Photochemical Mechanisms Producing Large Fluorescence Stokes Shifts

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Various adiabatic photochemical mechanisms are compared which lead to a product in the excited state and therefore often to strongly red-shifted fluorescence. The applicational aspects of this strong red shift are outlined with respect to scintillators, solar collectors, and biological fluorescence probes. As an example, the unusual fluorescence properties of a pyrazolocoumarin derivative are described.

INTRODUCTION

In the application of fluorescence dyes as labels or probes in biology or medicine, as doping dyes in fluorescent solar concentrators, and as laser or scintillator dyes, some of the inherent problems could be solved if the property of a large Stokes shift could be introduced into a dye while keeping the fluorescence quantum yield at a high level.

The Stokes shift $\Delta\nu_{St}$, normally measured as the energy difference between absorption and emission maxima, determines how strongly the secondary inner filter effect, the reabsorption of fluorescence photons by the dye, will affect the fluorescence output and its spectrum. If reabsorption is important, for small $\Delta\nu_{St}$, a relatively large part of the emitted photons is reabsorbed for sufficiently high dye concentrations or long pathlengths, and this acts like a scattering process, reducing the efficiency. This problem becomes especially important for light channeling devices such as fluorescence solar concentrators and position-sensitive liquid scintillator-filled

capillary arrays or for similar possible future applications, e.g., in optical computers.

A further benefit of large Stokes shifts $\Delta\nu_{St}$ is that the emitted photons are usually spectrally well separated from scattered excitation light and from impurity fluorescence, which is often present in biological or clinical samples because the latter usually exhibit small Stokes shift properties. In this way, sensitivities of, e.g., fluorescence immunoassays could be drastically increased.

In this paper, we investigate and compare various mechanisms able to produce large Stokes shifts. For promising applicational purposes, other factors have to be fulfilled simultaneously, such as a high fluorescence quantum yield and, in some cases, a very good photostability. In the first step, we disregard these other requirements and concentrate on the Stokes shift, while knowing that for specific cases the combination of two or three of these properties has already been achieved (see notes a and b in the legend to Fig. 1b).
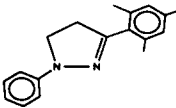
AN OVERVIEW OF PHOTOPHYSICAL AND PHOTOCHEMICAL MECHANISMS LEADING TO LARGE STOKES SHIFTS

Several mechanisms which can lead to red-shifted fluorescence are summarized in Fig. 1. They fall into

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a) PHOTOPHYSICAL

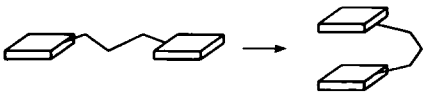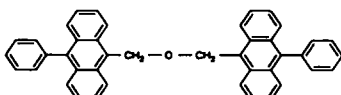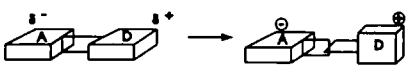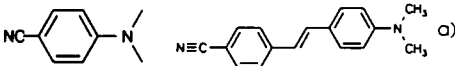| Mechanism	Description	Examples	Ref
"forbidden absorption"	S1 absorption, band very weak		(18)
medium relaxation	polar solvent relaxation around a large excited dipole	ICT or TICT molecules in polar solvents	(19)

b) PHOTOCHEMICAL
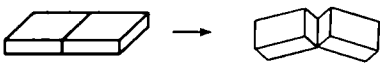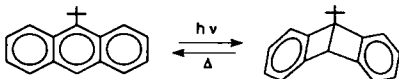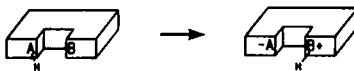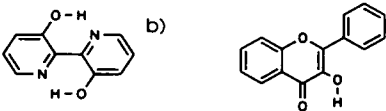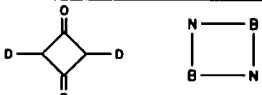
Mechanism	Sketch	Examples	Ref
EXCIMER EXCIPLEX			(13,20)
TICT		a)	(4)
BUTTERFLY			(12-15)
ESIPT		b)	(10-11)
KITE			(16,17)

Fig. 1. Photophysical (a) and photochemical (b) mechanisms able to produce large Stokes shifts. Notes to b: a) for donor–acceptor stilbenes [21] and a bipcrylcnyl derivative [22], linkage of a large Stokes shift and a high fluorescence quantum yield has been achieved; b) for this molecule, BP(OH)₂, linkage of a large Stokes shift, long-term photostability, and a good fluorescence quantum yield has been achieved [23,24].

two parts, namely, mechanisms involving only photophysical properties (forbidden absorption or polar solvent relaxation) and mechanisms necessitating an adiabatic photochemical reaction leading to an emissive product state [1–4].

Some mechanisms, such as the excimer/exciplex [5,6], the twisted intramolecular charge transfer (TICT) [7], and the excited-state intramolecular proton transfer (ESIPT) mechanisms [8], have been well-known for decades. The processes leading to the emissive products with red-shifted fluorescence have been well characterized. For the excimer/exciplex case, it is the formation of a complex of a ground-state with an excited-state molecule of the same or of a different kind and usually

involves diffusion processes or large intramolecular rearrangements (for the so-called intramolecular excimers, where two chromophores are chemically linked in a single molecule). Such diffusive motion can be used to probe the microviscous properties of the surrounding medium [4]. The formation of TICT states [3,7,9] involves mutual twisting of two chromophores directly connected by a single bond and simultaneous charge transfer from the donor to the acceptor chromophore. ESIPT [8,10,11] involves tautomerization, i.e., transfer of a proton from one to another basic site in the same molecule (or molecular cluster), which usually occurs through proton tunneling.

The other two photochemical mechanisms, Butter-

fly and Kite, are less well investigated. The name Butterfly mimics the reactive motion which involves the folding of an aromatic molecule. A well-known example is 9-t-butylanthracene, which, on excitation, folds about the 9,10-axis to arrive to a photochemical funnel leading to the ground state. Most of the folded ground-state molecules react back to the starting material; a small percentage, however, folds further to a stable Dewar isomer, which can be isolated and characterized [12]. The reaction tendency in the 10-cyano-substituted derivative is even stronger and can be used to probe free volume effects in glassy polymers [13]. If, on the other hand, the photochemical funnel corresponds to a less pronounced approach of S_1 and S_0 hypersurfaces, red-shifted emission from the adiabatically formed folded excited state should become possible. Such an out-of-plane deformation could be the source of several still unexplained cases of strongly red-shifted fluorescence [14–16] (See Fig. 1). A further possibility is in-plane deformations within the chromophore, named the Kite mechanism here. This has been studied theoretically for cyclobutadiene and its donor–acceptor derivatives [17]. In-plane deformation from a quadratic to a nonsymmetric but planar conformation can lead to large changes in the energy difference between the ground and the excited state. The Kite mechanism is the generalization of this concept (see the examples given below).

Fig. 2. Absorption and fluorescence spectra in solvents of different polarities at room temperature and at 77 K in ethanol for (a) NMC and (b) NPC.

PYRAZOLOCOUMARINS: A PROBABLE COMBINATION OF SEVERAL MECHANISMS

NMC and NPC are pyrazolocoumarin derivatives which exhibit anomalous emission behavior in terms of Stokes shift and of radiative rate constants [25].
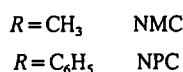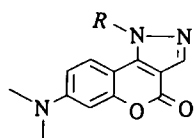

$R = CH_3$ NMC

$R = C_6H_5$ NPC

Figure 2 shows absorption and emission spectra in differently polar solvents and in a rigid glassy matrix. The Stokes shift is much larger for NPC than for NMC, and for both compounds, it increases with solvent polarity and can be reduced in a rigid matrix. We therefore have a CT mechanism (polar solvent relaxation) connected with a large-amplitude motion, i.e., probably one of the photochemical mechanisms discussed above. With respect to the discussions in the literature [14,26], one could argue that a TICT mechanism is involved, with the dimethylamino group as the donor part. But the strong difference between NMC and NPC and the fact that the
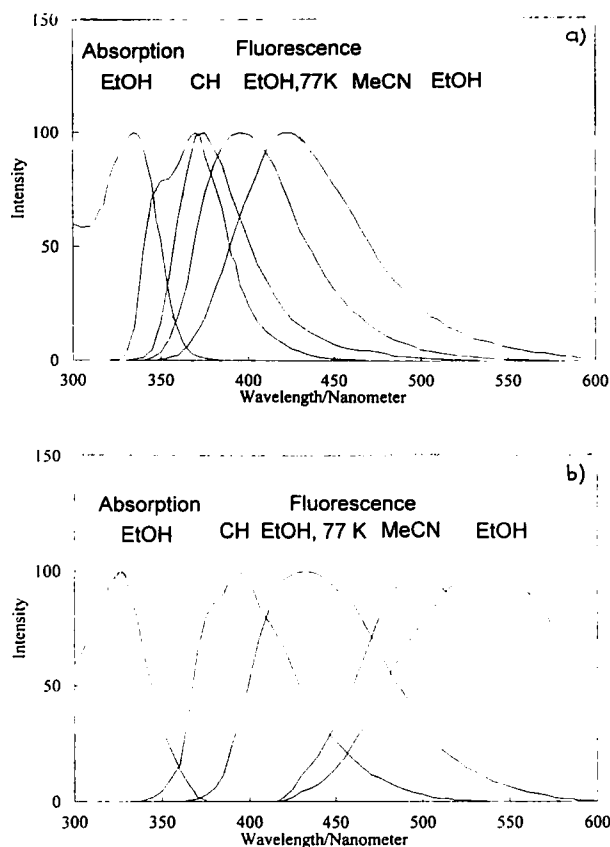
Stokes shift is smaller for NMC, although the acceptor character of the chromophore is expected to be larger, indicate that the more probable reaction site is at the amino nitrogen of the pyrazolo ring. Here, the TICT mechanism is improbable for phenyl as a donor in NPC, and impossible for NMC, such that we are led to conclude a probable Kite or Butterfly mechanism within the pyrazolo ring as depicted in Fig. 3. The photoreaction may even involve a combination of both mechanisms, as discussed in a photochemical study on indazole photoisomerization [27].

REABSORPTION IN LIGHT GUIDES: SOLAR CONCENTRATORS AND SCINTILLATION COUNTERS

Fluorescent solar concentrators and liquid scintillator-filled capillaries used in position-sensitive scintillation counters are both based on the principle of absorbing
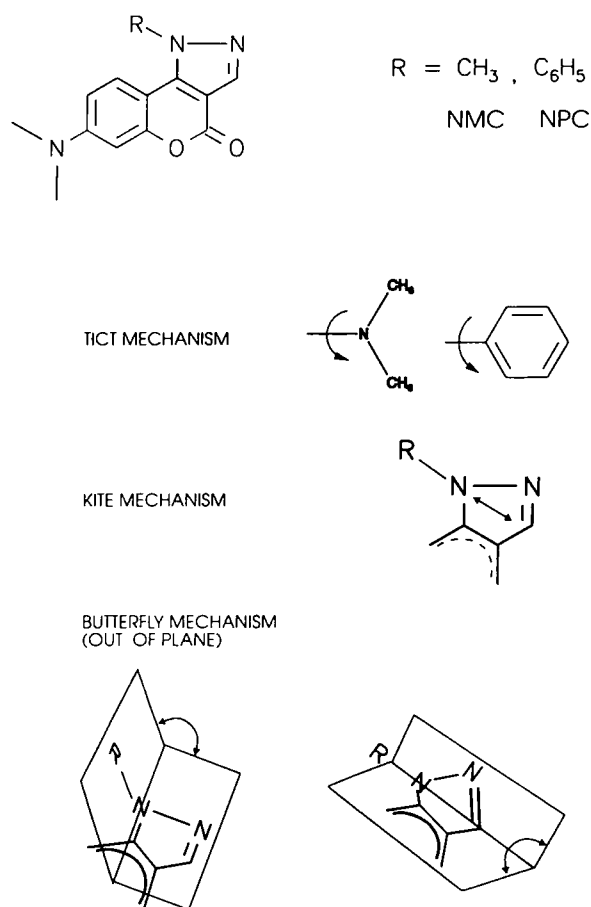
R = CH₃ , C₆H₅

NMC   NPC

TICT MECHANISM

KITE MECHANISM

BUTTERFLY MECHANISM
(OUT OF PLANE)

Fig. 3. Schematic illustration of a possible Kite and Butterfly distortion for the example of the pyrazolo ring in NMC and NPC.
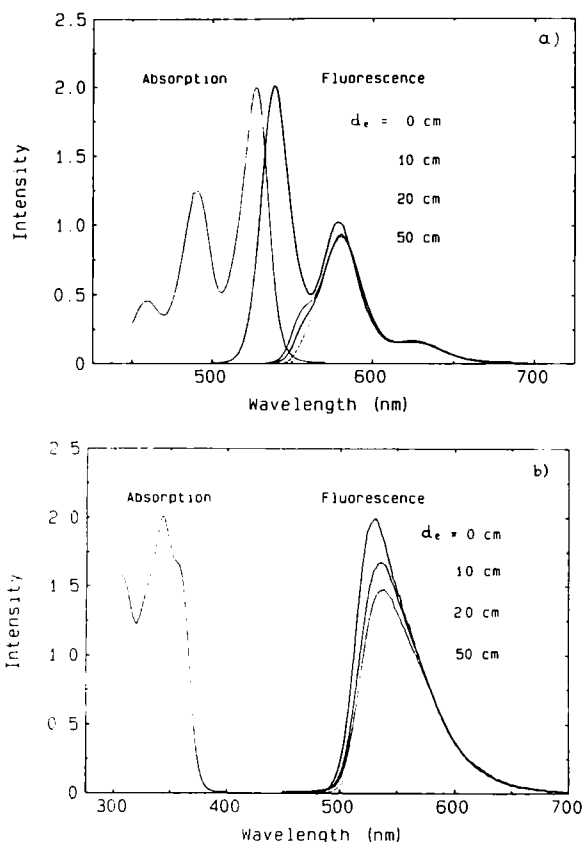
Fig. 4. Fluorescence spectra of (a) B-241 and (b) 3HF dissolved in toluene viewed in a capillary setup at various distances d_e (cm) from the excitation source. The spectra have been normalized in the red tail, including the spectrum taken for optically thin conditions (dilute solution), $d_e = 0$ cm.

a photon (energy v_a, or high-energy particle) within a relatively small distance d_a, transforming it into a different spectral region (emission energy v_e) and transporting this secondary photon over large distances, d_e $> >$ d_a. Because of this large difference in distances, reabsorption can constitute a problem. Figure 4 shows capillary measurements of the fluorescence loss through reabsorption as a function of the distance d_e. The pery-limid-based dye B-241, discussed for fluorescent solar concentrators due to its extremely high photostability and its fluorescence quantum yield of unity [28], has been compared to 3HF, an ESIPT compound with a large Stokes shift, and to PMP, one of the most widespread scintillator dyes [18].

For both B-241 and 3HF, the fluorescence intensity decreases with capillary length due to the following effects: (i) reabsorption by the dye itself, (ii) reabsorption by trace impurities, (iii) scattering losses (Rayleigh,

Tyndall etc.) and (iv) reflection losses due to imperfections of the totally reflecting surfaces. To demonstrate the influence of reabsorption alone, we have normalized the spectra in the red tail. Figure 4 shows that only the blue part of the spectrum is affected by reabsorption but that its extent is considerably stronger for B-241 than for 3HF. For the conditions we used (optical density, about 2 for 1 cm), reabsorption in the blue is nearly complete at a 10-cm capillary length.

ACKNOWLEDGMENTS

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