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Research paper

Excited-state symmetry breaking of linear quadrupolar chromophores: A transient absorption study

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ABSTRACT

The photophysical properties of two highly symmetrical quadrupolar chromophores were studied by both steady-state and transient absorption spectroscopy. Their excited-state behavior is dominated by the solvent-induced Stokes shift of the stimulated-emission band. The origin of this shift is attributed to symmetry breaking that confers a non-vanishing dipole moment to the excited state of both compounds. This dipole moment is large and constant in DMSO, whereas symmetry breaking appears significantly slower and leading to smaller excited-state dipole in toluene. Time-dependant increase of the excited-state dipole moment induced by weak solvation is proposed to explain the results in toluene.

1. Introduction

Since the 1990s, nondipolar chromophores have been the object of a continued research effort to develop new materials for nonlinear optics. In addition to conventional, seminal conjugated push-pull structures giving rise to nonlinear (second-order) polarizabilities through efficient intramolecular charge transfer (ICT) occurring upon the transition from HOMO to LUMO [1], new families of compounds have emerged that show a higher degree of molecular symmetry. They were aimed at allowing the appearance, and optimization, of nonlinear polarizabilities of more complex origin via non-vanishing elements of the corresponding tensors [2]. This has prompted numerous efforts in the design of octupolar derivatives with large optical nonlinear responses, fist aiming at large second-order optical responses (as these derivatives lack a center of symmetry) [3–8] and more recently third-order nonlinear responses [9–12]. In parallel, linear quadrupolar chromophores displaying the generic DπAπD or AπDπA structure (D standing for electron donor, A for acceptor, and π for pi conjugation) attracted particular attention due to their high potentialities for two-photon absorption (2PA) [13–26]. This third-order optical property offers many promises for the development of a variety of technologies (microfabrication, optical limitation, three-dimensional data storage, photodynamic therapy, two-photon fluorescence microscopy) [27].

It is worth mentioning here the theoretical framework developed by Terenziani et al. [21] to understand the photophysical and optical properties of quadrupolar chromophores. According to this work, coupling of the zwitterionic valence states of the molecule to nuclear motions localized in each arm of the molecule is capable of inducing symmetry breaking and allows the creation of polar states. Different types of chromophores were defined, exhibiting symmetry breaking either in the one-photon-allowed excited state or in the ground state, depending of the quadrupolar character of the molecule and the strength of the vibronic coupling. Moreover polar solvation was identified as an additional mechanism contributing to the induction of symmetry breaking. This solvent-induced mechanism relies on a classical “slow” (overdamped) solvation coordinate, as opposed to the above-mentioned quantum nuclear coordinates. As a consequence, symmetry cannot be recovered by fast exchange (tunneling) between the two polar minima (*false* symmetry breaking). Interestingly, several quadrupolar derivatives have been shown to display strong fluorescence solvatochromism despite their symmetrical structure, in relation with symmetry breaking in the excited state [21,28–30].

Ventelon et al. [14,16,17] designed some years ago several series of quadrupolar chromophores for 2PA, which bear a central acceptor group (phenyl or biphenyl or dihydrophenanthrene or dithienothiophene) connected on each side to diverse electron donor or acceptor moieties through a semi-rigid conjugated linker (phenylene-vinylene). Some of them were shown to display very large 2PA cross sections in the visible red or NIR regions. Fig. 1

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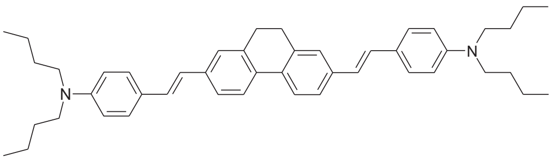

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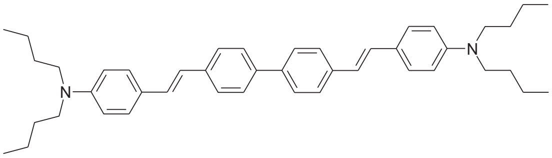

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Fig. 1. Structures of the push-push quadrupolar chromophores.

shows two examples of these chromophores, which the present article will deal with. Compound **1** has a dihydrophenanthrene core while **2** has a biphenyl one; both compounds share the same donor, NBu_2.

We report here a study of the photophysical properties of compounds **1** and **2** by steady-state and picosecond broad-band transient absorption spectroscopy. Our first aim was to characterize the general excited-state behavior of these molecules (lifetime, decay mechanism) and determine for reference purpose their excited-state absorption cross sections over a wide spectral range (360–800 nm) – proposed as Supplementary Information. More specifically, we wished to examine the question of the establishment of symmetry breaking, its dynamics and dependence on the polarity of the solvent. Such questions, discussed on a broad perspective by Vauthey [31], have been tackled recently by ultrafast spectroscopy, for several quadrupolar systems [29,30,32–36]. For the particular DπAπD molecule reported by Dereka et al. [36], the polarity of the solvent was shown to control the nature of the excited state. From symmetrical and quadrupolar in nonpolar solvents, it shifts to a purely dipolar state in highly polar solvents, with full localization of the excitation on one arm of the molecule. An intermediate case is identified in weakly polar media. The dynamics of excitation localization is reported to be controlled by the different time scales of solvent relaxation. In the present study, we used time-dependent Stokes shift of stimulated emission as a reporter of solvation dynamics, itself revealing the effective dipole moment of the molecules in the excited state.

2. Materials and methods

2.1. Samples

Compound **1** was synthesized as described in Ref. [14] and compound **2** as reported in Ref. [37]. The chemical purity of the sample was checked by NMR spectroscopy. Both compounds were found to be in an all-trans configuration, as represented in Fig. 1. Spectroscopy grade dimethyl sulfoxide (DMSO) and toluene were purchased from Aldrich and used as received.

2.2. Transient absorption setup

Transient absorption experiments were performed by the pump-probe with continuum technique. The source was a non-mode-locked dye laser described elsewhere [38], delivering 500-fs pulses at 610 nm, with 10 Hz repetition rate. It was used, through continuum generation, filtering and amplification in dye cells, to produce two synchronous sub-picosecond beams, tuned at 570 and 428 nm.

The pump-probe setup used for the present experiments has been previously described [39]. Excitation of the sample was done with the 428-nm beam while the 570-nm beam generated a continuum of white light used as the probe. The probe beam was delayed with respect to the pump beam in a motorized optical delay line and split into a sample and a reference channel. Pump and probe beams crossed on the sample, held in a 1-mm cuvette, at an angle of ca. 10° and their linear polarizations were set at the magic angle. The sample solution (50 mL) was recirculated, at room temperature, to avoid significant photolysis during the experiment. The transmitted beams were sent through optical fibers to the entrance slit a Jobin-Yvon 270M spectrograph (100 grooves/mm grating). Spectra were recorded on a 1024 × 128 Princeton Instruments CCD camera and accumulated over 500 pump shots.

Time-resolved differential absorbance spectra (ΔA = absorbance of the pumped sample minus absorbance of the unpumped sample) were calculated and corrected for the chirp of the probe pulse (dispersion of the arrival time on the sample), measured in a separate experiment by two-photon absorption in pure 1-chloronaphtalene.

2.3. Data analysis

The full transient absorption data, depending on both wavelengths and delay times, were globally fitted [40] to a discrete sum of exponentials, convoluted by a Gaussian representing the instrument response function (IRF). Singular value decomposition (SVD) allowed both dimensional reduction and noise filtering. The rms amplitude of the residue after fitting was of the order of 3 mOD. The full width at half maximum of the IRF (time resolution) was found to lie between 1.3 and 1.5 ps.

For each time component of the fit, the collection of wavelength-dependent pre-exponential factors constitutes a spectrum called decay-associated differential spectrum (DADS).

In order to follow the position of the stimulated-emission band as a function of time, deconvoluted transient absorption spectra, reconstructed from the preceding global multiexponential analysis, were used. The stimulated emission band was fitted by a sum of two lognormal functions, which allowed extracting the wavenumber of its minimum at each time. This position was then plotted as a function of time and fitted to a sum of exponentials.

3. Results and discussion

3.1. Steady-state absorption and fluorescence spectra

The steady-state absorption and fluorescence spectra of compounds **1** and **2**, in DMSO and toluene, are given in the lower panels of Figs. 2 and 3, respectively. Let us recall that DMSO is a strongly polar solvent (dielectric constant $\varepsilon = 46.45$, permanent dipole moment $\mu = 4.1$ D [41]) whereas toluene is nearly nonpolar ($\varepsilon = 2.38$, μ=0.3 D [41]). Table 1 gathers the values of the absorption and fluorescence maxima, together with the corresponding fluorescence quantum yields (measured using fluorescein in 0.1 M NaOH aqueous solution as a standard). It may be noted that the shape of the fluorescence emission spectra was checked to be independent of the excitation wavelength, for both compounds.

One notes that the solvatochromic shift of the absorption band (shift upon increasing solvent polarity) of both **1** and **2** is weak (~8 and 14 nm, respectively) and positive (towards longer wavelengths). Conversely, the solvatochromic shift of the fluorescence spectra is very large (80 nm for **1** and 90 nm for **2**) and positive.