Upconversion-induced delayed fluorescence in multicomponent organic systems: Role of Dexter energy transfer

A. Monguzzi,* R. Tubino, and F. Meinardi

Department of Material Science, University of Milano-Bicocca, via Cozzi 53, I-20125 Milano, Italy
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The efficiency of the upconversion-induced delayed fluorescence in a solution of multicomponent organic systems is limited by two steps of the overall process: (i) a triplet-triplet energy transfer between a phosphorescent donor and an emitting acceptor, and (ii) a bimolecular acceptor triplet-triplet annihilation generating acceptor singlet excited states from which the high-energy emission takes place. In this work, the energy transfer process has been investigated in a model system constituted by solutions of Pt(II)octaethylporphyrin, which acts as a donor, and 9,10 diphenylanthracene, which acts as an acceptor. At low temperature, the experimental data have been interpreted in the frame of a pure Dexter energy transfer by using the Perrin approximation. A Dexter radius as large as 26.5 Å has been found. At room temperature, the fast diffusion of the molecules in the solution is no longer negligible, which gives rise to a strong increase in the energy transfer rates.

I. INTRODUCTION

The generation of high-energy emission starting from photons with lower energy is a well known phenomenon. This upconversion processes, such as second-harmonic generation or two-photon absorption, usually require very high excitation power densities[1] of the order of MW/cm^2 or GW/cm^2, being therefore effective only by using laser sources. Recently, a completely new approach based on the exciton triplet-triplet annihilation (TTA) in organic molecules, which gives rise to an upconversion-induced delayed fluorescence, indirectly excited via energy transfer (ET) from a second moiety acting as a light harvesting, has been proposed.[2–7] In such a way the requested power density is reduced to the ultralow level of the solar emission power (as low as ≈ 0.1 W/cm^2) for which an efficient upconversion can be obtained.[5] This makes these processes suitable for the huge market of the photovoltaics,[8] which calls for methods for the conversion of the low-energy tail of the solar spectrum into a spectral range efficiently exploited by the solar cells, and that of the organic light emitting diodes, which requires efficient and low cost strategies to tune the device emission. However, for practical device application, the upconversion efficiency must be further improved, particularly in the solid state.

In organic multicomponent systems, the upconversion-induced fluorescence is the result of the following intermediate photophysical processes: (i) absorption of the light by a donor (D) molecule producing singlet excited states, (ii) intersystem crossing (ISC) switching the excitation from singlet to triplet states, (iii) energy transfer processes toward metastable triplet state of an acceptor molecule (A), and (iv) triplet-triplet annihilation giving rise to high-energy singlet excited states of the second moiety, from which the upconverted emission takes place. In these multicomponent systems, the donor must exhibit a large absorption cross section and a fast ISC rate, while the acceptor must have long-lived triplet states suitable for collecting the excitation from the donor[9] and for producing a singlet excited state via TTA. As

donors, hybrid materials such as organometallic compounds[3,10] are usually employed since the presence of heavy atoms strongly enhance their ISC rate.[11] The selection of the acceptor is more difficult, but conjugated molecules such as anthracene derivatives are reported to work well.[12–14] The bottlenecks limiting the overall process efficiency are the last two steps involving the ET and TTA processes, which can be sketched as follows:

$$D_3^* + A \rightarrow D + A_3^*,$$

$$A_3^* + A_3^* \rightarrow A + A_1^*,$$
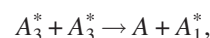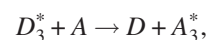
where the subscripts identify singlet (1) and triplet (3) states.

In this work, we focus our attention on the ET step to understand its role in the upconversion-induced delayed fluorescence of a model multicomponent system. To this end, we prepared solutions with different concentrations of acceptor as a quencher of red emission of the donor. Measurements of the ET efficiency on solutions at different temperatures allowed us to quantitatively evaluate the contribution of the molecular diffusion on the overall efficiency of the process.

II. EXPERIMENT

Pt(II)octaethylporphyrin (PtOEP) and 9,10 diphenylanthracene (DPA), both purchased from Aldrich and used as is, have been selected as the donor and acceptor moieties, respectively. Their molecular structures are reported in Fig. 1, with a sketch of the relevant energy levels. Mixed solutions have been prepared in 1,1,1-trichloroethane with a fixed concentration of PtOEP ($1.4 \times 10^{-4} M$), while the concentration of DPA has been varied from 10^{-5} to $5 \times 10^{-1} M$. Solutions have been carefully deoxygenated before the measurements by bubbling dry helium for 1 h. The oxygen singlets are, indeed, well known to be a formidable quencher of the triplet states of porphyrin complexes.[15,16] After the deoxygenation, the lifetime of the PtEOP emission in absence of the DPA increases from a few microseconds to 27 μs, which corresponds to a decay rate (K_0) of 3.7×10^4 Hz.
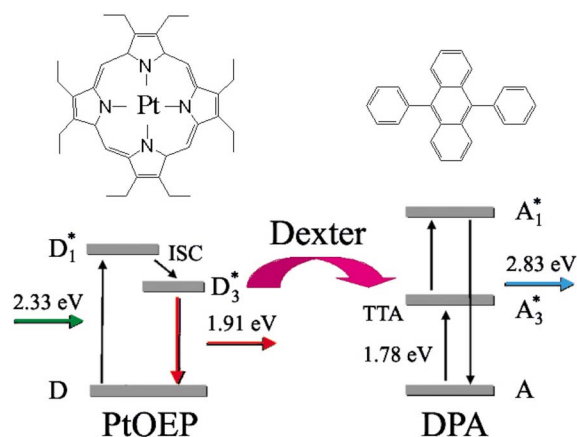
FIG. 1. (Color online) Molecular structures of Pt(II)octaethylporphyrin and 9,10 diphenylanthracene with an outline of the energy levels involved in the generation of the upconverted fluorescence (Ref. 2).

Steady-state photoluminescence (PL) measurements have been carried out by exciting the samples using a Coherent Verdi Nd:YAG laser at 2.33 eV (532 nm), with a power density of 325 mW/cm^2. The emission from the solutions has been detected by a nitrogen cooled charge coupled device (Spex 2000), which is coupled to a monochromator (Triax 190 from J-Horiba) with a bandpass of 0.5 nm. All of the measurements have been recorded with the solution inside a bath cryostat in helium atmosphere at 300 K [room temperature (RT)] and 77 K.

PL decay 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 ns.

III. RESULTS AND DISCUSSION

Resonant ET processes take place via interaction between transition dipole moments[17] (Förster ET) or via exchange interaction[18,19] (Dexter ET) provided that a good matching between relevant energy levels of donor and acceptor exist. However, in the first case, the transfer rate is also proportional to the product of the oscillator strength of the involved transitions, while in the second one, only a spatial overlap between the donor and acceptor wave functions is required. When weakly allowed or forbidden transitions are involved in the process, the Förster contribution is usually negligible because of their vanishing oscillator strength. From Fig. 1, it is evident that only between D_3^* and A_3^* triplet states does the resonance necessary to the transfer exist.[2] Therefore, for the ET between these states, only the exchange interaction should be considered. In such a case, the transfer rate (k_{ET}) between a donor-acceptor pair at a distance R can be written as[18]

$$k_{ET}(R) = \frac{2\pi}{\hbar}Z^2\int F_D(E)G_A(E)dE, \tag{1}$$

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 energy conservation requirement. Z is the exchange integral, an asymptotic form of which is

$$Z^2 = K^2\exp(-2R/L). \tag{2}$$

Here, K is a constant with the dimension of energy and L is the so-called effective Bohr radius, which measures the spatial extent of the donor and acceptor wave functions. In particular, Eq. (2) shows the dependence of the ET rate on the distance between donor and acceptor as a consequence of the molecular-wave-function exponential decay in the space.

In the case of Förster-type ET, the transfer rate is easily accessible with spectroscopic methods. On the contrary, 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-wave functions should be known for an exact evaluation of the parameter Z. Many models have been developed to simplify the original Dexter equations.[20–22] One of the simplest, the Perrin model,[22] follows from the observation that Eq. (2) implies an extremely fast ET rate at short distances ($R \ll L$), while the ET rate becomes negligible at $R > L$. Therefore, the Perrin model assumes the existence of a sort of active sphere of radius R_0 for each isolated donor-acceptor pair: 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

$$k_{ET}(R) = \begin{cases} 0 & \text{for } R > R_0 \\ \infty & \text{for } R < R_0 \end{cases}. \tag{3}$$

In Eq. (3), R_0 is defined as the Dexter radius, in the sense that at this distance, the ET rate is equal to the rate of the spontaneous decay of the donor in the absence of acceptors.

From an experimental point of view, the Dexter radius can be obtained from measurements of PL relative to the quantum yield of the donor, which is defined as the ratio between the donor PL intensity γ in the presence of a defined acceptor concentration (C_A) and that without it (γ_0). By using Eq. (3), this relative quantum yield can be written as[19]

$$\gamma/\gamma_0 = \exp(-C_A/C_0), \tag{4}$$

where C_0 is a constant related to the Dexter parameters, which is called critical transfer concentration (if concentration is expressed in units of cm^{-3}, $C_0 = 3/[4\pi/R_0^3]$). By using units of moles per liter for C_0, R_0 is equal to $7.346 C_0^{-1/3}$ (in Å).

Figure 2 shows representative PL spectra of PtEOP/DPA mixed solution as a function of the DPA content. At low DPA concentration, the typical red phosphorescence of the PtOEP at 1.91 eV (Refs. 16 and 23) is the main spectral feature, while the blue upconverted emission is only barely detectable at around 2.83 eV. As the DPA concentration increases,
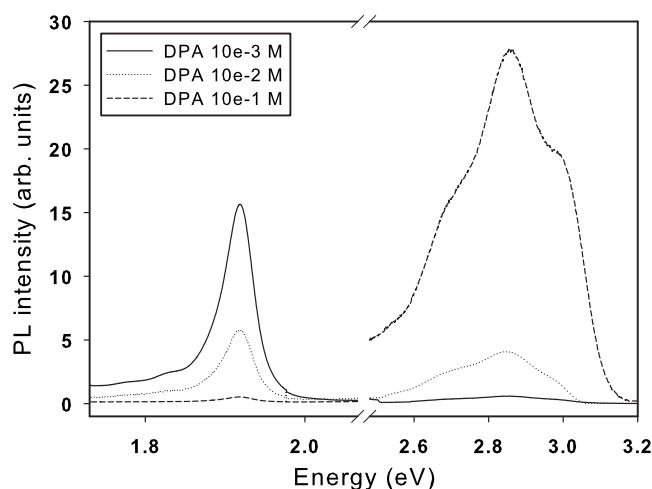
FIG. 2. PtOEP red phosphorescence and DPA blue fluorescence in 1,1,1-trichloroethane. Spectra have been collected at RT by exciting the solution at 2.33 eV. The PtEOP concentration was 1.4 $\times 10^{-4} M$, while those of DPA are reported in the inset.
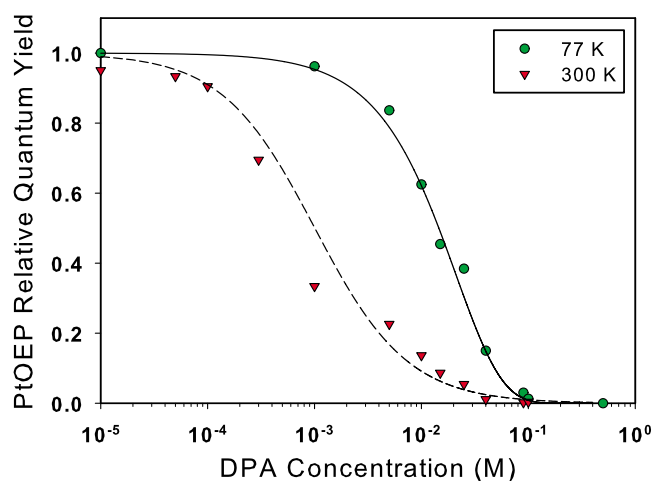

FIG. 3. (Color online) Relative PL quantum yields of the PtOEP PL as a function of the DPA concentration at 77 K (green circles) and 300 K (red triangle). The continuous line is the fit of the data collected at 77 K by considering a pure Dexter ET (Dexter radius of 26.5 Å). The dashed line has been calculated by adding the contribution of the molecular diffusion to the ET process.

the intensity of the peak at 1.91 eV is strongly reduced and a dramatic enhancement of the emission band at 2.83 eV is observed. This is the typical behavior of a donor-acceptor system, with the only peculiarity that the emission of the acceptor occurs at an energy higher than that of the emission of the donor because of the upconversion process. It should also be noted that the excitation power is not a relevant parameter in this study. It strongly affects the upconversion efficiency, which is a two particle process, but not the energy transfer process. In particular, the donor emission efficiency is expected to be completely power independent unless effects such as donor TTA occur, which shorten the lifetime of donor triplet excited states. With measurements as functions of the excitation power in the range between 0.01 and 1 W/cm^2, we checked that there is a linear dependence between donor PL intensity and excitation power density.

To verify whether the ET process can be fully described as a pure Dexter mechanism and to check if the Perrin approximation can be employed for these systems, we measured the relative PL efficiency of the PtEOP as a function of the DPA concentration. A first set of measurements have been performed on a frozen solution, where the molecule's diffusion is completely prevented. The obtained results are reported in Fig. 3 (circle). These data can be perfectly fitted by using Eq. (4) and are therefore fully consistent with an exchange driven transfer with a Dexter radius of 26.5 Å.

The same measurements carried out at room temperature (Fig. 3, triangle) show a different phenomenology. First of all, the ET process became much more efficient. For instance, while at 77 K concentrations of DPA larger than 2 $\times 10^{-2} M$ are necessary to obtain transfer efficiency in the range of 60%, at RT the same result is obtained with a 30 times smaller acceptor concentration. By considering that the Dexter ET, is temperature independent, as are all of the resonant ET processes, this finding suggests that, at RT, additional phenomena related to the molecular diffusion must be considered. In the frame of the model we are using, i.e., a Dexter ET within the Perrin approximation, the effect of the

diffusion can be easily taken into account. Indeed, the full process (Dexter ET plus diffusion) can be formally described as a donor quenching due to a direct collision with the acceptor moiety[24] by using the Dexter radius as the contact distance. In such a case, the ET rate in steady-state condition is

$$K_{ET} = 4\pi D R_0 C_A, \tag{5}$$

where D is the overall diffusion coefficient defined as the sum of the diffusion coefficient 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 according to Bondi[26] (8.7 and 4.5 Å for PtEOP and DPA, respectively). In such a way, the Einstein relation ($D = 3kT/6\pi\eta R_m$) gives diffusion coefficients of 6.3×10^{-6} cm^2/s for PtEOP and 1.2×10^{-5} cm^2/s for DPA. With these values, the overall diffusion coefficient is 1.8×10^{-5} cm^2/s. The relative PL quantum efficiency of PtEOP, taking into account the diffusion contribution, is then calculated as the ratio between the PtEOP decay rate with and without the donor $[\gamma/\gamma_0 = K_0/(K_0 + K_{ET})]$ and have been shown in Fig. 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.

The obtained results indicate that at RT molecular diffusion plays a key role in enhancing the ET efficiency in the investigated multicomponent systems for upconversion-induced fluorescence. Because of the involvement of long-living donor triplet states, the diffusion lengths are, indeed, orders of magnitudes larger than the Dexter radius. In the case of PtOEP/DPA solutions, despite a quite large Dexter radius of 26.5 Å arising from a perfect match between the donor-acceptor energy levels, the diffusion length of the PtEOP is 130 nm without DPA, and the overall diffusion

length goes up to 210 nm with a $10^{-3}M$ DPA concentration. Only for really large acceptor concentrations ($\geq 10^{-1}M$) does the migration become negligible and only the direct donor-acceptor ET become 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. The search for donor-acceptor pairs with a larger Dexter radius appears less effective in this case since the room for improvements is limited.

IV. CONCLUSIONS

In conclusion, the triplet-triplet exciton ET from PtEOP and DPA, a case of organic system for upconversion-induced delayed fluorescence, has been studied as a function of the temperature. At low T, the results can be well described as a pure Dexter ET by using the Perrin approximation, and a Dexter radius of 26.5 Å has been found. On the contrary, at RT, molecular diffusion is the main phenomenon controlling the ET efficiency, which becomes very high also for low acceptor concentrations as a consequence of overall molecular diffusion lengths. If we consider that the molecular migration is expected to affect not only the donor-acceptor ET but also the acceptor-acceptor TTA, our finding clearly explains why high upconversion efficiencies are usually reported for systems in solution,[3,6] while the performance of the corresponding films are much lower.[2,7] The study of the influence of migration on the TTA is in progress.

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*angelo.monguzzi@mater.unimib.it

[1] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, Berlin, 2002), p. 074902.

[2] F. Laquai, G. Wenger, C. Im, A. Büsing, and S. Heun, J. Chem. Phys. **123**, 074902 (2005).

[3] R. R. Islangulov, D. V. Kozlov, and F. N. Castellano, Chem. Commun. (Cambridge) **30**, 3776 (2005).

[4] S. Baluschev, P. E. Keivanidis, G. Wegner, J. Jacob, A. C. Grimsdale, K. Müllen, T. Mitieva, A. Yasuda, and G. Nelles, Appl. Phys. Lett. **86**, 061904 (2005).

[5] S. Baluschev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, and G. Wegner, Phys. Rev. Lett. **97**, 143903 (2006).

[6] S. Baluschev, V. Yakutkin, G. Wegner, B. Minch, T. Mitieva, G. Nelles, and A. Yasuda, J. Appl. Phys. **101**, 023101 (2007).

[7] S. Baluschev, V. Yakutkin, G. Wegner, B. Minch, T. Mitieva, G. Nelles, A. Yasuda, S. Chernov, S. Aleschenkov, and A. Cheprakov, Appl. Phys. Lett. **90**, 181103 (2007).

[8] T. Trupke, M. A. Green, and P. Würfel, J. Appl. Phys. **92**, 4117 (2002).

[9] R. Bensasson and E. J. Land, Trans. Faraday Soc. **67**, 1904 (1971).

[10] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, J. Appl. Phys. **90**, 5048 (2001).

[11] D. Beljonne, Z. Shuai, G. Pourtois, and J. L. Bredas, J. Phys. Chem. A **105**, 3899 (2001).

[12] J. Jortner, S. Choi, J. L. Katz, and S. A. Rice, Phys. Rev. Lett. **11**, 323 (1963).

[13] J. Partee, E. L. Frankevich, B. Uhlhorn, J. Shinar, Y. Ding, and T. J. Barton, Phys. Rev. Lett. **82**, 3673 (1999).

[14] T. Azumi and S. P. McGlynn, J. Chem. Phys. **39**, 1186 (1963).

[15] R. Bonnett, A. A. Charalambides, E. J. Land, R. S. Sinclair, D. Tait, and T. G. Truscott, J. Chem. Soc., Faraday Trans. 1 **76**, 852 (1980).

[16] A. K. Bansal, W. Holzer, A. Penzkofer, and T. Tsuboi, Chem. Phys. **330**, 118 (2006).

[17] T. Förster, Ann. Phys. (Paris) **437**, 55 (1948).

[18] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[19] M. Inokuti and F. Hirayama, J. Chem. Phys. **43**, 1978 (1965).

[20] O. Stern and M. Volmer, Phys. Z. **20**, 183 (1919).

[21] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **38**, 1187 (1963).

[22] F. Perrin, Compt. Rend. **178**, 1978 (1924).

[23] P. A. Lane, L. C. Palilis, D. F. O'Brien, C. Giebeler, A. J. Cadby, D. G. Lidzey, A. J. Campbell, W. Blau, and D. D. C. Bradley, Phys. Rev. B **63**, 235206 (2001).

[24] U. Gosele, M. Hauser, U. K. A. Klein, and R. Frey, Chem. Phys. Lett. **34**, 519 (1975).

[25] R. Cohen and J. Mercer, *DNAPL Site Evaluation* (CRC, Boca Raton, FL, 1993).

[26] A. Bondi, J. Phys. Chem. **68**, 441 (1964).