



Multicoordinational excited state twisting of indan-1,3-dione derivatives

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ABSTRACT

Excited state relaxation of indan-1,3-dione derivatives with different substituents attached to the phenyl ring and with the bridged amino group was investigated by means of the steady-state fluorescence and femtosecond time-resolved absorption pump-probe spectroscopy. Bridging of the amino group increases the fluorescence quantum yield and the excited state lifetime. Analysis of the results indicates that the phenyl ring twisting around a single central bond leads to the nonradiative state formation and to subsequent fast relaxation to the ground state. Double bond twisting takes place in molecules with the bridged amino group and causes a large Stokes shift and slightly slower excited state relaxation.

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1. Introduction

Indan-1,3-dione (ID) class molecules have large dipole moments in the ground state, which change significantly in the excited state [1]. The magnitude of the dipole moment and its change under excitation significantly depend on substituents attached to indan-1,3-dione or benzylidene moieties of the molecules. Most of these molecules in solvents have low fluorescence quantum yield, which strongly depends on the environment parameters. These properties make ID class molecules attractive for various applications in nonlinear optics as molecules with large dielectric susceptibility, which might be pooled in the electric field [2] or oriented by all optical alignment [3]. Good understanding of the excited state properties and relaxation dynamics is therefore very important for their perspective applications.

Excited state dynamics of one of this class compounds, *N,N*-dimethylaminobenzylidene indan-1,3-dione (DMABI), has been extensively investigated by means of ultrafast absorption and fluorescence spectroscopy [4]. It has been shown that significant charge redistribution and large scale conformational changes of the molecules take place in the excited state and are responsible for their fast excited state relaxation and its dependence on the environment viscosity. These flat in the ground state molecules have several torsional degrees of freedom, and twisting of one or simultaneously several bonds may take place in the excited state. Generally, bond twisting in the excited state leads to the fast non-radiative relaxation [5–9], with occasional formation of nonemis-

sive “dark” states [10–12], or to the appearance of the dual fluorescence bands [13–23]. The dual fluorescence is a well known signature of the intramolecular charge transfer in 4-(dimethylamino)benzonitrile (DMABN) class molecules, which form twisted internal charge transfer (TICT) states involving the twisting of the amino group [14]. Molecules composed of larger molecular fragments connected by single or double bonds often undergo fast nonradiative relaxation and have low quantum yield [5–9]. Structural changes introduced to the complex molecules influence their excited state dynamics and relaxation pathways by blocking some of the twisting motions and permitting the other ones [5], and in such a way enabling us to control their properties.

In this paper, we investigate a series of ID class molecules with different structure by using femtosecond time-resolved pump-probe absorption spectroscopy together with the steady-state absorption and fluorescence methods. The molecules possess a phenyl ring substituted with a disubstituted amino group, which is a typical electron-donor fragment of various widely investigated flexible molecules experiencing torsional motions in the excited state and exhibiting complex fluorescence properties. The best known representatives are famous DMABN and related molecules showing dual fluorescence. ID class molecules under investigation are more complex, since they have more rotational degrees of freedom, and consequently, may experience more complex conformational changes under excitation. Such flexible molecules usually do not exhibit dual fluorescence, but experience fast nonradiative relaxation and low fluorescence quantum yield [5–9]. Still, there are no clear rules enabling one to predict torsional motions responsible for the relaxation dynamics and fluorescence properties of such molecules.

Here, we will try to shed more light on the excited state dynamics by addressing molecules with different substituents as well as

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ones bearing two identical chromophores linked by a spacer (double molecules) and physical dimers linked by Van der Waals forces. We will demonstrate that molecule twisting around single or double bond connecting two molecule moieties is responsible for the excited state relaxation and formation of nonradiative “dark” states. As it will be shown the amino group twisting is not directly responsible for these processes, however its incorporation into the heterocycle prevents formation of nonradiative states due to the increased volume of one of the molecule moieties, and thus, slowed down rotation.

2. Experiment

The 2-(4-diethylaminobenzylidene)indan-1,3-dione (ID1) and 2-(4-diethylamino-2-hydroxy-benzylidene)indan-1,3-dione (ID2) were prepared in good yield via condensation of 1,3-indandione with 4-diethylaminobenzaldehyde and 4-diethylamino-2-hydroxybenzaldehyde in the absence of a catalyst [24]. 2-(4-diethylamino-2-oxiranylmethoxybenzylidene)indan-1,3-dione (ID3) was produced by alkylation of 2-hydroxy-4-diethylaminobenzaldehyde with epichlorohydrin, followed by condensation with 1,3-indandione. The double structure ID4 requires an additional reaction step with 1,3-benzenedithiol to bind the (4-diethylamino-2-hydroxybenzylidene)indan-1,3-dione units into the dimeric structure. The relative compounds ID5–ID8 were synthesized following the procedure used to prepare ID1–ID4 except that instead of aryl aldehydes, 6-formyl-3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline was used. Their synthesis is described in detail in Ref. [25]. Investigated materials were purified by column chromatography and purity of the products was confirmed by NMR and elemental analysis.

The steady-state absorption and fluorescence spectra of the ID derivatives dissolved in various organic solvents were measured with a Perkin–Elmer Lambda 950 and a Perkin–Elmer LS50B spectrometer, respectively. The fluorescence spectra were corrected for the instrument sensitivity. In order to avoid reabsorption and spectra distortion, the solutions used for fluorescence investigations had a maximal absorbance of about 0.2 in the 1 cm quartz cuvette. In this case, the concentration of solutions was about 10^{-5} mol/l. The solutions with even lower absorbance (<0.05) were used to estimate fluorescence quantum yield. Quantum yields were estimated by comparing spectrally integrated emission intensities with that of the standard. Quinine sulphate dissolved in 0.1 M H_2SO_4 , and exhibiting $53 \pm 2.3\%$ quantum yield at an excitation wavelength of 366 nm was used as a standard in these estimations. Different refractive indices of the standard and the solutions under investigation were taken into account.

Nonlinear transient absorption was investigated by means of conventional femtosecond pump–probe absorption spectroscopy. The spectrometer was based on an amplified femtosecond Ti:Sapphire laser Quantronix *Integra-C* generating 130 fs duration pulses at 805 nm (1.55 eV) at the 1 kHz repetition rate. A fraction of the laser output radiation converted to the second harmonic (402 nm) was used to excite the samples, whereas white continuum generated in a 2-mm thick sapphire plate was used to probe the transient differential absorption. The investigations were performed in the 2-mm cuvette, where solutions had a maximal absorbance of about 0.2–0.4.

3. Results

3.1. Steady-state spectroscopy

The ID derivatives addressed in this work (see Fig. 1) may be classified into two groups: the first group (ID1–ID4) with the diethylamino group *para* attached to the phenyl ring with or with-

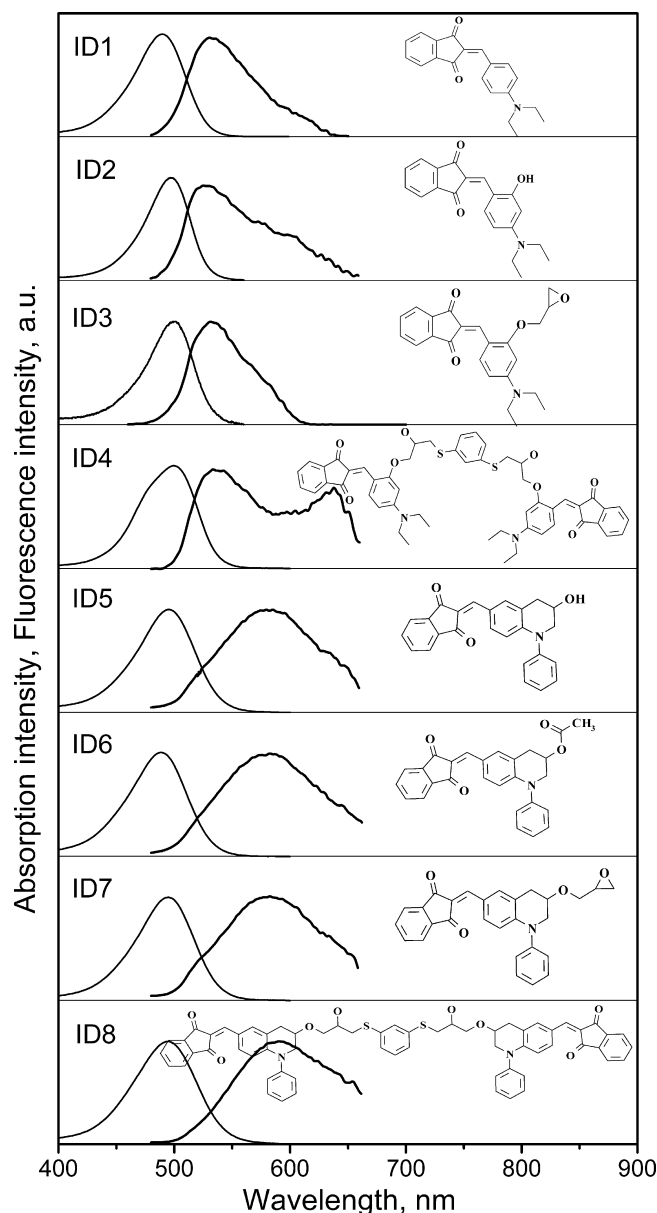


Fig. 1. Normalised steady-state absorption (thin lines) and fluorescence spectra (thick lines, $\lambda_{ex} = 450$ nm) of the investigated indan-1,3-dione compounds in ethanol solution.

out additional hydroxyl or oxiranylmethoxy groups *ortho* attached to the phenyl ring of the benzylidene moiety, or covalently linked into double molecules; the second group (ID5–ID8) with the disubstituted amino group incorporated into the 1-phenyl-1,2,3,4-tetrahydroquinoline, with additional hydroxyl, acyl or oxiranylmethoxy attachments to the heterocycle, or covalently linked into double molecules. Fig. 1 represents the steady-state absorption and emission spectra of the investigated molecules in ethanol solution. Absorption band positions of all the molecules are almost identical, indicating negligible influence of the structural changes to the ground state and Franck–Condon excited state energies.

Fluorescence spectra of the first group molecules in ethanol have a main fluorescence band at about 525 nm. An additional band is also observed at about 625 nm. Intensity of this band differs for different molecules and also depends on the solvent, chromophore concentration as well as excitation wavelength. Since its relative intensity increases with molecular concentration, it may unambiguously be attributed to physical dimers. The 625 nm band

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