Excitation Energy Transfer and Trapping in Dye-Loaded Solid Particles

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The photophysics of several systems composed of a single dye or pairs of dyes attached to solid particles has been studied in the dry solid state at high dye concentrations taking into account light scattering and inner filter effects. Interaction among dye molecules and singlet-singlet energy transfer are relevant in these conditions, as has been demonstrated for pairs of dyes with suitable spectral overlap. For single dyes, after correction for radiative energy transfer, fluorescence quenching is observed as the surface concentration increases. This effect is explained by two different trapping models. Irrespective of the nature of the traps, concentration quenching may be of static (trap absorption) and dynamic (energy transfer) nature. The unraveling of energy trapping mechanisms is a key to the development of efficient photoactive solid materials.

Key words: solid particles; energy trapping; dye aggregation; quenching radius

Introduction

The photophysical and photochemical study of dyes in heterogeneous media is relevant to different fields. The development of photosensitizers,[1] photocatalysts,[2] nanosized reactors,[3] and visible light–driven solar cells,[4] among other real or foreseeable applications, either require or are advantageously driven in constrained environments. In general, light collection efficiency is a key for the development of useful photoactive materials. Accordingly, high dye concentrations are needed to afford substantial absorption of incident light. Moreover, energy transfer among different dyes may be a suitable strategy to broaden the excitation spectrum and/or to canalize the excitation energy to accomplish the desired objective. High local concentrations, however, give rise to deactivation processes either by the formation of dye aggregates or enhanced energy trapping. In general, a compromise has to be found between the large dye concentrations needed for substantial light absorption and excited-state deactivation due to dye-to-dye interactions at such concentrations.

Frequently, the cited applications are carried out in systems composed of particles or particle aggregates of micrometer size, adding complexity to the study as compared with experiments carried out in solution or nanoparticle suspensions. Several factors have to be taken into account in this case: 1) interactions between dyes and the surface; 2) reabsorption and reemission processes present at high overall concentrations; 3) multiple light scattering; 4) formation of ground-state aggregates; and 5) other interactions leading to excited state deactivation. The quantitative analysis of these effects is rather challenging and has attracted the attention of photochemists and spectroscopists for a long time. Different methods have been developed and applied to inorganic phosphors, colored solids, and dyes adsorbed on solid substrates.[5,6] The calculation of inner filter effects has been also addressed[7] with the help of current theories of light scattering.[8;9]

Energy transfer processes have been less studied in these conditions. During the past years, several methods and models have been developed in our laboratory to account for reabsorption and reemission of fluorescence,[10–13] singlet-singlet nonradiative energy transfer (NRET),[14,15] and calculation of absolute fluorescence quantum yields.[16] Systems composed of single dyes or pairs of dyes with substantial spectral overlap (donor-acceptor systems) were studied. Dyes were physically or chemically attached to cellulose microparticles and other supports. Solids were studied by reflectance and fluorescence spectroscopy in the form of optically thick (negligible transmission) and thin samples. In particular, optically thick layers were found convenient for the determination of absolute fluorescence quantum yields, as the determination of the fraction of absorbed photons can

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be performed accurately in this case. Moreover, in this way the interplay between radiative and NRET processes can be conveniently studied. Most systems were composed of physisorbed dyes, allowing a systematic study of the effect of concentration on the photophysical properties. Details of experimental and theoretical aspects are given in the corresponding references.

Photophysics in Constrained Environments

Rigidization of dyes by attachment to solid surfaces may lead to enhanced fluorescence quantum yields,[17] while intermolecular interactions open currently new deactivation channels due to the proximity among dye molecules, particularly when they are distributed at random. Absorption and fluorescence spectra are affected on attachment as well. Spectral shifts arise from the interaction of the dye with the solid surface and depend strongly on the particular microenvironment. Surface heterogeneity is responsible for spectral broadening. Dye aggregation was recognized as one of the most important factors impairing photoactivity.[13] Self-aggregation can be controlled by the simultaneous attachment of a second dye, as it has been demonstrated for methylene blue (MB) coadsorbed with pheophorbide-a (Pheo)[14] or in the presence of chemically attached rhodamine 101 (R101).[15] In both cases, MB aggregation is reduced in comparison with the same dye adsorbed separately on the same support. In the first case, the decrease in micropolarity caused by the presence of Pheo, which has a hydrophobic character, enhances repulsion among positively charged MB molecules, thus reducing aggregation. In the later case, since R101 is polar and positively charged, the reasons for the inhibition of MB aggregation are not completely clear. In general, changes in medium polarity can be used to control dye aggregation.

Light Scattering and Reabsorption and Reemission Processes

Light scattering phenomena common to micrometer-size particulate solids complicate the evaluation of photophysical properties enormously, particularly when reabsorption and reemission processes take place. Reabsorption affects fluorescence spectra and reduces fluorescence quantum yields. The last property can be useful for some applications, such as searching for solid photosensitizers, because

excitation energy lost by emission is injected back into the system, thus repopulating the excited state. Though current solids are nonideal scatterers, our experience shows that a very simple approach based on the Kubelka-Munk theory of light scattering leads to sound results.[10,11]

Intermolecular Interactions

Aside from ground-state molecular aggregation, interactions between excited and ground-state molecules have a strong influence on spectroscopic and photophysical properties. Depending on their nature, interactions may affect the excited state relaxation and lead to deactivation. The occurrence of concentration-dependent Stokes shifts, resulting in a displacement to higher wavelengths of the fluorescence maximum as the dye concentration increases, once spectra are corrected for inner filter effects, while the absorption spectrum remains unchanged, is a common observation in these systems.[10–12,14,15] The effect is noticed even at average intermolecular distances in excess of 10 nm. This behavior may be ascribed to a gradual perturbation of the excited-state microenvironment with the increase of the dye concentration due to the interaction of the excited state with ground-state neighbor molecules.[18]

In two-dye systems, nonradiative (Förster) energy transfer leads to donor excited-state deactivation followed by acceptor excitation[14,15] rather than to energy trapping by molecular aggregates or statistical traps. It was demonstrated that very high energy transfer efficiencies can be achieved without any particular molecular order. To make evident Förster resonance energy transfer, full account of reabsorption and reemission has to be made. A general overview of energy flow in these systems is given in SCHEME 1 for a two-dye system. In the scheme, the various fractions of the incoming energy flowing out from each subsystem, A* or B*, or node, represented by a dot in the diagram, are defined for an optically thick sample. Donor dyes act as antennae for the collection of excitation light, thus broadening the excitation spectrum and improving light collection efficiency for polychromatic irradiation.

Quantities in SCHEME 1 are as follows: I_0 is the incident photon flow; R the total reflectance; α_{0i} the fraction of absorbed photons exciting species i; Φ_i the fluorescence quantum yield of species i in the absence of NRET; E_{ij} the efficiency of NRET from i to j; P_{ij} the fraction of photons emitted by i and reabsorbed by j; and Q_i the fraction of radiation emitted by i that escapes out of the system. All fractions can be calculated
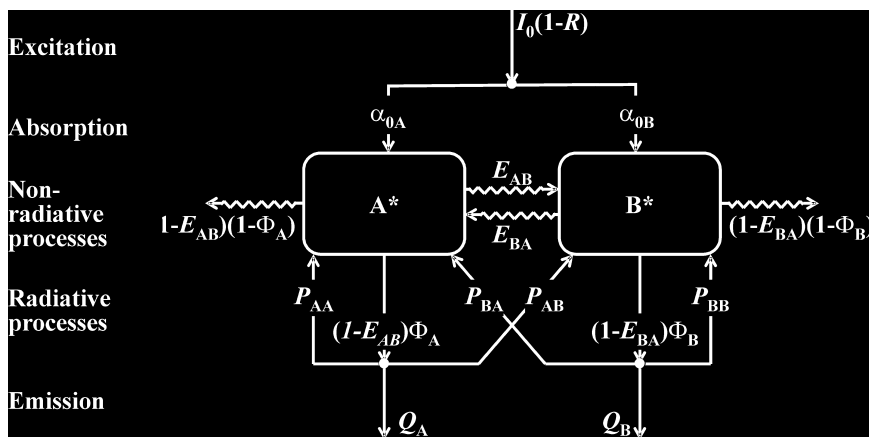
SCHEME 1.

from experimental data, mainly fluorescence and reflectance spectra, without the need of adjustable parameters.[14] SCHEME 1 is quite general as it allows for both forward and backward energy transfer. A simpler description, adapted to the case under study will be given later.

Energy Trapping Mechanisms

In general, single-dye fluorescence quantum yields, once corrected for dye aggregation and inner filter effects, decrease steadily with dye concentration.[12,14] Concentration quenching may take place even when no spectroscopic evidence on aggregation is found.[12]

The trapping effect of dimeric species has been demonstrated for MB adsorbed on cellulose microparticles (average size $20\,\mu$m), after calculation of the dimerization equilibrium constant, $K = 225$ nm^2, from spectroscopic data (units reflect the fact that surface concentrations are expressed in molecules per nm^2; in more common units, $K = 1.36 \times 10^{10}$ dm^2 mol^{-1}). Aggregates, particularly H-type dimers, are known to behave as energy traps due to the enhancement of radiationless deactivation.

On the other hand, rhodamine 6G (R6G) adsorbed on the same support was studied. Results showed that fluorescence quantum yields—corrected for inner filter effects—decrease on increasing dye concentration, even when no evidence on ground-state aggregation is found. Average lifetimes decrease also, but more slowly than quantum yields. As dye molecules have restricted motion on the support surface during the excited state lifetime, diffusional quenching can be excluded.

A trapping mechanism similar to that considered for donor–acceptor systems is proposed. Traps formed

by special configurations of dye pairs are assumed to act as acceptors of the excitation energy conveyed both radiatively and nonradiatively from the free dye pool. Energy transfer to traps should be responsible for the decrease in average lifetimes, while direct absorption and reabsorption should be responsible for static quenching.

Since the nature of the traps is unknown in the case of R6G, two models are developed involving (a) dimers or (b) statistical traps. In both cases, trapping centers are assumed to be nonfluorescent. In model (a), the dimerization constant is used as a fitting parameter. For model (b), a Poisson distribution of dye molecules is assumed and, as in Perrin's model,[19] a quenching radius is obtained by fitting. In both cases Förster theory[18,20] is applied, considering a two-dimensional random distribution of dye monomers and traps:

$$\frac{\Phi}{\Phi_{\mathrm{M}}} = 1 - E = \int_0^{\infty} \exp\left(-x - \Gamma(2/3)\,(\delta/\delta_0)\,x^{1/3}\right) \cdot dx \tag{1}$$

$$I(t) = I(0) \exp\left(-x - \Gamma(2/3)\,(\delta/\delta_0)\,x^{1/3}\right) \tag{2}$$

where Φ and Φ_{M} are the monomer fluorescence quantum yields in the presence of traps and for the free monomer, respectively; E the trapping efficiency; $x = t/\tau$, where τ is the monomer lifetime in the absence of traps; Γ the gamma function; δ the trap surface concentration (see below); and $\delta_0 = 1/\pi R_0^2$, where R_0 is the Förster critical distance for energy transfer. Calculation of E is afforded using a simplified flow diagram as given in SCHEME 2.

Symbols in this scheme are equivalent to those given in SCHEME 1 and are to be interpreted as follows. From the incoming photon flow, I_0 (photons per second at the excitation wavelength), a fraction R, the reflectance
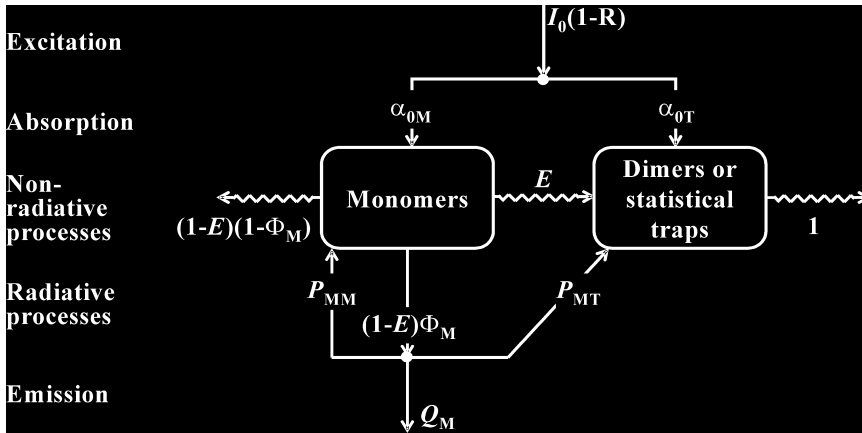
SCHEME 2.

of the system, is scattered back. Thus, $I_0(1 - R)\alpha_{0M}$ is the photon flow absorbed by the monomeric dye, M, α_{0M} being the fraction of absorbed light exciting the monomer. From this quantity, a fraction E is nonradiatively transferred to traps. The quantity $(1 - E)\Phi_M$ is an effective monomer emission quantum yield, Φ_M being the value in the absence of trapping. Accordingly, $(1 - E)(1 - \Phi_M)$ is the fraction of excited monomers decaying by any other mechanism, as internal conversion or intersystem crossing. Finally, monomer emission is partially reabsorbed by the monomer itself with a probability P_{MM} and by traps with a probability P_{MT}. The quantity $Q_M = 1 - P_{MM} - P_{MT}$ is thus the fraction of the emission which escapes out of the system and leads to the observed fluorescence quantum yield, Φ_{obs}, obtained experimentally. It should be noticed that the sum of the fractions emerging from each subsystem or node is 1. As a special case, traps decay quantitatively to their ground state by a single deactivation pathway and, therefore, the decaying fraction is 1.

A simple calculation based on these quantities yields for the NRET efficiency:

$$E = 1 - \frac{1}{\Phi_M} \frac{\Phi_{obs}}{\Phi_{obs}P_{MM} + \alpha_{0M}Q_M} \qquad (3)$$

EQUATION (3) is a special case of Eq. (A7) in Reference 14. All quantities in this equation other than E are accessed either experimentally, as Φ_{obs} and Φ_M, or calculated on grounds of remission function[8,9] and fluorescence spectra.

The two models differ in the way in which δ is calculated. If equilibrium between monomers and dimers is considered EQUATION (4) is used, whereas EQUATION (5), which assumes a Poisson distribution of
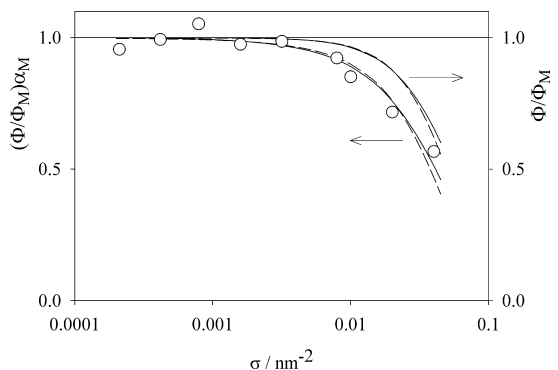

FIGURE 1. $(\Phi/\Phi_M)\alpha_M$ for R6G on cellulose as a function of dye surface concentration σ (expressed in molecules per nm^2). Open circles, experimental results; solid lines, dimerization model; dashed lines, statistical trap model (see text). $(\Phi/\Phi_M)\alpha_M$ displays total quenching, whereas Φ/Φ_M displays dynamic quenching according to EQUATION (1). The difference between both quantities shows the relative importance of static quenching.

dyes, is applied for the quenching radius model.

$$K = \frac{\delta}{(\sigma - 2\delta)^2} \qquad (4)$$

$$\frac{2\delta}{\sigma} = 1 - \exp\left(-\pi r_Q^2 \sigma\right) \qquad (5)$$

where r_Q is the quenching radius. In both cases, σ represents the surface dye concentration assuming a specific area of $60\,\mathrm{m^2\,g^{-1}}$.[15]

Results given in FIGURE 1 show that both models account quantitatively for the observed facts. Calculation relies on the assumption that the spectrum of dimers or statistical traps is the same as the spectrum of the free monomer. Thus, neglecting a small absorbance of the support, the fraction of absorbed radiation exciting
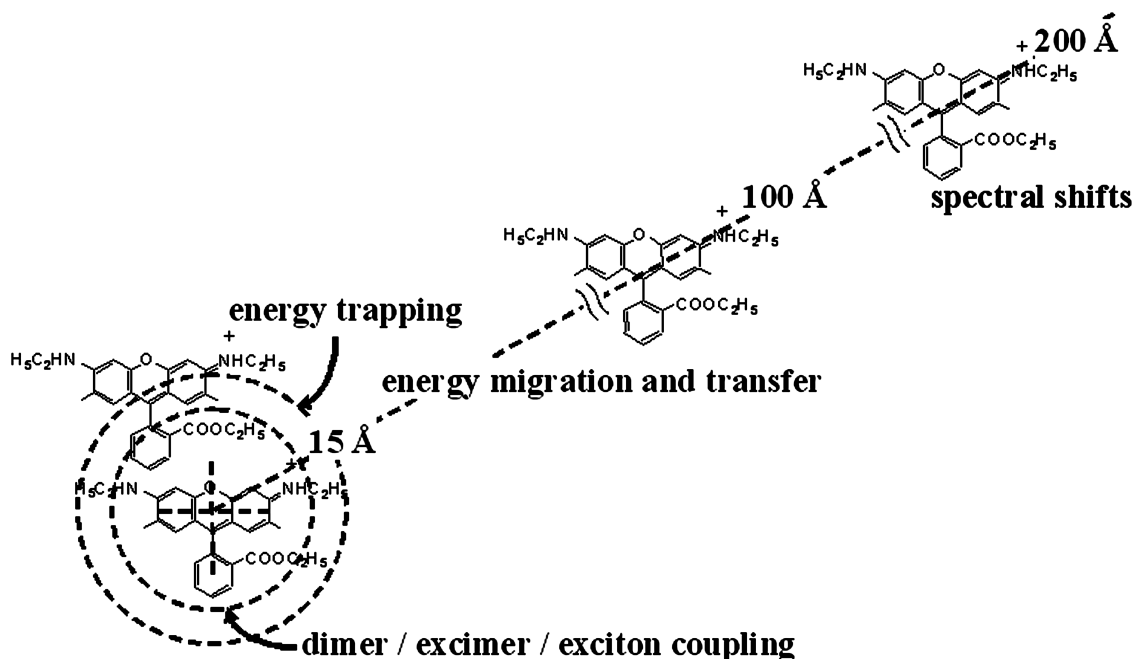
SCHEME 3.

the free monomer, α_M, does not depend on wavelength. Rearrangement of EQUATION (3) leads to:

$$\frac{\Phi}{\Phi_M} \cdot \alpha_M = (1 - E)\alpha_M = \frac{1}{\Phi_M} \frac{\Phi_{obs}}{\Phi_{obs}P_{MM}/\alpha_M + Q_M} \tag{6}$$

and, in these conditions, according to Reference 14 the right side of EQUATION (6) is independent on α_M. Results shown in FIGURE 1 were calculated using this equation from experimental Φ_{obs} values and raw reflectance and fluorescence data. The free monomer quantum yield, Φ_M, is the limiting value of Φ_{obs} as $\sigma \to 0$. Theoretical curves are based on EQUATION (1); K or r_Q, depending on the applied model, were obtained from best fittings. The assumption of identical spectra for monomers and traps allows calculation of α_M as $1 - (2\delta/\sigma)$ since the fraction of radiation exciting monomers is equal to the actual fraction of free monomers in the sample. This assumption allowed also the estimation of the critical Förster radius, R_0.

Application of model (a) shows that nearly 20% of the dye molecules should be in the dimeric state at the highest dye concentration. Though this aggregation degree is quite high, spectral changes might be obscured if the monomer and the dimer spectrum do not differ noticeably. If model (b) is applied, a quenching radius of nearly 1.5 nm is found, which is

in the order of molecular dimensions. This means that trapping centers are consistent with two closely lying dye monomers. These results are in accordance with the low aggregation tendency of R6G found in different media. Fluorescence decays (not shown) may be fitted through EQUATION (2) with a concentration-independent decay time, $\tau = 3.2$ ns. Decay analysis is consistent with both kinds of trapping and with the steady state analysis. While the exact nature of traps cannot be ascertained in the case of R6G, it is clear that concentration quenching may be both static (through trap absorption) and dynamic (by energy transfer from free monomers). The study of more concentrated samples, as would be needed to distinguish between the two models, was not possible due to instrumental limitations imposed by the low reflectance of samples. It may be observed from FIGURE 1 that, in both cases, the prevailing quenching mechanism at high dye concentrations is NRET, as already observed for donor-acceptor systems.

In summary, short-range interactions are responsible for the formation of traps, while long-range interactions lead to resonance energy transfer. At even longer distances, dye-to-dye interactions lead to concentration-dependent Stokes shifts. A general picture of the effect of molecular interactions on the photophysics of single-dye systems is shown in SCHEME 3.

Concluding Remarks

The photophysics of dyes attached to micrometer size particles may be described through a simple energy flow scheme considering radiative and nonradiative energy transfer processes. The involved quantities may be calculated from experimental data through model equations without the need of adjustable parameters. Based on these results, Förster theory allows the investigation of excitation energy transfer and trapping and the retrieval of quenching parameters. The same processes are common to donor–acceptor and single-dye systems, and a general mechanism leads to the explanation of energy trapping. In the first case, excitation energy trapped by acceptor molecules may be used to improve light collection efficiency in a broad region of the spectrum. In the absence of acceptors, excitation energy is lost by trapping as the dye concentration increases.

Acknowledgments

Conflict of Interest

The authors declare no conflicts of interest.

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