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Model studies of spectral and photophysical characteristics of a series of donor–acceptor–polyenes of different length

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Abstract

The photophysical behaviour of a series of donor–acceptor–polyenes of different length: 4-dimethylamino-4′-cyanostilbene (DCS), 4-dimethylamino-4′-cyano-1,4-diphenylbutadiene (DCB) and 4-dimethylamino-4′-cyano-1,4-diphenylhexatriene (DCH) has been studied by means of steady state and time resolved fluorescence and low temperature measurements. Quantum chemical calculations were performed for comparison. For all three dyes, the fluorescence quantum yields show a maximum in the most polar solvents. A pronounced solvatochromic behaviour is only observed for the emission spectra whereas the absorption spectra remain nearly unaffected. The non-radiative decay decreases in the order DCS > DCB > DCH. Similarly, the radiative rate constant decreases in this order, contrary to the usual behaviour for a lengthening of the π-system. The chain-length dependence of the dipole moments of the relaxed excited state μ_e is better described by the Onsager radius derived from molecular length rather than from the density approach. Both calculations and experiments support the conclusion that the emissive state is not a TICT state.
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1. Introduction

For several decades, the photophysical and solvatochromic properties of donor–acceptor–stilbene of DCS (for structures see Scheme 1) have been studied in detail [1–12], while the information about the closely related structure with longer chain length like DCB and DCH remains limited [13,14]. Recently, we reported a study of the photophysical and solvatochromic behaviour of dimethylamino-cyano-diphenylbutadiene (DCB) [15,16]. The possible involvement of a twisted intramolecular charge transfer (TICT) state has been studied for the case of DCB by comparing the photophysical properties of this compound with those of a twisted model compound, the sterically hindered dimethylated derivative DMDCB. There was no evidence for the involvement of a TICT state for this pair of compounds [15]. Also the observed dipole moments for Franck Condon and equilibrated S_1 states differ strongly. This

could not be explained on the basis of the quantum-chemically derived excited state properties including polarizability effects and neither by the solvatochromic equations based on the Onsager theory [16]. Here we report a study of the photophysical properties and the solvatochromic behaviour of a series of structurally related molecules in which the donor (dimethylamino) and acceptor (cyano) substituents are separated by *trans*-stilbene (DCS), all-*trans*-diphenyl-butadiene (DCB) and all-*trans*-diphenyl-hexatriene (DCH). The solvent polarity does not significantly affect the absorption properties of these three dyes. In contrast, a pronounced solvatochromic fluorescence shift of these dyes in differently polar solvents is observed. Moreover, the strongly different solvatochromic slopes for absorption and fluorescence are not compatible with the usual assumption of the same state for absorption and emission or with the validity of a point dipole in a solvent continuum Onsager model [17]. Several alternative models for explaining this behaviour have been discussed [16]. From the similarity of the polarity dependence of the photophysical properties, it is concluded that the three

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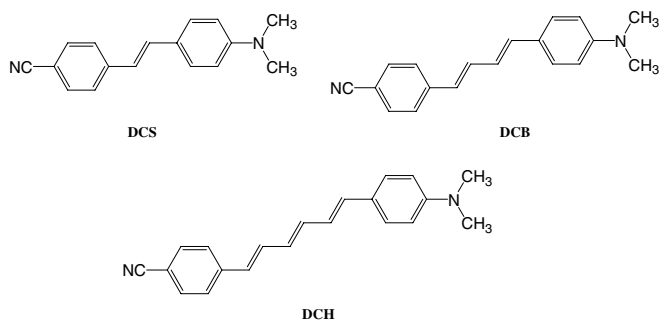
Scheme 1. Investigated compounds.

compounds behave similarly in a mechanistic sense and that the involvement of a TICT state is not supported. Further questions to be dealt with in this work are: how does the chain-length affect solvatochromism, dipole moments, as well as radiative and nonradiative decays?

2. Experimental

2.1. Materials

The structures of the investigated compounds are shown in Scheme 1. All compounds were already known. The preparation and chemical identification of DCB was done according to known literature [18]. DCS [19] was obtained from 4-cyanobenzyltriphenylphosphonium bromide and 4-dimethylaminobenzaldehyde by a Wittig reaction following a published procedure [20]. DCH has been synthesized according to Ref. [18]. The solvents for the spectroscopic measurements: *n*-hexane, dibutyl ether (ButOBut), diethyl ether (EtOEt), tetrahydrofurane (THF), butyronitrile (BCN), ethanol (EtOH) and acetonitrile (ACN) were Uvasol grade from Merck. Dipentyl ether (POP) was from Fluka puriss. The solutions were prepared to optical densities of 0.09–0.10 for steady-state fluorescence measurements. All solutions were prepared under red light and care was taken to verify that photochemistry during the experiments was negligible. Neither absorption nor fluorescence spectra were affected by the measurements.

2.2. Spectroscopy

Absorption spectra were recorded on an AT1 Unicam spectrometer UV4, and the steady-state fluorescence spectra were recorded with a SLM Aminco-Bowman AB2 spectrofluorimeter and were corrected for instrumental sensitivity. The emission correction curves were created using a calibrated tungsten lamp from SLM instruments.

Fluorescence decay curves were recorded with the time-correlated single-photon counting technique [21] using an Ar-pumped Ti-sapphire laser as excitation source (excitation wavelength 367 nm, instrument response function 55 ps), and the equipment described in Ref. [22]. The decays were analyzed by the Marquardt algorithm, which is implemented in the commercial global analysis program

[23] by iterative reconvolution of the instrument response function with a sum of exponentials (Eq. (1)):

$$I(t) = \sum_{i=1}^{n} \beta_i \exp(-t/\tau_i) \tag{1}$$

where $I(t)$ is the intensity of the fluorescence at time t, β_i is the preexponential factor for the fraction of the fluorescence intensity of component i, τ_i is the fluorescence decay time and n is the total number of exponentials necessary for the fit. The results were judged by the statistical parameter χ^2 ($\leqslant 1.2$) and by the shape of the autocorrelation function of the weighted residuals.

Some of the fluorescence decay measurements were performed using synchrotron radiation from the Berlin synchrotron facility BESSY II as excitation source (excitation at the maximum of the absorption band) in conjunction with an excitation monochromator (Jobin Yvon, II, 10 UV). It delivers a 1.25 MHz pulse train with characteristic pulse widths of 30–50 ps. The fluorescence was detected by a microchannel plate photomultiplier (MCP, Hamamatsu R 1564-U-01) cooled to −30 °C, which was coupled to an emission monochromator (Jobin Yvon, II, 10 VIR) by means of quartz fiber optics. The signal from a constant fraction discriminator (CFD, Tennelec 454) was used as the start pulse for the time-to-amplitude converter (TAC, Tennelec TC864) operating in the reverse mode. The BESSY II synchronization pulse was used as the stop pulse. The MCP pulses were amplified by a homemade amplifier (INA 10386) and coupled into the CFD. A multichannel analyzer (Fast Comtec MCDLAP) was used for data accumulation.

2.3. Fluorescence quantum yield

The fluorescence quantum yield, Φ_f, at 298 K was calculated from the integrated intensity under the emission band using the following equation [24]:

$$\Phi_f = \Phi_f^{ref} \frac{n^2 A_{ref}}{n_{ref}^2 A} \frac{\int I_f(\lambda_f)\,d\lambda_f}{\int I_f^{ref}(\lambda_f)\,d\lambda_f} \tag{2}$$

where n_{ref} and n are the refractive indices of the solvents, A_{ref} and A ($\leqslant 0.1$) are absorbances at the excitation wavelength, Φ_f^{ref} and Φ_f are the fluorescence quantum yields, and the integrals denote the computed area of the fluorescence bands, each parameter for the reference and sample solution. Quinine bisulfate in 0.05 M sulfuric acid ($\Phi_f = 0.52$) [25] was taken as fluorescence reference. Most values have been remeasured, the relative experimental error of the quantum yields was found to be around ±5%.

2.4. Low temperature measurements

Temperature dependent fluorescence spectra were measured with a homemade cooling apparatus that allows simultaneously freezing and controlling the temperature of four samples in quartz cuvettes by pumping cold nitrogen gas through the cryostat. The temperature precision