

Research Article

Diffusion Enhanced Upconversion in Organic Systems

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Received 29 March 2008; Accepted 5 May 2008

Recommended by Mohamed Sabry Abdel-Mottaleb

The upconverted fluorescence generation in a solution of multicomponent organic systems has been studied as a function of the temperature to investigate the role of resonant energy transfer processes and of the molecular diffusion on the overall emission yield. The strong blue emission observed exciting the samples at 532 nm derives from a bimolecular triplet-triplet annihilation between 9,10 diphenylanthracene molecules, which produces singlet excited states from which the higher energy emission takes place. Diphenylanthracene excited triplet states are populated by energy transfer from a phosphorescent donor (Pt(II)octaethylporphyrin) which acts as excitation light harvesting. At low temperature, the experimental data on the efficiency of the transfer have been interpreted in the frame of a Dexter energy transfer in the Perrin approximation. At room temperature, the fast diffusion of the molecules has been found to be the main factor which affects the energy transfer rates and the overall photon upconversion efficiency.

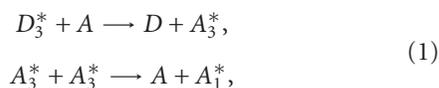
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1. INTRODUCTION

The well-known upconversion processes such as second-harmonic generation or two-photon absorption usually require very high excitation power densities [1], typically of the order of MW/cm², being effective only by using laser sources. Recently, a novel approach has been proposed based on the exciton triplet-triplet annihilation (TTA) between organic molecules, which gives rise to an upconverted fluorescence indirectly excited via energy transfer (ET) from a second molecular species acting as a light harvesting [2–7]. In such a way, the requested power density to have upconverted photons is reduced to the level of the solar emission (as low as ≈ 0.1 W/cm²) [5]. Obviously, this makes these processes suitable for applications in the field of organic photovoltaics [8], which requires for methods for the conversion of the low energy tail of the solar spectrum.

In these multicomponent systems, the upconverted light is the result of several intermediate photophysical processes: (i) absorption of the excitation light by a phosphorescent donor (*D*) molecule producing triplet excited states; (ii) energy transfer processes towards metastable triplet state of an acceptor molecule (*A*); (iii) triplet-triplet annihilation giving rise to high-energy singlet excited states of the second species, from which the upconverted fluorescence takes place. The donor must exhibit large absorption cross-

section, while the acceptor must have as long as possible long lived triplet states suitable to collect the excitation from the donor [9] by ET and to generate singlet excited state via TTA. Hybrid materials like organometallic compounds [3, 10] are usually employed as donors, since the presence of heavy atoms strongly enhances their ISC rate [11], thus giving a high population of excited triplet states. Conjugated molecules like polyacenes are reported to work well [12–14] as acceptors, due to the extremely low oscillator strength of their *T*^{*}-*S*₀ electronic transitions. The key passages which can limit the overall process efficiency are the steps involving the ET and the TTA, which can be sketched as



where the subscripts identify the singlet (1) and triplet (3) states.

The results presented in this paper focused our attention on the ET step, in order to understand its role in the upconversion-induced delayed fluorescence of a model multicomponent systems. To this goal, we prepared solutions at a different acceptor concentration, which has been considered as a simple quencher of the red emission of the donor. Measurements of the ET efficiency on solutions at different temperatures allowed us to evaluate quantitatively

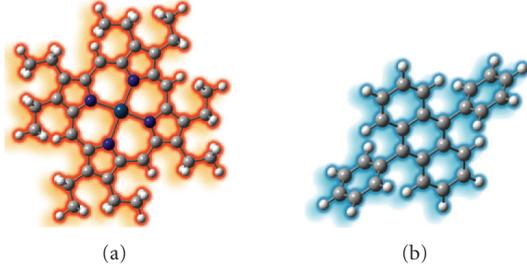


FIGURE 1: Molecular structures of (a) Pt(II)octaethylporphyrin and (b) 9,10 diphenylanthracene.

the contribution of the molecular diffusion on the overall efficiency of the process.

2. EXPERIMENTAL

CW photoluminescence (PL) measurements have been carried out by exciting the samples using a Coherent Verdi Nd:YAG laser at the wavelength of 532 nm with a power density of 0.3 W/cm². The emission from the solutions has been detected by a nitrogen cooled CCD (Spex 2000) coupled to a monochromator (Triax 190 from J-Horiba) with a bandpass of 0.5 nm. All the measurements have been recorded with the sample inside a bath cryostat in helium atmosphere at room temperature (RT) and 77 K.

PtOEP (Pt(II)octaethylporphyrin) and DPA (9,10 diphenylanthracene), both purchased from Aldrich and used as-is, have been selected as the donor and acceptor moieties, respectively. Their molecular structures are reported in Figure 1. Mixed solutions have been prepared in 1,1,1-Trichloroethane with a fixed concentration of PtOEP (1.4×10^{-4} M) while the concentration of DPA has been varied from 10^{-5} to 4×10^{-2} M. Solutions have been carefully deoxygenated before the measurements by bubbling dry helium for 1 hour [15, 16]. After the deoxygenation, the measured lifetime of the PtOEP emission in absence of the DPA is 27 microseconds which corresponds to a decay rate (K_0) of 3.7×10^4 Hz.

Time resolved PL measurements, carried out to control the effects of the deoxygenation, have been performed with the same monochromator but using a pulsed laser at 355 nm for the excitation (Laser-Export Co. LCS-DTL-374QT), and, for the detection, a photomultiplier connected to a board for time correlated photon counting measurement (ORTEC 9353 100-ps Time Digitizer/MCS). The overall time resolution was better than 100 nanoseconds.

3. RESULTS AND DISCUSSION

Considering that the ET occurs between D_3^* and A_3^* triplet states, whose transition to the ground state is weakly allowed or forbidden at all, therefore, we expect that only Dexter ET via exchange interaction can take place [17–19].

In such a case, the transfer rate (k_{ET}) between a donor-acceptor pair at a distance R can be written as [18]

$$k_{ET}(R) = \frac{2\pi}{\hbar} Z^2 \int F_D(E) G_A(E) dE, \quad (2)$$

where $F_D(E)$ and $G_A(E)$ are the normalized donor emission and acceptor absorption spectra, respectively. The integral of the products of these two functions is the mathematical expression of the resonance involved levels as required by the energy conservation principle. Z is the exchange integral which can be expressed by his asymptotic form

$$Z^2 = K^2 \exp\left(\frac{-2R}{L}\right), \quad (3)$$

where K is a constant with the dimension of an energy, and L is the so-called effective Bohr radius measuring the spatial extent of the donor and acceptor wavefunctions. In particular, (3) shows the dependence of the ET rate on the distance between donor and acceptor, as a consequence of the molecular-wavefunctions exponential decay in the space.

For processes controlled by exchange interactions, $F_D(E)$ and $G_A(E)$ spectra are only hardly detectable as they involve forbidden transitions. Moreover, the shape of the molecular wavefunctions should be known for an exact evaluation of the parameter Z . For these reasons, many models have been developed to simplify the original Dexter equations [20–22]. The Perrin model [22] follows from the observation that (3) gives at short distances, when $R \ll L$, an extremely fast ET rate, while the ET rate becomes negligible at $R > L$. The Perrin model assumes for each isolated donor-acceptor pair the existence of a sort of active sphere of radius R_0 : if the donor acceptor distance is shorter than R_0 , the energy is totally transferred from the donor to the acceptor, while there is no transfer for larger distances. In this frame, the $k_{ET}(R)$ assumes the simple form

$$k_{ET}(R) = \begin{cases} 0 & \text{for } R > R_0, \\ \infty & \text{for } R < R_0. \end{cases} \quad (4)$$

In (4), R_0 is defined as the *effective radius*, in the sense that at this distance the ET rate equals the rate of the spontaneous decay of the donor in absence of acceptors.

R_0 can be obtained experimentally from measurements of PL relative quantum yield (QY) of the donor, by defining the QY as the ratio between the donor PL intensity ϵ in the presence of a defined acceptor concentration (C_A), and that without it (ϵ_0). By using (4), this relative QY can be written as [19]

$$\frac{\epsilon}{\epsilon_0} = \exp\left(\frac{-C_A}{C_0}\right). \quad (5)$$

C_0 is a constant related to the Dexter parameters (L, K) called critical transfer concentration. Using units of moles per liter for C_0 , the value of R_0 in Ångstrom is equal to $7.346 C_0^{-1/3}$.

In Figure 2, PL spectra of PtOEP/DPA mixed solution are reported as a function of the DPA content. At low DPA concentration, the typical red phosphorescence (PH) of the PtOEP at 635 nm [16, 23] is clearly detected (Figure 2(b)). As the acceptor concentration increases, the intensity of the peak at 635 nm is reduced and a strong enhancement of the DPA emission band at 435 nm (FL) is observed, as in a typical donor-acceptor system (Figure 2(a)). The only difference in this case is that the emission of the acceptor occurs at an

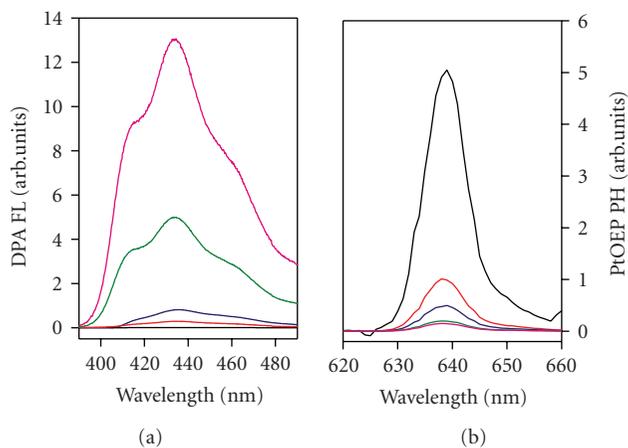


FIGURE 2: (a) DPA FL spectrum and (b) PtOEP PH intensity at different DPA concentration in PtOEP (1.4×10^{-4} M)/1,1,1-Trichloroethane solution. Spectra have been collected at RT exciting the solution at 532 nm.

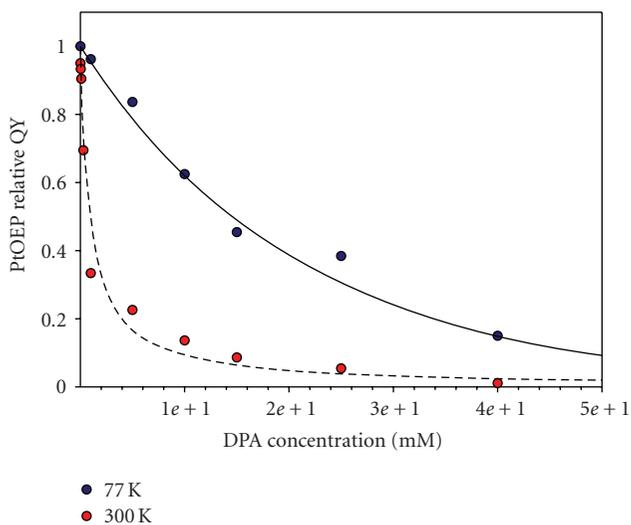


FIGURE 3: Relative PL quantum yields of the PtOEP PL as a function of the DPA concentration at 77 K (blue circles) and 300 K (red circles). The dashed line has been calculated by combining the contribution of the molecular diffusion and the ET process as a contact interaction. The continuous line is the fit of the data collected at 77 K considering a pure Dexter ET (Dexter radius 26.5 Å).

energy higher than that of the emission of the donor because of the upconversion process.

To verify whether the ET process can be fully described as a Dexter mechanism and to check if the Perrin approximation can be employed for these systems, we measured the relative PL efficiency of the PtOEP used in (5) as a function of the DPA concentration. In Figure 3 (blue circles), the measurements performed on frozen solution are reported, where the molecules diffusion is completely prevented. These data can be perfectly fitted using (5) and are therefore consistent with an exchange driven transfer with an effective radius R_0 of 26.5 Å. A second set of measurements is carried

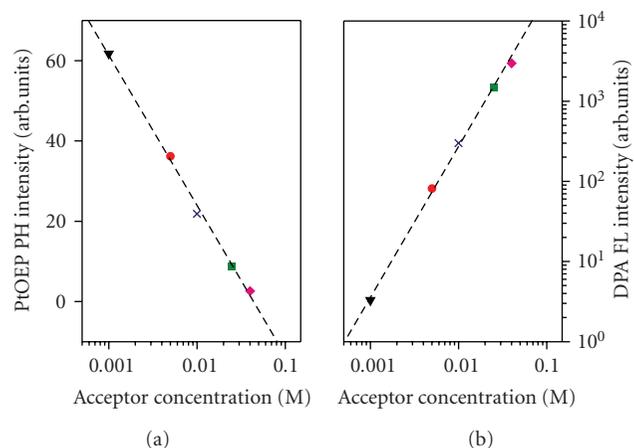


FIGURE 4: (a) PtOEP PH intensity at different acceptor concentration. Dashed line is the fit with a linear function. (b) Corresponding DPA FL intensity. Dashed line is the fit with a linear function with $m = 1.9$.

out at RT (Figure 3, red circles). Indeed the full process (Dexter ET plus diffusion) can be formally described as a donor quenching due to direct collision with the acceptor moiety [24] using the Dexter radius as the contact distance. In such a case, the ET rate in steady state condition is

$$K_{ET} = 4\pi DR_0 C_A, \quad (6)$$

where D is the overall diffusion coefficient defined as the sum of the diffusion coefficients of donors (D) and acceptors (A). Diffusion coefficients are evaluated from the viscosity of the solvent ($\eta = 1.2$ cP at RT [25]) and from the effective molecular radii (R_m) estimated accordingly to Bondi [26]. In such a way, the Einstein relation ($D = 3kT/6\pi\eta R_m$) gives an overall diffusion coefficient of 1.8×10^{-5} cm²/s.

The relative PL quantum efficiency of PtOEP, taking in to account the diffusion contribution, is then calculated as the ratio between the PtOEP decay rates with and without the donor [$\epsilon/\epsilon_0 = K_0/(K_0 + K_{ET})$] and has been shown in Figure 3 (dashed line). This curve matches well the corresponding experimental data. It must be pointed out that in this comparison no adjustable parameters (K_0 , D , R_0) are involved. By considering that for DPA concentration values higher than 1×10^{-2} M $K_{ET} \gg K_0$, from (6) we can deduce that in the absence of competitive de-excitation channels, PtOEP PH intensity is inversely proportional to the concentration of acceptor C_A . In Figure 4(a), the values of PH intensity varying C_A of three orders of magnitude are reported, and by using a semilogarithmic scale to plot concentrations, we expect a decrease of PH intensity. The data reported in Figure 4(a) are indeed strictly consistent with the prevision of collision ET/diffusion model proposed by (6) (dashed line). For TTA is a second-order process, the blue light intensity should be proportional to the square of acceptor triplet excited states population [27]. In such a way by considering that the number of excited acceptors is proportional to C_A (see (6)), then also upconverted light intensity should be proportional to the square of acceptor

concentration. In Figure 4(b), the FL intensity versus the DPA concentration (by using logarithmic scale) has been plotted at fixed concentration of donor. The experimental data fit well with a linear function with an angular coefficient $m = 1.9$ which is in very good agreement with the considerations done on the TTA process (the quadratic dependency gives an exact value of 2 for the slope m).

Obtained results indicate that in the investigated multi-component system, ET is the main mechanism to populate DPA triplets, and that there are not competitive alternative channels through which donor centers can lose the absorbed energy. At RT it is clear that the molecular diffusion plays a key role in enhancing the ET efficiency. In fact, because of the involvement of long-living donor triplet states, the diffusion lengths of excited molecules are the order of magnitudes larger than the effective radius R_0 of the ET. In the case of PtOEP/DPA solutions, the overall diffusion length goes up to 210 nm with a 10^{-3} DPA concentration. Only for really large acceptor concentrations ($\gg 10^{-2}$ M), the effect of migration can be considered negligible and only the direct donor-acceptor ET is effective. This implies that in order to enhance the efficiency of the ET of these systems in solution, it is necessary to improve the molecular mobility by using solvents with low viscosity and/or small molecular species.

4. CONCLUSIONS

The effects of the molecular diffusion on the triplet-triplet exciton ET between PtEOP and DPA, an organic system model for upconversion-induced delayed fluorescence, have been studied as a function of the temperature. At low T, the results can be well described as a Dexter ET by using the Perrin approximation with an effective radius of 26.5 Å. On the contrary, at RT the molecular diffusion is the main phenomenon which affects the ET efficiency, which is very high also for low acceptor concentrations as a consequence of overall molecular diffusion lengths. As shown, RT experimental data can be strictly interpreted by using an ET/diffusion combined model. These findings clearly explain why high upconversion efficiencies are usually reported for systems in solution [3, 6], while the performance of the corresponding films, where donors and acceptors moieties are not able to move, is much lower [2, 7].

ACKNOWLEDGMENT

This work has been supported by the Italian MURS (project Synergy) by Fondazione Cariplo and by RTN Nanomatch (Marie-Curie RTN NANOMATCH, Grant no. MRTN-CT-2006-035884).

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