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Upconversion-induced fluorescence in multicomponent systems: Steady-state excitation power threshold

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We have analyzed the dynamics of the upconversion-induced delayed fluorescence for a model multicomponent organic system, in which high concentrations of triplet states can be sustained in steady-state conditions. At different excitation powers, two regimes have been identified depending on the main deactivation channel for the triplets, namely, the spontaneous decay and the bimolecular annihilation. The excitation power density at which triplet bimolecular annihilation becomes dominant is the threshold (I_{th}) to have efficient upconversion generation. The simple equation obtained for I_{th} allows us to predict the theoretical efficiency of a generic system on the basis of few parameters of the constituent molecules.

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I. INTRODUCTION

In the last few years many researches have been focused on the development of multicomponent molecular systems for upconversion-induced fluorescence, where high-energy photons are generated upon excitation with lower-energy light.[1–6] These systems exploit bimolecular triplet-triplet annihilation (TTA) processes to generate high-energy singlet states from which the emission takes place. Since the direct optical excitation of metastable triplet states is very difficult, because of their extremely low absorption cross section, they are excited via energy transfer from a second moiety possessing partially allowed triplet to singlet transitions. In such a way efficient upconversion has been demonstrated also for excitation power densities comparable with the solar irradiance (1 $\mathrm{kW\,m^{-2}}$, AM 1.5 global spectrum), i.e., orders of magnitude lower than the power densities required in classical upconversion processes such as the second-harmonic generation or the two-photon absorption.[7] Therefore these systems can be employed to improve the efficiency of the solar cells by upconverting the long-wavelength tail of solar spectrum which is barely exploited by both the organic and inorganic photovoltaic devices.[5]

The systems for upconversion-induced fluorescence are basically composed by two different molecular moieties. The first one is an organometallic complex with large absorption cross section at the selected wavelength. The presence of the heavy atom enhances the intersystem crossing (ISC) rate[8,9] thus producing a large number of triplet states from which the energy transfer to the triplet state of the second moiety takes place. The latter should have long-lived triplet states to produce the large steady-state population suitable for the TTA process.[10–12] The steady-state path followed by the energy from the absorption to the upconverted emission is sketched in Fig. 1. The overall yield is mainly influenced by two factors: the efficiency of the energy transfer and that of the TTA. Recently we have investigated the energy-transfer step demonstrating that it can be described as a Dexter resonant energy transfer strongly assisted by energy migration processes.[13] The Dexter radius, as well as the optimal concentration to obtain a complete energy transfer to the emitting moiety, has been calculated for a model system. About the TTA, starting from the 1960s the processes controlling the triplet exciton dynamics in crystals and solutions of polycyclic aromatic hydrocarbon have been carefully investigated, including the triplet-triplet energy transfer,[14–16] the triplet diffusion,[10,11,17,18] and the triplet-triplet interaction inducing the so-called delayed fluorescence,[19] i.e., the same process responsible for the upconversion-induced fluorescence in our multicomponent systems. On the basis of these studies parameters such as the TTA rate or the triplet diffusion coefficient are now well known for many oligomers. Up to now the difficulty to sustaining high concentrations of excited triplets upon direct excitation allowed only for time-resolved studies describing a situation far from the working condition at which the multicomponent systems for upconversion-induced fluorescence are supposed to operate. In this paper we present a quantitative description of the TTA kinetics in a model multicomponent system under steady-state conditions and demonstrate a simple equation giving the efficiency of the upconverted emission as a function of the exciting power. By using this equation it is easy to recognize which properties of the different moieties composing the system can be optimized to enhance the devices performances.

II. EXPERIMENT

The investigated model system is based on the Pt(II)octaethylporphyrin (PtOEP) as light absorber and energy donor (D) and on the 9,10 diphenylanthracene (DPA) as the moiety which acts as acceptor (A) and in which the TTA process occurs. Both the molecules have been purchased by Sigma-Aldrich and used as is. A sketch of the molecule structure, as well as an outline of the relevant molecular energy levels, is shown in Fig. 1. PtEOP/DPA solutions of PtOEP (1.4×10^{-4} M and 1.0×10^{-1} M, respectively) in 1,1,2-trichloroethane have been prepared. This solvent has been selected for its low viscosity, which allows for a fast molecular diffusion. Since the PtOEP phosphorescence is strongly quenched by the molecular oxygen following the $T_1^*(\mathrm{PtOEP}) + {}^3\Sigma_g^-(\mathrm{O}_2) \rightarrow S_0(\mathrm{PtOEP}) + {}^1\Delta_g(\mathrm{O}_2)$ reaction scheme, 5.5 helium has been bubbled in the solutions for at least 1 h before the measurements to deoxygenate the

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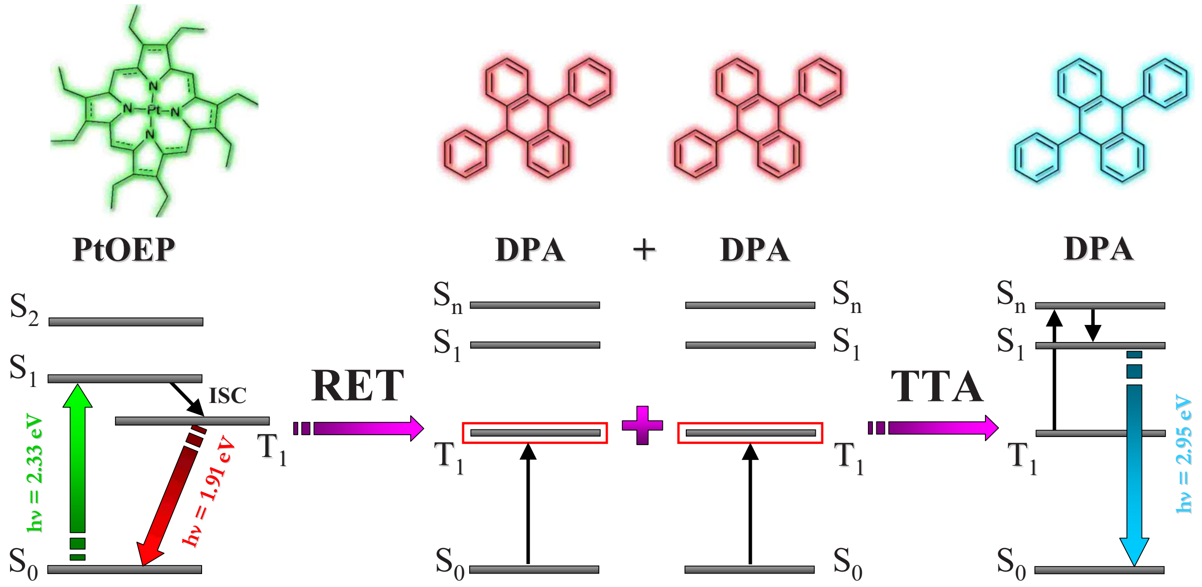

FIG. 1. (Color online) Sketch of the PtOEP and DPA molecule with an outline of molecular energy levels involved in the upconversion-induced fluorescence.

samples. Absorption measurements have been carried out with Varian Cary 50 UV-Vis spectrophotometer (bandpass 1 nm). For the steady-state photoluminescence (PL) measurements, a Coherent Verdi cw laser at 2.33 eV (532 nm) has been used as excitation source and a nitrogen-cooled charge-coupled device (CCD) (Spex 2000) coupled to a polychromator (Triax 190 from J-Horiba) with a bandpass of 0.5 nm for signal detection. Time-resolved PL measurements have been excited at 3.49 eV (355 nm) with the III harmonic of a Nd:YAG (YAG stands for yttrium aluminum garnet) laser (Laser-Export Co. LCS-DTL-374QT) and detected in photon counting mode with a Hamamatsu R943–02 photomultiplier connected to an Ortec 9353 multichannel scaler. The overall time resolution was better than 100 ns. All the measurements have been done at room temperature (RT) and have been corrected for the instrumental spectral response.

III. RESULTS AND DISCUSSION

Figure 2 shows the well-known absorption/emission spectra of the PtOEP/DPA solutions. Following the excitation into the sharp absorption band of the PtOEP around 2.32 eV, both its red phosphorescence centered at 1.92 eV and the broad blue fluorescence at 2.6–3.1 eV due to the presence of the DPA are observable. The relative red to blue intensity is strongly power dependent. The dynamics of the system can be described by using three coupled rate equations:

$$\partial T_D/\partial t = \alpha(E)I_{\mathrm{exc}} - k_D^T T_D - k_{\mathrm{tr}} T_D, \tag{1a}$$

$$\partial T_A/\partial t = k_{\mathrm{tr}} T_D - k_A^T T_A - \gamma_{TT} T_A^2, \tag{1b}$$

$$\partial S_A/\partial t = 0.5\gamma_{TT}^S T_A^2 - k_A^S S_A = 0.5 f \gamma_{TT} T_A^2 - k_A^S S_A. \tag{1c}$$

Giving, respectively, the population of the PtOEP excited triplets (T_D), of the DPA excited triplets (T_A), and of the DPA excited singlets (S_A). [The exciting power density is position dependent, both along the laser propagation direction because of the progressive attenuation of the beam traveling in the solution and in transversal direction because of the Gaussian beam shape. Therefore, even if not explicitly indicated, Eq. (1) are local relations, in which all the quantities must be integrated and averaged over the overall excited volume (V) to calculate the correct PL intensity. As instance $I_{\mathrm{exc}} \equiv 1/V \int_V I_{\mathrm{exc}}(x,y,z)dxdydz$.] Since ISC in the PtOEP molecules takes place very rapidly,[8,9] we have supposed that all the excited PtOEP singlets are immediately converted in the corresponding triplets, as also suggested by the lack of any PL due to singlet PtOEP recombination. Therefore in Eq. (1a) the rate of T_D generation is simply given by the number of photons per second arriving on the sample (I_{exc}) multiplied by the PtOEP absorption coefficient $\alpha(E)$. The excited

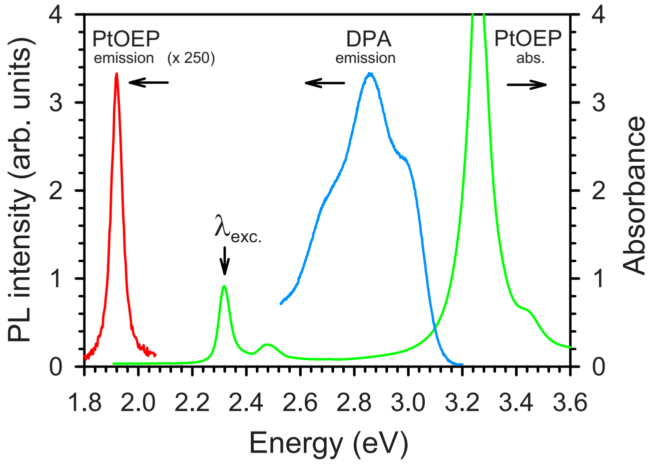

FIG. 2. (Color online) Absorption and emission spectra of a PtEOP/DPA solution in 1,1,2 trichloroethane (PtEOP and DPA concentrations: 1.4×10^{-4} and 1.0×10^{-1} M, respectively). The PL excitation power density was 1×10^{15} photons s^{-1} cm^{-2}.

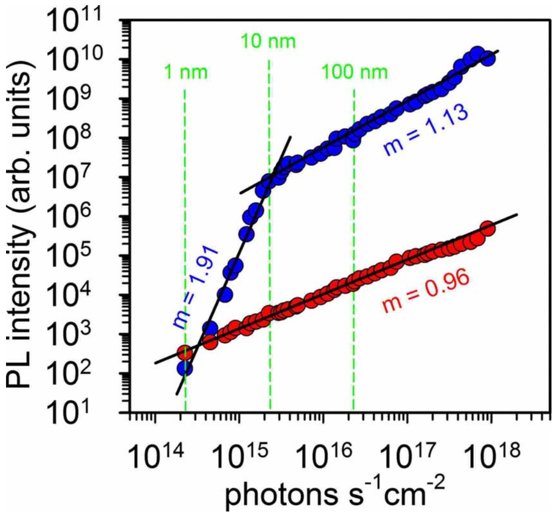

FIG. 3. (Color online) DPA fluorescence (blue circles) and PtOEP phosphorescence (red circles) intensity vs the excitation power density for a PtEOP/DPA solution in 1,1,2-trichloroethane (PtEOP and DPA concentrations: 1.5×10^{-4} and 1.0×10^{-1} M, respectively). The green vertical lines indicate the power density supplied by the sun at 532 nm under AM 1.5 condition integrated over 1, 10, and 100 nm, respectively.

PtOEP triplets can decay spontaneously with a rate k_D^T, or transfer their energy to the DPA molecules with a rate k_{tr}. The DPA triplets [Eq. (1b)], indirectly excited from the PtOEP ones, can decay nonradiatively with a k_A^T rate or annihilate with a probability depending on γ_{TT} which is the second-order rate constant characterizing the TTA process. Finally the DPA singlets [Eq. (1c)] are created from the TTA process and decay with k_A^S rate. It should be noted that γ_{TT}^S, the rate constant of singlet formation by TTA, is not equal to γ_{TT} since also the spin-statistical weight (f) of the singlet excited-state generation from a TTA process must be considered. In the presented case f is 0.4.[20–22] Equation (1) can be solved for steady-state conditions. However in the following we will discuss separately the two limiting cases of fast and slow TTA in order to underline the basic physical behavior of the two different regimes. In the first case we assume that the DPA TTA is much more probable than the triplets spontaneous decay, i.e., $\gamma_{TT}T_A^2 \gg k_A^T T_A$, as expected at high excitation power where T_A is very large. On the opposite, at low excitation power the TTA becomes negligible with respect to the DPA spontaneous radiative/nonradiative decay, which is now the main triplet deactivation channel ($k_A^T T_A \gg \gamma_{TT}T_A^2$). In this case Eq. (1a) gives the S_A steady-state concentration as a function of the excitation power density,

$$S_A = 0.2\frac{\gamma_{TT}}{k_A^S}\left[\frac{k_{\mathrm{tr}}/k_A^T}{k_D^T + k_{\mathrm{tr}}}\right]^2[\alpha(E)I_{\mathrm{exc}}]^2 \propto I_{\mathrm{exc}}^2. \qquad (2)$$

Since the upconverted PL is proportional to S_A ($I_A = \beta\Phi_A k_A^S S_A$, with β being the detection efficiency of the experimental setup and Φ_A being the DPA emission quantum yield), a logarithmic plot of I_A vs I_{exc} yields a straight line with slope 2. Figure 3 shows these data (blue circles) for power densities ranging from 10^{14} to 10^{18} photons $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$.

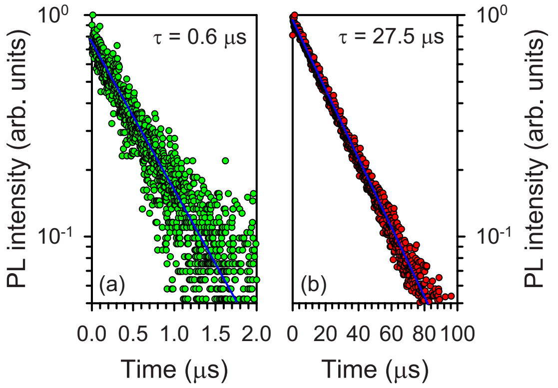

FIG. 4. (Color online) Decay of the 1.91 eV PtOEP phosphorescence in 1,1,2 trichloroethane solution (b) without DPA and (a) with a 1.0×10^{-1} M DPA concentration. The continuous lines are the fits of the experimental data with single exponential functions. The obtained phosphorescence lifetimes are, respectively, 27.5 and 0.61 μs.

As expected the experimental data for low power densities, approximately up to 2×10^{15} photons $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$, can be well fitted with a straight line of slope of 1.91, really close to the predicted value. The behavior of the data collected for higher excitation power will be discussed later, while now we will focus our attention on the evaluation of γ_{TT} from the analysis of this first set of data.

To avoid absolute PL intensity measurements, it is possible to remove the dependence of the DPA fluorescence intensity from the instrumental parameter β by considering the ratio between the DPA blue and the PtOEP red emissions. The latter, analogously to I_A, can be written as $I_D = \beta\phi_D k_D^T T_D = \beta\phi_D k_D^T/(k_{\mathrm{tr}}+k_D^T)\alpha(E)I_{\mathrm{exc}}$ [from Eq. (1a)]. The I_D dependence on the excitation power is in this case expected to be linear, regardless of the excitation power intensity, and indeed the corresponding data reported in Fig. 3 (red circles) follow very well this law being fitted by a straight line with slope of 0.96. The relative DPA/PtOEP emission intensity can be written as

$$\varepsilon \equiv \frac{I_A}{I_D} = 0.2\frac{\phi_A(\gamma_{TT}/k_D^T)(k_{\mathrm{tr}}/k_A^T)^2}{\phi_D(k_{\mathrm{tr}} + k_D^T)}\alpha(E)I_{\mathrm{exc}}. \qquad (3)$$

Equation (3) shows that in the low excitation power limit, the relative DPA/PtOEP emission PL increases linearly with the excitation power density and allows us to evaluate γ_{TT} from few parameters which can be easily measured or collected from the literature. In particular, the DPA is a well-known molecule whose photoluminescence quantum yield is reported to be close to 1 (ϕ_A is 0.95 for diluted solution[23]) and its triplet decay rate is 2×10^2 Hz.

The parameters describing the PtOEP properties have been directly measured since the energy-transfer process is specific of the particular system investigated. We obtained a PtOEP PL decay time, in the absence of any acceptor moiety, of 27.5 μs implying $k_D^T = 3.63\times10^4$ Hz. In the mixed DPA/PtOEP solution, with a 1.0×10^{-1} M DPA concentration, the PL decay shortens down to 0.61 μs (see Fig. 4), still following a single exponential decay behavior. This implies that: (i) for the employed DPA concentration the energy-transfer efficiency from the PtOEP is extremely high (about 98%), which means that almost all the absorbed photons produce triplet states on DPA; (ii) the PtOEP spontaneous decay rate is negligible with respect to the energy-transfer rate so $k_{\text{tr}} \cong 0.61\ \mu\text{s}^{-1} = 1.63 \times 10^6$ Hz; (iii) at such high concentration of DPA the energy-transfer process is not assisted by any molecular diffusion, in agreement with our previous results.[13] The last two quantities needed to evaluate γ_{TT} from Eq. (3) are the PtOEP absorption coefficient $\alpha(E)$, which is $8.3\ \text{cm}^{-1}$ (Fig. 2) and the ϕ_D, which is 0.41.[24]

In the low excitation power limit, the data reported in Fig. 3 gave an experimental ratio between the DPA and PtOEP emissions of 1.99, from which, using the parameter above reported, γ_{TT} is $3.6 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$. γ_{TT} is related to the triplet diffusion coefficient (D) and to the effective triplet-triplet interaction distance (a) through the equation, $\gamma_{TT} = 8\pi Da$.[10] Since the triplet diffusion coefficient in solution depends on the molecule diffusion, it can be easily calculated from the viscosity of the solvent (0.12 cP at RT) and from the DPA effective molecular radius (4.5 Å) estimated according to Bondi,[25] resulting to be $D = 1.6 \times 10^{-4}\ \text{cm}^2\ \text{s}^{-1}$. The DPA effective triplet-triplet interaction distance is therefore $a = 9.1 \times 10^{-8}$ cm. There are no data about the triplet-triplet cross section in DPA, but these values can be compared to those of anthracene which has a quite similar electronic structure. In anthracene crystals the exciton diffusion is $2 \times 10^{-4}\ \text{cm}^2\ \text{s}^{-1}$, incidentally not too far from that of the DPA molecule in our solution, but its γ is only $2.1-2.4 \times 10^{-11}\ \text{cm}^3\ \text{s}^{-1}$, i.e., more than 1 order of magnitude smaller than that we have obtained for DPA. This difference can be easily explained by considering the different behavior of the triplet-triplet annihilation process in solution and in an ordered environment as a crystal. When two triplets come together they can annihilate by producing either a singlet or triplet state or can scatter without reaction. Studies of the triplet-triplet annihilation in presence of magnetic field demonstrated that the ratio between the scattering probability and the probability of formation of a singlet state upon triplet-triplet interaction is much larger in crystals than in solutions (for anthracene this ratio is about 30).[26]

In the high excitation power limit the main DPA triplet decay channel is the triplet-triplet annihilation because, as outlined before, $\gamma_{TT}T_A^2$ becomes larger than $k_A^T T_A$. In such a case Eq. (1) must be solved by neglecting the term $k_A^T T_A$ in Eq. (1b). Under steady-state condition the singlet concentration ($\underline{S}_A$) is now

$$\underline{S}_A = 0.2\frac{1}{k_A^S}\left[\frac{k_{\text{tr}}}{k_D^T + k_{\text{tr}}}\right]\alpha(E) I_{\text{exc}} \propto I_{\text{exc}}, \tag{4}$$

which shows that $\underline{S}_A$ becomes proportional to the excitation power density as well as the PL intensity which depends, as in the case of slow TTA, on $\underline{S}_A$. It is interesting to observe that in this regime $\underline{S}_A$, and therefore also the upconverted PL signal, does not depend on γ_{TT}. As a consequence Eq. (4) cannot be used to extract any additional information about the TTA process. For excitation power densities larger than 2×10^{15} photons $\text{s}^{-1}\ \text{cm}^{-2}$ the data in Fig. 3 display exactly the behavior predicted by Eq. (4) (slope ≈ 1) thus demonstrating the reliability of the proposed model.

The excitation power density at which $k_A^T T_A = \gamma_{TT} T_A^2$ is especially interesting because it represents the point at which the DPA spontaneous decay and the DPA TTA give the same contribution to limit the DPA triplet concentration. This excitation power density, at which the TTA becomes the main DPA triplet deactivation channel, can be considered the threshold (I_{th}) corresponding to the achievement of the maximum upconversion efficiency. For lower excitation powers, on the contrary, the energy supplied to the system is mainly lost through the DPA spontaneous decay, thus resulting ineffective to induce upconversion. I_{th} corresponds to the point at which Eqs. (2) and (4) assume the same value, i.e., where the logarithmic plot of I_A vs I_{exc} changes the slope from 2 to 1. By equating Eqs. (2) and (4) it is easy to find

$$I_{\text{th}} = \frac{(k_A^T)^2}{\alpha(E)\gamma_{TT}}\left(\frac{k_{\text{tr}}}{k_{\text{tr}} + k_D^T}\right) \equiv \frac{(k_A^T)^2}{\phi_{\text{tr}}\alpha(E)\gamma_{TT}}, \tag{5}$$

in which we have defined an energy-transfer quantum yield as $\phi_{\text{tr}} = (k_{\text{tr}}/k_{\text{tr}} + k_D^T)$.

Equation (5) directly shows which parameters rule the upconversion efficiency and can be used to understand where there is room for significant improvements. In the following we will comment briefly each of these parameters. First of all I_{th} depends on the square of k_A^T. It is therefore possible to strongly reduce I_{th} by preparing molecules with extremely long-lived triplets. However in anthracene and anthracene derivatives k_A^T is still rather small (of the order $10^2\ \text{s}^{-1}$), and it seems not easy to enhance this parameter.

γ_{TT} depends on the triplet exciton diffusion length, on the exciton interaction distance, and on the probability that the triplet-triplet interaction give rise to an excited singlet state. In crystals the triplet exciton diffusion distance may be rather large but we have already pointed out that the probability to form singlet upon triplet-triplet interactions is small. In amorphous solids this probability may be much larger, but the exciton diffusion is expected to be smaller. Concentrated solutions are from a photophysical point of view the ideal systems displaying fast diffusion (in solvents with low viscosity) and high probability to generate singlet excited states upon TTA. However they offer only limited applications in real devices.

In these multicomponent systems, characterized by very large acceptor concentration required to maximize γ_{TT}, ϕ_{tr} can be easily very close to 1 if the donor species has been properly selected. For instance, in the investigated system the PtOEP PL decay measurements in presence of DPA give $\phi_{\text{tr}} = 97.8\%$. Therefore this parameter cannot be further enhanced significantly. The last parameter in Eq. (5) is $\alpha(E)$. In order to decrease I_{th}, $\alpha(E)$ must be enhanced both by using donor molecules with large absorption cross section and by employing in the multicomponent system relatively high donor concentration. However, if the goal is to obtain efficient systems under white light illumination, as for instance in the case of upconverters for solar cell applications, also the width of the absorption band of the donor moiety is to be considered. Indeed, in this condition $\alpha(E)$ in Eq. (5) must be replaced with $\bar{\alpha} \equiv \int \alpha(E) dE$ which gives the total number of absorbed photons. It is evident that the value of $\bar{\alpha}$ can be easily tuned by changing the absorption bandwidth. To understand the influence of this parameter on the performances of a system for upconversion may be useful to consider the efficiency of the PtOEP/DPA solution investigated in this paper under exposition to the sunlight. In AM 1.5 condition the solar irradiance at 532 nm is about 2×10^{14} photons $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}\,\mathrm{nm}^{-1}$. Since the PtOEP absorption bandwidth is about 10 nm this gives an exciting power of 2×10^{15} photons $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$ nearly as large as the I_{th}. In other words, the solar irradiance is for the investigated system sufficient to achieve the maximum upconversion efficiency. Larger absorption bandwidth (100 nm) would of course generate more upconverted photons but maintaining the same efficiency. On the contrary, with an hypothetical absorption bandwidth of only 1 nm our system would be highly inefficient even if with the upconverted blue emission still detectable (see Fig. 3).

IV. CONCLUSION

The analysis of the TTA kinetics in multicomponent system for upconversion-induced fluorescence, in which high concentration of triplet states can be sustained in steady-state condition, allowed us to define a power threshold indicating the minimum excitation density required to make the TTA the main decay channel. The simple expression of I_{th} clearly shows how the various molecular properties affect the overall upconversion efficiency. It can be used both as a figure of merit of the upconverted fluorescence generation and to focus proper strategies to enhance the performance of these systems in order to design efficient upconverting devices. In particular we have demonstrated that for applications involving white light excitation, the absorption bandwidth of the light harvesting moiety is the molecular property with the largest possibility of improvements.

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