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Thioindigo, and sulfonated thioindigo derivatives as solvent polarity dependent fluorescent on-off systems

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ABSTRACT

The synthesis of a novel series of 5,5′-sulfonamide thioindigo derivatives, including a new synthetic methodology (*via* microwave assisted synthesis), together with a comprehensive electronic spectral and photophysical characterization is described. The study made in solution, as a function of the solvent polarity, showed -rationalized by TDDFT calculations- that in nonpolar solvents the high efficiency of the radiative deactivation channel (50% in dioxane and 70% in benzene) is due to an S_1 (of π,π* origin) in the *trans* form, whereas in polar solvents the low fluorescence quantum yield (1% or less) is due to the adiabatic stabilization of the *trans* and saddle S_1 forms, making the sloped type CI (Conical Intersection) with S_0 energetically accessible thus becoming an efficient competitive decay channel to the radiative pathway. It is shown that thioindigo and all the 5,5′-sulfonamide thioindigo derivatives exhibit "on-off" fluorescence that can be tuned by the solvent polarity. The presence of a dark *cis* form with an S_1 (of n,π* origin) was confirmed by the appearance of a new absorption band, upon irradiation, assigned by TDDFT to an S_2 (of π,π* origin) state.

1. Introduction

Thioindigo, **TI** (Fig. 1) is a synthetic molecule structurally related to indigo, which was first reported in 1906 by Friedlander [1]. In the 1930's driven by the demand of new pigments from the industry, the works of Formanek [2], Hixson and Cauwenberg [3,4], lead to a development on the study of this molecule. One of the relevant differences on using thioindigo derivatives (relative to the indigo derivatives) is that substitution in thioindigo leads to major color differences with a more wide range of wavelength maxima and therefore of colours [5–8]. The stability, nature and tuning of color and excited state decay mechanisms of thioindigo and of its derivatives was also the subject of both experimental and theoretical studies [9–19]. In particular Wyman and co-workers found that, in contrast with indigo (Fig. 1), thioindigo displays *trans-cis* photoisomerization (presumably *via* the triplet state although this was not unequivocally established) [13–15,20–22]. Brode and Wyman [22,23], showed that the absorption spectra does not change with time for the derivatives in the 5 and 7 positions (in aqueous sulfuric acid) [22]. Later on, Dalgliesh and Dokunikin worked on the synthesis and photochemical properties of the first sulfonated thioindigo derivatives, 5,5′-dimethylsulfonyl-thioindigo and 6,6′-dimethylsulfonylthioindigo, reporting that the presence of donor groups lead to a bathochromic shift, and withdrawing groups to a hypsochromic effect [24]. Other thioindigo derivatives were subsequently synthesized [17,25,26] together with hemithioindigos [27], metal-complexes [28] or derivatives obtained through the addition to the carbonyl group [29,30].

Inspired by the studies of *cis-trans* isomerization with thioindigo Wyman, Vlahakis and co-workers were able to dope liquid crystal films pointing to what was one of the first indications of an on/off switcher [31,32]. More recently thioindigo derivatives have been used for applications in solar devices [33], ion transport [34] and in inorganic supports [35,36].

The main difference in the photophysical properties of thioindigo relative to indigo lies in the fact that with the latter the internal conversion deactivation channel (available through a very efficient excited state proton transfer - ESPT) is dominant with more than 99.99% of the quanta loss made through this channel with negligible triplet state formation and fluorescence [37–41]; in contrast, in the case of **TI** the dominant deactivation is fluorescence (solvent dependent) with com-

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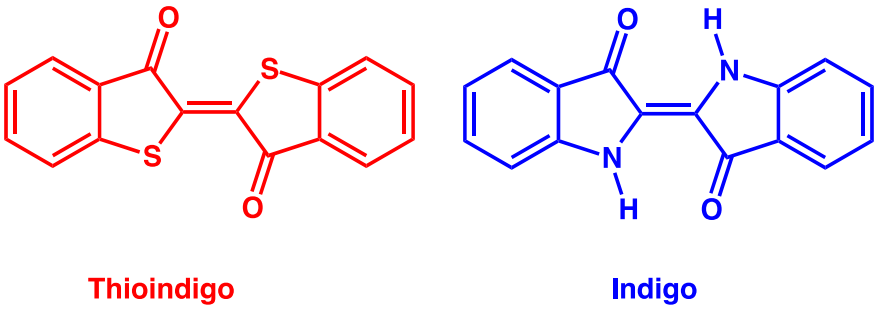

Fig. 1. Structures of indigo and thioindigo.

petitive $S_1 \sim\sim > S_0$ internal conversion and singlet-to-triplet state formation [5]. It is also very interesting to note that recent works on indigo derivatives -by replacing the hydrogen of the N-H groups with different groups, which blocks the ESPT in indigo- have revealed the presence of *trans-cis* photoisomerization [42,43].

In this work the synthesis, electronic spectral and photophysical properties of thioindigo and of different 5,5′-sulfonamide thioindigo derivatives in polar and non-polar solvents is described. The data is further rationalized by TDDFT calculations.

2. Experimental section

2.1. Material and methods

Thioindigo, triethylamine, *tert*-butylamine, allylamine, aniline and chlorosulfonic acid was acquired from Aldrich and used without further purification. The solvents used (benzene, dioxane, methanol, dimethyl sulfoxide, and dimethylformamide) were all of spectroscopic grade and were used without further purification. Water used was ultra-pure at pH = 5.4, purified using a Direct Q3 Merk Millipor equipment. Microwave-assisted synthesis was performed using a CEM Discover S-Class single-mode microwave reactor, featuring continuous temperature, pressure and microwave power monitoring. Absorption spectra were recorded on a Cary 5000 UV-Vis-NIR. Fluorescence spectra were recorded in a Horiba-Jobin-Yvon Spex Fluorolog 3–2.2. spectrophotometer and corrected for the instrumental response of the system. The fluorescence quantum yields of the compounds were determined using thioindigo as standard ($\phi_F = 0.54$; dioxane) [5]. The molar absorptivity coefficients (ε_{SS} Table 1) were obtained from the plot of the absorption *vs.* concentration obtained with solutions with concentrations ranging from 8×10^{-5} to 3×10^{-5} mol dm^{-3}. In all cases R^2 values ≥ 0.99 were obtained.

The fluorescence decay times were obtained by the Time-Correlated Single Photon Counting (TCSPC) technique with nanosecond time resolution in an equipment described elsewhere [44], and further analysed using the method of modulating functions implemented by George Striker [45].

Room temperature singlet oxygen phosphorescence was detected at 1270 nm using a Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (products for research model PC176TSCE-005), following laser excitation of the aerated solutions at 532 nm with an adapted Applied Photophysics flash kinetic spectrometer. The singlet oxygen quantum yields were obtained by plotting the signal intensity (at 1270 nm) *vs.* the applied laser energy in a procedure elsewhere [46] reported and by using tetraphenylporphyrin (TPP) in benzene ($\lambda = 532$ nm, $\phi_\Delta = 0.66$) as the standard.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AMX with an operating frequency of 400 and 101 MHz, respectively. ^{1}H assignments were made using 2D COESY and NOESY experiments while ^{13}C assignments were made using HSQC experiment. When TLC monitoring was necessary it were used silica slates 60 F250 acquired on Merck and Fluka. The solvents used on the synthesis and purification of the compounds were purified and dried if necessary by conventional method. Dichloromethane was placed in reflux with Calcium chlorate during 3 h, distilled and then stored with molecular sieves (4 Å). Ethyl Acetate was placed in reflux with potassium carbonate during 3 h, distilled and then stored with molecular sieves (4 Å). Ether was dried by reflux with sodium stripes, then distilled and stored with molecular sieves (4 Å). High-resolution mass spectra (HRMS) were recorded with a TOF VG Autospect M spectrometer with electrospray ionization (ESI).

All calculations were of the DFT type, carried out using GAMESS-US [47] version R3. A range corrected CAMB3LYP [48] functional, with 65% HF exact exchange at long range and 19% at short range, was used in both ground- and excited-state calculations. TDDFT calculations, with similar functionals, were used to probe the excited-state potential energy surface (PES). The solvent was included using the polarizable continuum model with the solvation model density to add corrections for cavitation, dispersion, and solvent structure. In TDDFT calculation of FC (Franck-Condon) excitations the dielectric constant of the solvent was split into a “bulk” component and a fast component, which is essentially the square of the refractive index. In “adiabatic” conditions only the static dielectric constant is used. Hessians were computed by numerical differentiation of analytically computed first derivatives. A 6-31G** basis set was used in either DFT or TDDFT calculations. CAMB3LYP slightly overestimates excitations with a scaling correction applied to the reported values ($E_{reported} = E_{TDDFT} \times 0.92–0.25$) [49]. Excitations were corrected for Zero Point Vibrational Energy by, essentially, the frequency of the relaxing vibrational mode (± 0.05 eV).