

Charge Transfer in Molecular Functional Materials: A Spectroscopist's View

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Molecular functional materials are the Holy Grail of modern materials science, with promising applications in the fields of molecular electronics and photonics. Molecular materials (mm) have already found an appealing and rewarding application in organic-light emitting devices, first devised in the 1980's, they are present in the market nowadays. From a different perspective, fundamental biological processes often involve supramolecular arrangements of functional molecules, as nicely demonstrated by the light harvesting complexes central in photosynthetic processes. A thorough understanding of these processes will unveil some fundamental mechanisms of life, offering at the same time important clues for the optimal engineering of molecular devices. Molecular materials of interest for applications, molecular functional or intelligent materials, are materials that respond in a qualitatively different way to different inputs: *non-linearity* is the qualifying property for *functional (intelligent) behaviour*.

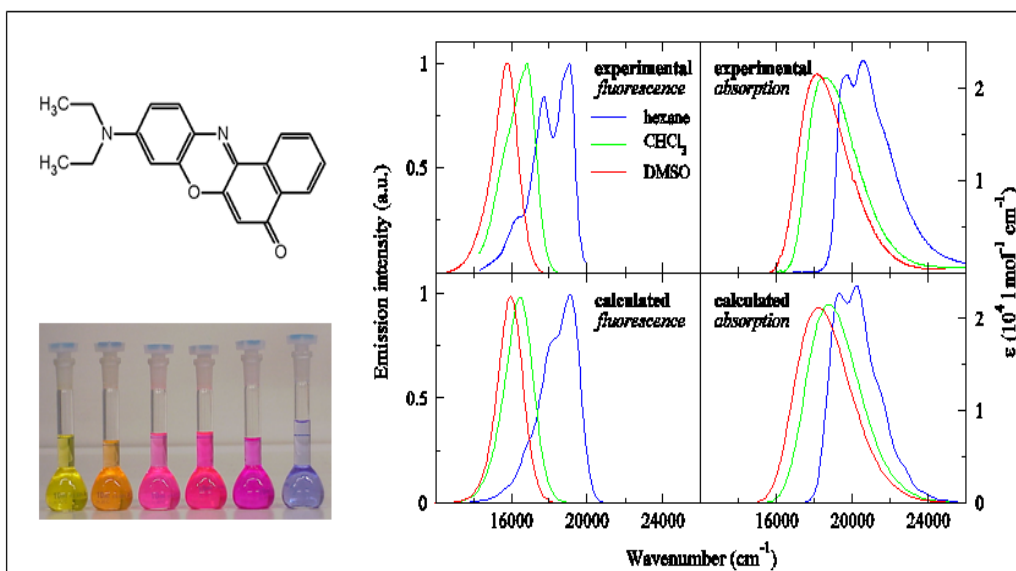


Fig. 1 Solvatochromism: Nile-red, a typical D- π -A chromophore. Top left: the chemical structure; bottom left: solutions of Nile-red in solvents of different polarity (from left to right: cyclohexane, toluene, carbon tetrachloride, chloroform, dichloromethane, DMSO). Right: absorption and fluorescence spectra of Nile-red in different solvents: top panels report experimental data, bottom panels show spectra calculated spectra in the essential state approach (see Ref. 4 for details).

Here I will shortly touch upon environmental effects on linear and non-linear optical spectra of π -conjugated molecules with electron-donor (D) and acceptor (A) groups that represent a wide family of molecules extensively studied for NLO applications. Perhaps the simplest demonstration of the importance of local environment is found in the solvatochromism of D- π -A molecules. Solvatochromism (from the Greek word chroma for color) describes the fact that the color of a molecule (a chromophore) changes with the solvent, as shown in Fig. 1 for the commercial dye Nile-red. Of course, the change of color of the solution from yellow in hexane to blue in DMSO is

due to a variation of the position of the absorption spectrum: the absorption spectra of solutions of Nile-red shown in Fig. 1 move to the red as the polarity of the solvent increases from hexane to DMSO. This well-known result is easy to understand: Nile-red has a weakly polar ground state and a largely polar excited state. The excited state is then more stabilized than the ground state in polar solvents and both absorption and fluorescence bands red-shift with increasing solvent polarity. Opposite behavior (inverse solvatochromism) is expected for dyes with a strongly polar ground state that become less polar upon excitation.

While the basis of solvatochromism is well known and well understood [1] optical spectra (see e.g. Fig. 1) carry much more information than absorption or emission frequencies. In fact, an impressive evolution of the bandshape with the solvent polarity is commonly observed, while non-specular absorption and fluorescence shapes deserve an explanation. All these features can be rationalized based on essential state models that we have developed in the last years [2-5]. The idea is very simple: the D- π -A molecule resonates between a neutral and a charge separated structure: $D-\pi-A \leftrightarrow D^+-\pi-A^-$, and the low-energy physics of the system can then be described based on just two electronic states. To understand band-shapes and polarity effects one must account for the coupling between the two electronic states and a molecular vibration. To account for the fact that the molecule readjusts its geometry with the charge distribution, we need an effective solvation coordinate that accounts for the reorientation of polar solvent molecules around the solute. The model works very well and explains the wildly different behaviour of both neutral dyes (those whose ground state is dominated by the neutral D- π -A structure) as represented by Nile-red in Fig. 1, and of zwitterionic dyes (whose ground state is dominated by the $D^+-\pi-A^-$ structure), as exemplified by the dye in Fig. 2.

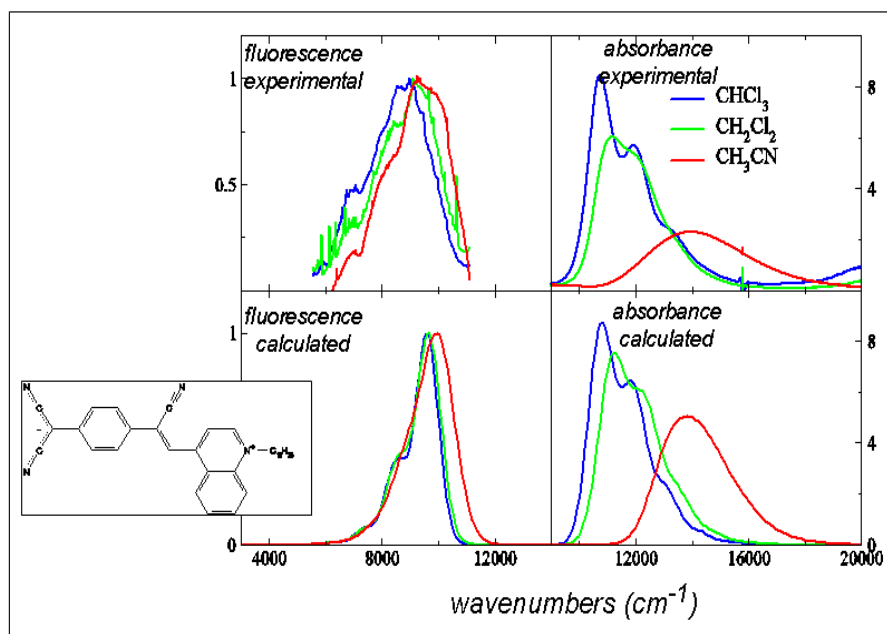


Fig. 2 The inverse solvatochromism of a D- π -A chromophore with a zwitterionic ground state (see Ref. 5 for details).

The model is semi-empirical in nature: model parameters in fact are extracted from the analysis of absorption and/or fluorescence spectra. However, these same parameters can be used to predict other spectral properties as well: based on this model we were able to rationalize Raman [3], time-resolved [6], and non-linear spectra [7] of DA dyes in solution. I do not want to go into any details here, but I just call attention on a specific non-linear process: two-photon absorption (TPA). In linear spectroscopy (weak electromagnetic field, or low-intensity light) just a single photon can be

absorbed at a time, provided of course that the energy of the transition from the ground to the excited state matches the photon frequency: $E_e - E_g = \hbar\omega$. For strong fields, as those generated at the focus of a laser beam, non-linearity takes place and two photons can be absorbed on a single shot. Of course, energy has to be conserved and TPA only occurs if the energy of the transition matches twice the photon frequency: $E_e - E_g = 2\hbar\omega$. TPA is a fascinating phenomenon that can be exploited in many different fields, ranging from nanofabrication to in-vivo optical microscopy. In general, different selection rules apply to one-photon absorption (OPA) and TPA spectra. D- π -A molecules, however, have no symmetry elements and the same transition can be promoted both by linear and two-photon absorption processes. For this reason (as sketched on the top of Fig. 3) one expects exactly superimposed OPA and TPA spectra (provided of course that in both cases the spectra are plotted against the energy of the transition and not the photon frequency). However, when vibrations are taken into account the intensity of the different vibronic lines can lead to different OPA and TPA spectral profiles resulting for D- π -A chromophores, to a blue-shift of the TPA with respect to the OPA (cf Fig. 3) [7]. This prediction (dating back to 2001) was experimentally confirmed in 2004 [8] and is in line with more recent data [8].

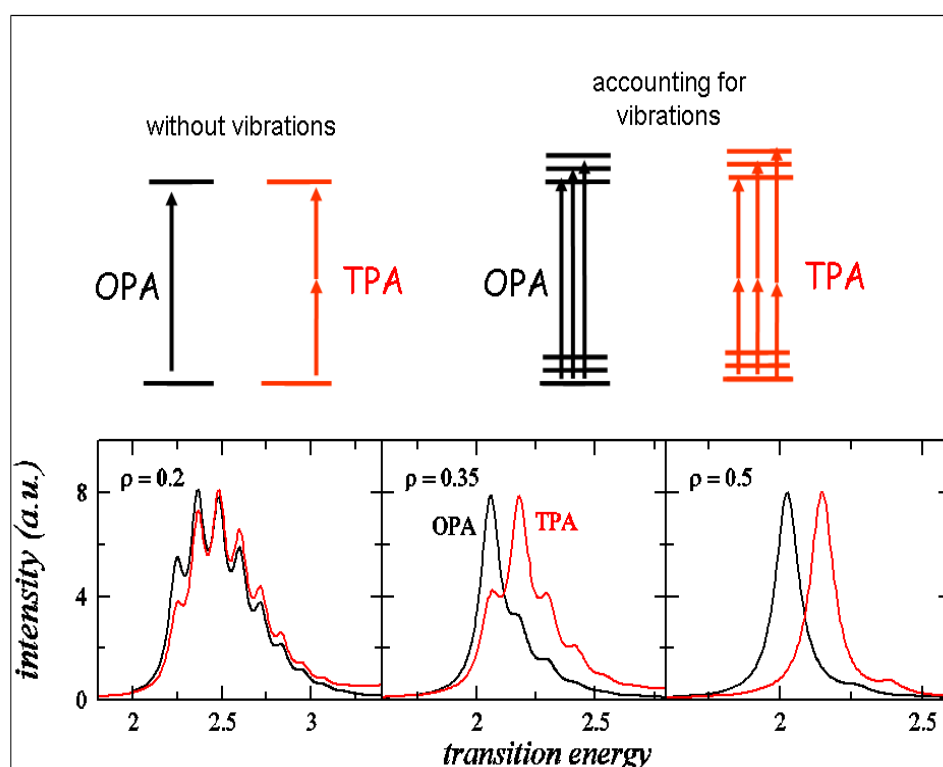


Fig. 3 Comparing one-photon absorption (OPA) and two-photon absorption (TPA) spectra calculated for D- π -A chromophores with different charge distribution (see ref. 7 for details). The diagrams on top schematically represent OPA and TPA processes when only electronic states are considered (OPA and TPA processes lead to the same state and therefore the relevant transition energies are exactly the same) or accounting for vibrations (vibrations are responsible for the structures in OPA and TPA bands and the intensity of each vibronic line needs not to be the same in the two processes leading to an apparent blue shift of the TPA band with respect to the OPA band).

The proposed approach is not limited to polar D- π -A chromophores. Quadrupolar (D- π -A- π -D or A- π -D- π -A), octupolar (DA₃ or AD₃) and, more generally, multipolar chromophores can in fact be treated along similar lines (see Fig. 4 for typical structures). Multipolar chromophores have a non-polar ground state and, upon absorption of a single photon, they are vertically driven to a non-polar excited state (vertical excitation), so that the absorption is not solvatochromic. However, emission occurs from a relaxed excited state, and this state may have a lower symmetry than the ground state,

corresponding in multipolar dyes to a state where the excitation is confined on a single molecular arm.

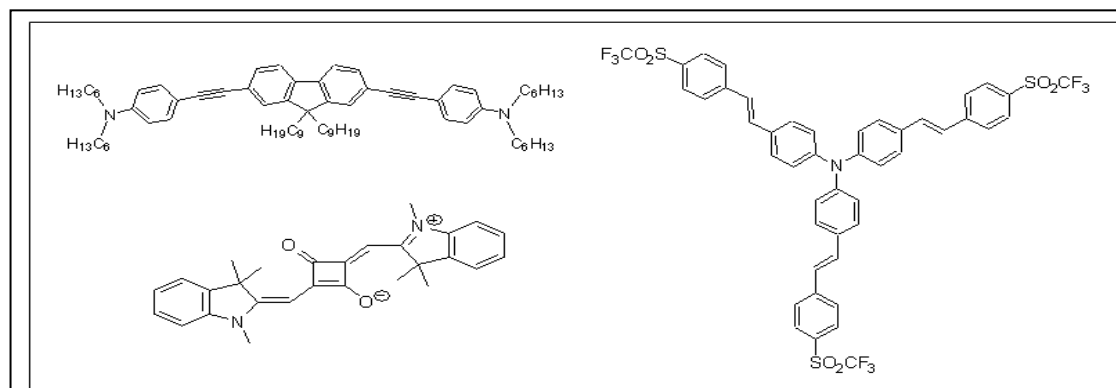


Fig. 4 Examples of quadrupolar (left) and octupolar chromophores.

As far as quadrupolar dyes are concerned, we demonstrated that symmetry breaking is conditional. We expect symmetry breaking in the excited state for chromophores with not too strong donor and acceptor groups (class I chromophores, see ref. 9 for a more detailed discussion). However, other chromophores do not undergo symmetry breaking either in the ground or in the excited state and do not show any appreciable solvatochromism in absorption or fluorescence. This variegated behavior is well rationalized within our essential state models: we can reproduce nicely linear absorption and fluorescence spectra as well as TPA spectra of quadrupolar dyes [9]. In this respect, it is interesting to state that, in agreement with experimental observation, we expect much larger TPA intensities for class II than for class I chromophores. At variance with quadrupolar dyes, in octupolar dyes, due to the excited state degeneracy, symmetry breaking is unconditional in the excited state [10]. In other terms, we always expect for octupolar dyes a similar behavior as observed for class I quadrupolar dyes. Linear and TPA spectra of octupolar chromophores are rationalized in a model that just accounts for 4 electronic states, provided that the coupling with molecular vibrations and polar solvation is properly accounted .

This short description of optical spectra of polar and multipolar chromophores in solution demonstrates that the chromophores (or at least their spectra) are extremely sensitive to the polarity of the surrounding medium. This immediately suggests that putting together several polar and multipolar chromophores will lead to important spectroscopic effects. In the first place each chromophore, being a largely (hyper)polarizable unit, will readjust its charge distribution in response to the electrical field generated by the (fractional) charges on nearby molecules. In other terms the nature of the ground state of each chromophore changes in response to the surrounding. These *ground state* effects are usually well described in a mean-field approximation [11]. However, other spectroscopic effects are expected, related to the interaction between oscillating transition dipole moments (excitonic effects) [11]. The well-known excitonic model for optical spectra of molecular aggregates and crystals requires some extension to be applied to largely (hyper)polarizable molecules like our polar and multipolar chromophores. Moreover, the dipolar approximation for intermolecular electrostatic interactions has to be relaxed to describe properly optical spectra of multichromophoric assemblies [12]. We have recently summarized our work on intermolecular electrostatic interactions in multichromophoric assemblies of polar and multipolar chromophores in two papers [13]: I refer the interested reader to these papers for more details.

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