THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2009, *113,* 1171–1174
Published on Web 01/26/2009

Multicomponent Polymeric Film for Red to Green Low Power Sensitized Up-Conversion

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Received: November 12, 2008; Revised Manuscript Received: December 29, 2008

The realization of red to green photon energy up-conversion in a multicomponent polymeric organic solid film with good photochemical stability is presented. Up-converted light is obtained by using an ultralow excitation power density in the range of 1 mW cm^{-2}, suitable to recover the low energy tail of the solar emission spectrum.

Introduction

Recently, much research has been focused on the study of multicomponent organic systems in which the process of obtaining up-converted photons based on a bimolecular triplet−triplet annihilation (TTA) has been found to be extremely efficient in respect to well-known standard approaches, as well as two-photon absorption and second harmonic generation.[1−10] The investigated sensitized up-conversion process is the result of the several different photophysical intermediate steps outlined in Figure 1: (i) absorption of the incident photons by a light harvesting moiety; (ii) transfer of the excitation from singlets to triplets manifold by intersystem crossing (ISC); (iii) triplet−triplet energy transfer (ET) from the excited molecule (donor) toward metastable triplet states of a second (acceptor) moiety;[11,12] (iv) generation of excited singlet states by bimolecular TTA between acceptor excited triplets followed by emission of higher energy photons.[13−16]

In liquid solution systems, both high ET efficiency and TTA rate are ensured by fast molecular diffusion.[12,17] In this case, even a power density corresponding to the level of the solar emission (0.1 W cm^{-2}) is sufficient to produce efficiently up-converted photons. This, combined with the fact that even noncoherent light sources can be employed,[1,4] make these systems particularly suitable for the requests of the recent photovoltaic applications, whose efficiency would be greatly improved by the recovering of the low energy tail of the solar emission spectrum (energies under 1.1 eV/1130 nm for crystalline silicon based devices and under 2.00 eV/620 nm for low cost plastic cells);[18,19] with this perspective, these multicomponent systems are currently widely studied both in solution and in the solid state.[20−22,24]

Whereas green to blue up-conversion has been successfully obtained in polymeric films,[22] only preliminary results on a plastic film for low energy photons have been presented.[24] In this case, the fluorophore employed as acceptor is rubrene (5,6,11,12-tetraphenylnaphthacene), a highly photochemically unstable molecule, extremely sensitive to the presence of the oxygen.[25]

We present the realization and the photophysical study of a polymeric multicomponent organic solid film, in which light up-converted from the red (1.96 eV/633 nm) to the green region of the visible (VIS) spectrum (2.41 eV/515 nm) has been obtained by employing an ultralow (1 mW cm^{-2} or 3.2 × 10^{15} photons s^{-1} cm^{-2} at 1.96 eV) incident power density.

Experimental Section

The selected compounds are all commercially avaliable and have been used as received. BPAE (molecular formula $C_{30}H_{18}$, MW 378.46, CAS 119654-64-7 (CAS registry no. supplied by author)) and PdPh$_4$TPB (molecular formula $C_{60}H_{36}N_4Pd$, MW 919.37, CAS 119654-64-7 (CAS registry no. supplied by author)) have been provided by Sigma-Aldrich, whereas cellulose acetate MW 100 000 has been provided by Acros Organics. The film (BPd-AC) was obtained by drop casting a 2 g solution of cellulose acetate (5% in DMF) to which 0.5 mL of BPAE solution (2 × 10^{-2} M) and 1.0 mL of PdPh$_4$TPB solution (3 × 10^{-4} M) have been added. The solution has been bubbled with pure nitrogen for at least 4 h, to remove molecular oxygen, which is an efficient quencher of the PdPh$_4$TPB phosphorescence.[27] The drops have been deposited on a glass substrates, heated at 95 °C for 5 min, and cooled to room temperature (the glass transition temperature of cellulose acetate is about 67−68 °C). The procedure has been repeated to give a suitable optical density at the selected energy. A second film (Pd-AC) with only the polymer and the porphyrin has been prepared; also a liquid DMF solution sample (BPd-DMF) without the polymer has been prepared by using the same concentrations of compounds as in sample BPd-AC. Before any measurements, the films have been exposed to the air for three days to check their stability.

In Figure 2 are reported the absorption and emission spectra of the chromophores in DMF solution samples. Absorption has been recorded by a Cary Varian 50 spectrophotometer. Photoluminescence (PL) spectra have been carried out by exciting the samples with a Mira Ti:sapphire laser at 2.95 eV and a He−Ne laser at 1.96 eV. The He−Ne laser has been modulated with an optical switch (CONOPTICS 350-160 with the 25 D driver) for the time-resolved measurements. The emitted light has been collected with a CCD (spectra in the VIS), or with a Hamamatsu R5509R photomultiplier (spectra in the NIR) working in time-correlated photon counting mode and connected to an ORTEC 9353 100 ps multichannel scaler (overall time

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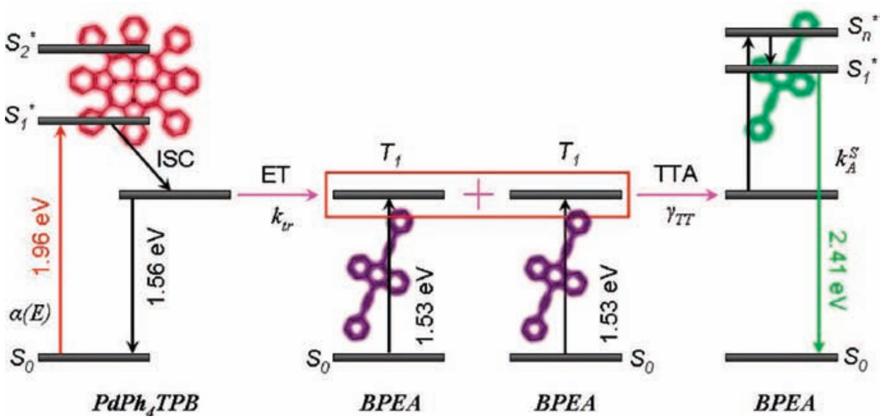

Figure 1. Molecular structures of the selected compounds PdPh$_4$TBP and BPEA and outline of the energy levels involved in the sensitized up-conversion process.

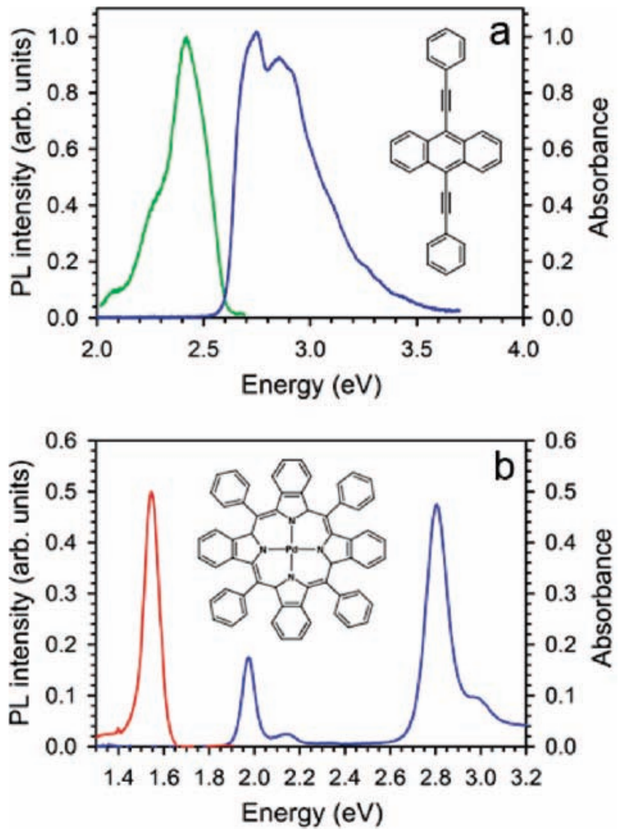

Figure 2. (a) BPEA normalized absorption and normalized fluorescence spectra in DMF solution. Emission spectrum has been obtained by exciting the sample at 2.95 eV at room temperature. (b) PdPh$_4$TBP absorption and luminescence in DMF solution. Emission spectrum has been obtained by exciting the sample at 1.96 eV at room temperature.

resolution better than 3 μs). All the measurements have been carried out in air at room temperature.

Results and Discussion

The light harvesting molecule employed is the palladium(II) *meso*-tetraphenyltetrabenzoporphyrin (PdPh$_4$TBP); metallated porphyrins are suitable to our purposes because they generally possess several well-separated absorption bands also in the near-infrared region.[28,29] Moreover, the presence of the heavy metal ion increases the intersystem crossing rate (ISC), which efficiently populates the donor triplet states.[30] As acceptors and final emitters, the class of polyacenes and their derivatives has shown to work well: the weak oscillator strength of their $T_1{}^*-S_0$ electronic transition allows the accumulation (or sensitization) of the excited-state population on the acceptor triplet states. Moreover, polyacenes generally exhibit a fluorescence quantum yield close to 90%.[31,32] We have selected 9,10-bis(phenylethynyl)anthracene (BPEA), which possesses triplet energy levels well matching the energy of the $T_1{}^*-S_0$ donor electronic transition.[21,33] Besides its remarkably high emission efficiency in the visible region, this molecule possesses a good solubility in a variety of solvents, and chemical and thermal stability.[32,34]

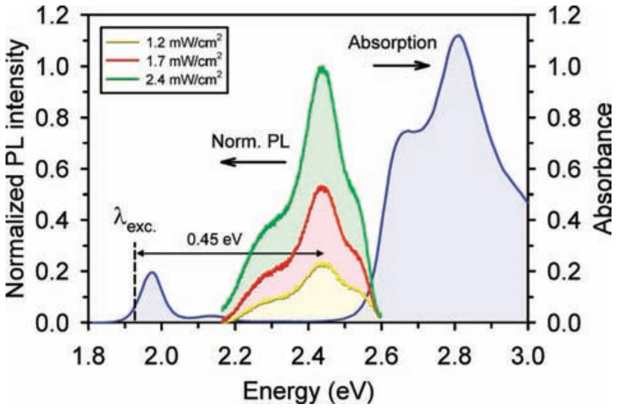

Figure 3. VIS absorption (blue line) spectrum and normalized PL spectra as a function of the incident power density (excitation energy 1.96 eV, dashed line) of sample BPd-AC.

The polymer selected as inert host matrix is the cellulose acetate, which is transparent in the spectral range needed, and it is commonly used to incorporate dyes.[35,36] All the selected materials are easy to handle, and they are chemically and photochemically stable.

Figure 3 shows the absorption spectrum of the film sample BPd-AC. The band centered at 1.97 eV is the typical *Q* band of metallophorphyrin-based molecules.[23] Its position is the same as that for the PdPh$_4$TBP/DMF solution sample (Figure 2b). The more intense and broad absorption band peaked around 2.81 eV originates instead from the overlap between the Soret absorption band of the PdPh$_4$TPB and the $S_0-S_n{}^*$ absorption band of BPEA (see Figure 2). When the sample in the PdPh$_4$TPB band is excited at 1.96 eV, the up-converted photoluminescence (PL) at 2.41 can be easily detected. Its intensity grows more than linearly by increasing the excitation power as it will be discussed below.

The overall up-converted PL generation rate is mainly determined by the efficiency of diffusion assisted ET in

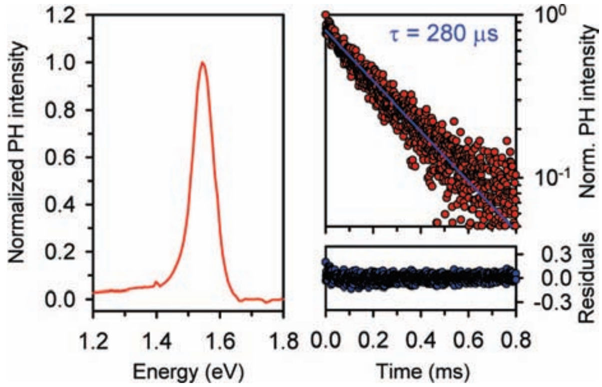

Figure 4. Sample Pd-AC normalized PH spectrum and decay at 1.56 eV (excitation at 1.96 eV, 500 Hz).

sensitization of acceptor triplets population and by TTA rate between triplet excitons. To evaluate the efficiency of the $PdPh_4TPB$ to BPEA energy transfer, we have compared the PL decay time of the $PdPh_4TPB$ in the sample BPd-AC and in the sample Pd-AC, which does not contain the acceptor molecules. Figure 4 shows the $PdPh_4TPB$ luminescence (PH) spectrum and its decay behavior (at 1.56 eV) in the sample Pd-AC; by excluding short times after the excitation pulse, the PH decay can be fitted with a single exponential function with a lifetime $\tau_0 = 280\ \mu s$. The nonexponential character at short times is probably due to an excitation energy migration in the donor center's framework. Anyway, this effect can be considered negligible in our system, because it does not heavily affect the main emission properties of the donor at long times, which are critical for diffusion controlled triplet−triplet ET processes.[12]

The measured τ_0 has the same value as that in low concentration solution samples, which indicates that the molecular oxygen has been successfully removed and thus that no efficient additional nonradiative decay channel is effective in the host matrix, even after the forced exposition of the sample to the air without any kind of sealing.[26] On the contrary, the decay time τ of PH in sample BPd-AC is shorter than the time resolution of our experimental setup ($\ll 3\ \mu s$). Because the efficiency ϵ of a luminescence quenching process, in this case the ET, can be expressed by $\varepsilon = (1 - \tau/\tau_0)$, even by considering $\tau \sim 3\ \mu s$, from experiments we obtained $\varepsilon = 0.99$, which indicates that donor/acceptor energy transfer is almost complete.

Because the system has been studied in solution with promising results, we analyzed its performance in the solid state. Figure 5 shows the dependence of the up-converted PL intensity as a function of the excitation power density at 1.96 eV for sample BPd-DMF and for sample BPd-AC. The PL is several orders of magnitude more intense in sample BPd-DMF compared to sample BPd-AC. In the case of PL due to the indirect excitation of the emitting species following an up-conversion process, it could be demonstrated that for low excitation power densities, the intensity I_A of up-converted PL due to TTA process for small polyacenes is given by

$$I_A \propto \gamma_{TT}[k_{tr}\alpha(E)I_{exc}]^2 \tag{1}$$

where γ_{TT} is the bimolecular rate constant of the TTA, I_{exc} the excitation power density, k_{tr} is the donor PH decay rate (in the case of ET with efficiency ~1, $k_{tr} = 1/\tau$), and $\alpha(E)$ is the donor absorption coefficient.[16,37,38] In a double logarithmic plot of I_A vs I_{exc}, the data are expected to follow a linear function with slope equal to 2 as showed by Eq. 1.

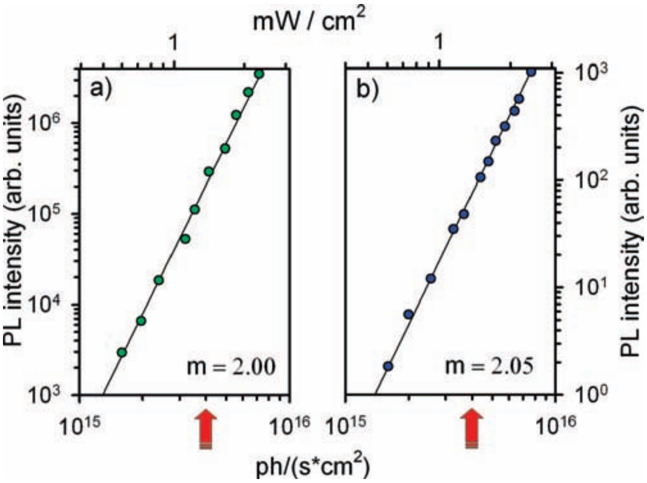

Figure 5. Up-converted PL intensity at 2.41 eV as function of the excitation power density for liquid solution (DMF) sample BPd-DMF (a) and for sample BPd-AC (b) collected at room temperature. The red arrows indicate the photons flux provided by the sun (AM 1.5 global spectrum) at 630 ± 10 nm, corresponding to the wavelength of maximum absorption of the *Q* band of $PdPh_4TBP$ (1.97 eV).

Indeed, the data in Figure 5 follow very well this behavior for both the samples (slopes 2.00 and 2.05 for samples BPd-DMF and BPd-AC, respectively), demonstrating that the TTA process is at the base of the observed PL. Even though in both samples TTA occurs and by considering that the absorption coefficient $\alpha(E)$ is almost equal, it is clear that the overall up-conversion efficiency is different, about 3 orders of magnitude lower in solid film than in liquid solution. By supposing that (i) ET efficiency is ~100% in both cases, (ii) the triplets annihilation distance *a* should not depend from the matrix, and (iii) the emission quantum yields are not different in the film, the lower efficiency observed in BPd-AC can be directly related only to the low triplet excitons mobility.[22,39−41]

Conclusions

We successfully realized a solid multicomponent polymeric film to obtain a sensitized red to green photon up-conversion, by using an ultralow excitation power density of the order of 1 mW cm^{-2}, strictly comparable with the solar irradiance in the selected energy range (Figure 4). The films have been fabricated by using commercially available compounds possessing good photochemical stability, even the forced exposure to the air. The photophysical mechanisms that determine up-conversion yield (triplet−triplet ET between donor/acceptor moieties and bimolecular TTA between acceptor triplets) in the multicomponent film have been investigated with respect to the corresponding system in solution. Because the up-converted photons generation rate at room temperature in the solid samples is not affected by the ET efficiency ($\varepsilon \sim 1$), the obtained results show that the key factor limiting the performance of the solid-state device is the low mobility of triplets excitons in the plastic matrix; host polymers with increased diffusion coefficient must be considered.[22]

Acknowledgment. This work has been supported by the Italian MURST (project Firb Synergy), and by Fondazione Cariplo.

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JP809971U