor of three. The lines are guides to the eyes.

different MOEP dispersed in PS show that PtOEP has the highest absorption at 532 nm. Furthermore, the spin-orbit coupling in the PtOEP in comparison with the other MOEPs is increased as a consequence of the difference in atom mass of the central metal cation. This, together with the above discussed Q-band position of PtOEP, can explain the up to 18-fold increase of the polymer emission intensity that is seen in blends of PF2/6:PtOEP in comparison with the blends of other MOEPs. Therefore, it is evident that the up-conversion is the result of an energy-transfer mechanism common to all the MOEPs and the PFs, the efficiency of which can be tuned by means of chemical modification of the metallated porphyrins.[15]

Temperature is another important parameter that strongly influences the up-conversion process. Figure 5 shows the change of the integral of PF2/6 emission intensity upon variation of the sample temperature. The quantum efficiency of the emission of a PF for the temperature interval studied increases by around 10 % with decreasing temperature.[6] Here, we show that even at temperature intervals around room temperature a significant change of the PF emission intensity can be observed. A 2-fold increase of PF emission intensity is seen upon decreasing the sample temperature to values easily reached by using a one-stage Peltier cooler. In addition, we have observed a decrease of the up-conversion efficiency caused by local heating during laser irradiation. This secondary effect will be discussed elsewhere.

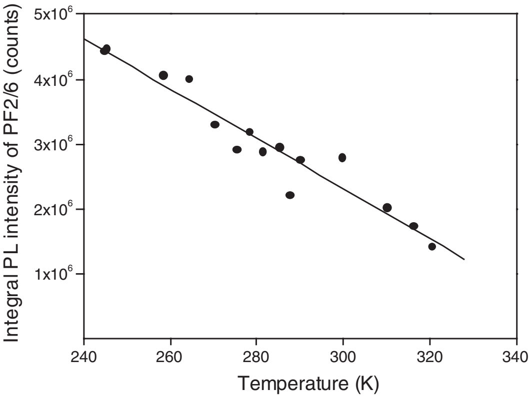

Fig. 5. Temperature dependence of the integral PL intensity of the film of PF2/6 doped with 3 wt.-% PdOEP. Excitation wavelength is 532 nm, laser intensity was kept at 80 kW cm^{-2}. The solid line is a linear fit to the data points.

In the present up-conversion experiment energy-transfer processes inside and among the dopant molecules as well as processes in the active matrix need to be considered.

The presence of the heavy metal atom in the dopant molecule increases the probability of singlet–triplet conversion creating a reservoir of triplet states, from which further energy conversion does occur finally leading to photoluminescence (PL) from PF2/6. Taking into account that the lifetime of the triplet states in this reservoir is inversely dependent on the temperature[16] and the experimental data presented by Figure 5, one can conclude that in a quasi-cw excitation regime, the multiphoton excitation channel is dominant. The different absorption cross sections for the first and second pump photon, together with all the additional relaxation channels occurring during the energy transfer between the dopant molecule and the active host matrix, result in the sublinear behavior shown in Figure 3.

In order to estimate the efficiency of the up-conversion process in PF2/6:PdOEP using the same optical set-up and registration scheme, we performed direct excitation of the active host polymer by pumping at 405 nm with a quasi-cw violet laser diode, close to the absorption peak of PF2/6. Figures 2a,c show the data obtained by the two different modes of PF excitation: one by direct excitation at 405 nm and the other by indirect excitation at 532 nm. Taking into account that about 10 % of the incident laser light is absorbed by the PdOEP component in the sample, we recalculated the experimentally measured laser intensity. A ratio of about 1:5000 between the integral intensities of the PL emission of PF when pumped at 532 nm and at 405 nm was derived.

In conclusion, we demonstrate here, for the first time, quasi-cw up-conversion in films of PF doped by various MOEPs. The pump intensities are five orders of magnitude lower than the pump intensities used and reported so far in experiments to achieve TPA excitation of similar magnitude in PF type polymers.[7] We also prove the ability to increase the efficiency of the proposed up-conversion scheme by controlling the experimental parameters such as temperature and absorption features by proper choice of the central metal moiety in the MOEP. We believe that this method for excitation of polyfluorenes can be successfully extended to other combinations of blue-emitting organic- and polymer-matrix materials and other metallated macrocycles.

Experimental

The PF2/6 (poly(9,9-bis(2-ethylhexyl-fluorene-2,7-diyl)), was synthesized according to Nothofer et al. [17]. MOEP: PtOEP, PdOEP, ZnOEP, CuOEP, free base OEP, were purchased from Porphyrin Systems GbR and used as obtained. Solutions of PF2/6:MOEP were prepared in toluene with a mass concentration of 10 mg mL^{-1}. Films of the PF2/6:MOEP blends were prepared via spin-coating of the solutions onto quartz substrates. Reference samples of PF2/6 and MOEP films were prepared in the same manner. In the case of MOEP, PS and PMMA were used as inert matrices. The film thickness was adjusted to about 80 nm, as measured by a TENCOR P-10 Surface Profiler. Absorption spectra were recorded with a UV-vis Perkin-Elmer spectrometer (Lambda2). A Xe-lamp equipped spectrofluorometer (SPEX FluoroLog II (212)) was used to obtain PL and PL-excitation spectra of films and dilute solutions.

A home-built vacuum chamber was used for the up-conversion experiments. Dynamic vacuum higher than 10^{-4} mbar was reached using a turbo pump. An electronically controlled one-stage Peltier element was used to define the temperature of the sample. As pumping sources an intracavity frequency-doubled (532 nm) diode pumped cw-Nd:YAG laser (Verdi V10), a green line (543 nm) He–Ne laser, and a violet (405 nm) laser diode (Nichia Corp.) were used. A combination of specially designed mirrors—with high transmittance for the regions below 490 nm and above 655 nm, reflectivity higher than 99 % for the region between 490 nm and 655 nm, and low absorption color filters—were used in order to eliminate scattered light from the pump laser beams. Achromatic lenses for focusing and collecting of the emitted PL were used. The spot sizes of the pump lasers were as follows: about 10 μm diameter at 532 nm and 543 nm; about 4 μm at 405 nm. An arbitrary function generator was used to synchronize the laser shutter and the registration system. The irradiation time used was 200 ms. The collected emission signal was dispersed in a 0.3 m monochromator equipped with a 150 lines mm^{-1} grating and registered by an optical multichannel analyzer (OMA, Hamamatsu Photonics, PMA50).

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Synthesis and Characterization of Magnetic Iron Sulfide Nanowires

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A variety of inorganic nanowires have been synthesized in the last three to four years.[1] Among these, magnetic nanowires are of interest because of their potential applications in magnetic recording and other areas. Nanowires and nanorods of magnetic metals, such as Fe, Co, and Ni,[2] and their alloys[3] have been prepared by employing template-directed synthesis. Although there are reports of nanotubes, nanorods, and nanowires of several metal chalcogenides,[4,5] oxides,[6] and nitrides[1,6] there is no report to date on iron sulfide nanowires, possibly because of the inherent difficulty in the synthesis and control of stoichiometry of these materials. The Fe–S system has a complex phase diagram, with broad range of compositions of $Fe_{1-x}S$ (pyrrhotite) phases[7] occurring between FeS and FeS_2, showing interesting magnetic[8–10] and electrical properties.[11] Fe_7S_8 is a well-defined phase in this region, showing ferrimagnetism with $T_N = 600$ K.[9] We deemed it important to synthesize iron sulfide nanowires by virtue of their interesting chemistry and magnetic properties. In this communication, we report the first successful synthesis of semiconducting nanowires of $Fe_{1-x}S$ ($x \approx 0.12$, 0.09), of which the $Fe_{0.88}S$ (Fe_7S_8) nanowires are ferrimagnetic, showing magnetic hysteresis at room temperature.

In order to synthesize $Fe_{1-x}S$ nanowires, a hybrid composite (**I**) with ethylenediamine was first prepared by solvothermal procedure (see Experimental). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the composite **I** showed the presence of a high yield of lengthy nanowires with diameters in the range of 80–150 nm and lengths of several micrometers as shown in Figure 1. The infrared (IR) spectrum showed characteristic peaks of the amine, although the bands due to C–N and N–H stretching frequencies were considerably shifted towards lower values due to the bound nature of the amine. Energy dispersive X-ray (EDX) analysis of several samples of **I** carried out over different regions of each sample gave an average Fe/S ratio of

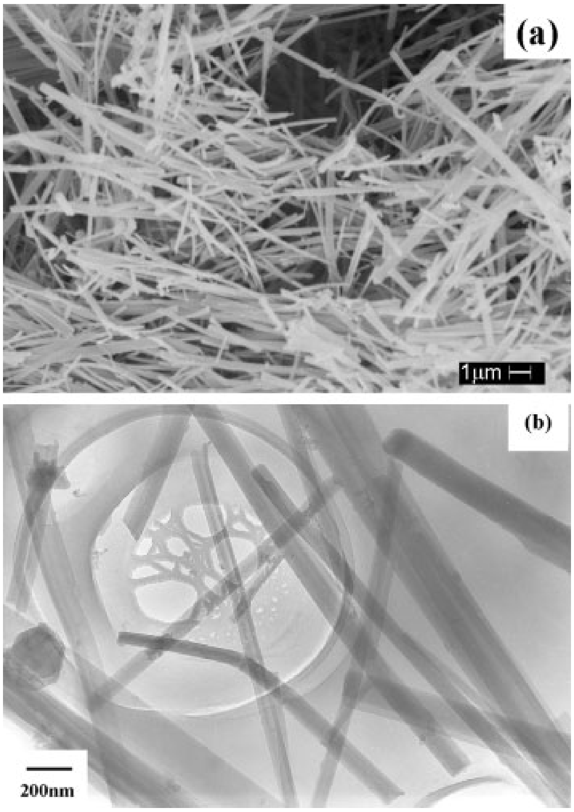

Fig. 1. a) SEM image of the organic–inorganic composite, $Fe_{1-x}S(en)_{0.5}$, **I**. b) Low-magnification TEM image of composite **I**. Apart from nanowires, some layer-rolled kind of structures are also observed (as seen in the center of the image).

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