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1,3-Bis(phenylamino)squaraine – Photophysical and photochemical properties

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ABSTRACT

A novel squarylium dye possessing donor–π–acceptor structure that features a fixed imine phenyl ring as an electron donor and 3,4-dihydroxycyclobut-3-ene-1,2-dione moiety as an electron acceptor was synthesized. The structure of the dye was elucidated by means of NMR and IR spectroscopy and elemental analysis. The compound was studied using steady-state absorption and emission spectroscopy, as well as the time-resolved spectroscopy. The measurements were carried out in solvents of different polarity. The dye absorbs in the visible light region about 400 nm and emits light with low fluorescence quantum yield, below 1×10^{-3} M. An increases polarity of solvent results in a blue-shift of absorption band and red-shift of emission band, respectively.

The rate constants of radiative and non-radiative deactivation of excited state depend on the viscosity of solvent used. The bimolecular quenching of excited singlet state of squaraine depends on the rate of diffusion process.

1. Introduction

Squarylium dyes often also called squaraines are derived from quadratic acid (squaric acid). According to IUPAC nomenclature they are derivatives of 1,2-dihydroxycyclobuten-3,4-dione.

There are two types of bis-substituted derivatives of squaric acid: 1,2-bis donor substituted and 1,3-bis donor substituted. The merocyanines belong to the first group are essentially and have no distinctive properties, whereas the second type represents an unique group of chromophore, which is neither a merocyanines nor cyanine and has exceptional light absorption characteristics [1]. The most of very important squarylium dyes possess an arylamine or a heterocyclic moiety as the end electron donating groups. The symmetric D–A–D (donor–acceptor–donor) arrangement of squaraine dyes has an interesting effect on the formation of intramolecular charge-transfer states. Basing on the Kamat's and et al. studies [2] on the photochemistry of bis[4-(dimethylamino)phenyl] squaraine and quantum chemical calculations may be suggested that 1,3-bis(aminophenyl)squaraine is polarized, with the phenylimino moiety being an electron donor (D) and the central C_4O_2 unit being an electron acceptor. The squaraines also form a solute–solvent complex in organic solvents, the equilibrium constant of which is dependent on D–A–D charge-transfer character of the squaraine [2]. The next feature of squaraine is the emission from the three different excited states, e.g. free squaraine, solute–solvent complex, and a twisted excited state as a result of C–C bond rotation [2].

Squaraines belong to so-called photosensitizing dyes, that absorb strongly in the visible light region and are very important for various imaging applications and solar energy conversion [2,3].

The dye under study was synthesized by a condensation reaction of squaric acid and aniline. A characteristic feature of this compound is a presence of nitrogen atom in the system of conjugated double bonds. There are not any amine and iminium terminals in dye structure. Form our knowledge, such compounds are very rare described in literature. Therefore, in order to improve the knowledge on the physicochemical properties of squaraines, the synthesis and spectroscopic properties of 1,3-bis(phenylamino) squaraine are described in article.

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2. Experimental

2.1. Materials and general methods

All reagents and solvents (spectroscopic grade) were purchased from Aldrich (Poland) and used without further purification.

^{1}H spectra was recorded in DMSO-d_6 on a Bruker Ascend™ spectrometer operating at 400 MHz. Chemical shifts are reported in ppm using tetramethylsilane TMS as an internal standard. Coupling constants (J) are given in Hz.

IR spectra were recorded on a Bruker Vector 22 FTIR Spectrophotometer (Germany). Samples were prepared by mixing FTIR-grade KBr (Sigma–Aldrich) with 1% (w/w) of dye, and grinding to a fine powder. Spectra were recorded over the 400–4000 cm^{-1} range. Characteristic absorptions are given in cm^{-1}.

The elemental analysis was made with a Vario MACRO 11.45-0000, Elemental Analyzer System GmbH (Germany), operating with the software VARIOEL 5.14.4.22.

Melting point was measured on the Boëthius apparatus (type PHMK 05, Germany).

Absorption and emission spectra were recorded at room temperature using an Agilent Technology UV–vis Cary 60 Spectrophotometer, a Hitachi F-7000 spectrofluorimeter and UV–VIS-NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon), respectively. The spectra were recorded in following solvents: water (H_2O), dimethylsulfoxide (DMSO), acetonitrile (CH_3CN), *N*,*N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (MP), methanol (MeOH), ethanol (EtOH), acetone, tetrahydrofuran (THF) and diethyl ether. The final concentration of the dye in the solution was 1.0×10^{-5} M. The spectroscopic measurements were performed in mentioned above solvents containing 10% of 1-methyl-2-pyrrolidinone. For this purpose a suitable amount of the dye was dissolved in 1-methyl-2-pyrrolidinone, than 0.1 mL of the concentrated (ca. 1 mM) stock solution was added to a 10 mL volumetric flask containing spectroscopic grade solvents under the study. They were characterized by a static dielectric constant (ε) and a refractive index (n) at 20 °C. The solvent polarity function $f(\varepsilon,n)$ is given by Eq. (1) [1].

$$f(\varepsilon,n) = \frac{(2n^2+1)}{(n^2+2)} \cdot \left[\frac{(\varepsilon-1)}{(\varepsilon+2)} - \frac{(n^2-1)}{(n^2+2)}\right] \quad (1)$$

The fluorescence quantum yield for the dye in solvents were determined as follows. The fluorescence spectra of a diluted dye solution (A ≈0.1 at 366 nm) was recorded by excitation at the maximum of absorption band of the standard. Dilute Coumarin I ($\Phi = 0.64$) was used as referene [5]. The fluorescence spectra of Coumarin I was obtained by excitation at 366 nm. The fluorescence quantum yield of dye (ϕ_{dye}) was calculated using Eq. (2):

$$\phi_{\text{dye}} = \phi_{\text{ref}} \cdot \frac{I_{\text{dye}} A_{\text{ref}}}{I_{\text{ref}} A_{\text{dye}}} \cdot \frac{n^2_{\text{dye}}}{n^2_{\text{ref}}} \quad (2)$$

where: ϕ_{ref} is the fluorescence quantum yield of the reference, A_{dye} and A_{ref} are the absorbance of the dye and reference at the excitation wavelength, I_{dye} and I_{ref} are the integrated emission intensity for the dye and reference, n_{dye} and n_{ref} are the refractive indexes of the solvents used for dissolve of dye and reference, respectively.

The fluorescence lifetimes were measured using a single-photon counting system UV–VIS-NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus utilizes for the excitation a picosecond diode laser generating pulses of about 55 ps at 370 nm. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals with a resolution of few picoseconds possible. The dye was studied at concentration able to provide equivalent absorbance at 370 nm (0.2 in the 10 mm cell) to be obtained. The fluorescence decay was fitted to two exponentials.

The fluorescence quenching measurements were performed using a single-photon counting system UV–VIS-NIR Fluorolog 3 Spectrofluorimeter (Horiba Jobin Yvon). The apparatus uses a picosecond diode laser (370 nm) generating pulses of about 50 ps for the excitation. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals in the range of single picoseconds possible. The dye was studied at a concentration able to provide equivalent absorbance at 370 nm (0.2 in the 10 mm cell). The rate constant for the quenching of 1,3-bis(phenylamino) squaraine by all quenchers under studies were determined in 1-methyl-2-pyrrolidinone. The concentration of dye was 2×10^{-5} M and that of the quenchers was in the range from 1×10^{-4} M to 5.0×10^{-3} M. The fluorescence quenching at 440 nm was measured in deaerated solution by bubbling with argon.

2.2. Synthesis

1,3-Bis(phenylamino)squaraine was synthesized according with general method: squaric acid (0.290 g, 2.5 mmol) was heated under reflux in a mixture of 1-butanol (40 mL) and toluene (20 mL), and water was distilled off azeotropically using a Dean–Stark trap. After 1 h, aniline (5 mmol) was added and the reaction mixture refluxed for additional 4 h. The suspension was then cooled to room temperature and the solvent removed on a rotary evaporator. The residue was crystallized from 1-butanol and the solid dried in an oven at 50 °C [1,6].

Dye was obtained as a yellow solid (0.38 g, 59%), mp. 328 °C.

^{1}H NMR (DMSO-d_6), δ (ppm): 7.1196–7.1566 (t, 2H, Ar); 7.3625–7.4021 (t, 4H, Ar); 7.7874–7.8073 (d, $J = 7.96$ Hz, 4H, Ar); 11.2766 (s, 2H, –NH–).

IR (KBr) ν (cm^{-1}): 3087.87, 3058.58, 2992.99, 2967.42 (=C–H); 2777.99, 2746.84, 2680.45 (NH_2^+); 1615.30, 1591.09 (C=O); 1552.29 (N–H); 1499.64, 1450.55, 1425.97, 1410.77 (C–C); 1337.62, 1317.78, 1294.63 (N–C); 1261.90, 1245.62, 1184.03, 1164.73, 1145.56, 1098.39, 1079.20 (C–O); 825.69, 751.13, 688.38 (“oop”); 825.69 (substituent para).

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.73; H, 4.545; N, 10.606. Found: C, 72.66; H, 4.558; N, 10.561.

2.3. Computational details

Gaussian 09 [7] software package was used for calculations.

For the optimization of geometry of the ground and first excited state of the **SQ** dye molecule the B3LYP/6-311++G(d,p) method was used. Frequencies analysis were performer at the same level. All calculations were performed in the gas phase (no intermolecular interactions were considered). For visualization of the surfaces of molecular orbitals the Gabedit software [8] was used.

3. Results and discussion

3.1. Synthesis

Structure and purity of 1,3-bis(phenylamino)squaraine was confirmed by FTIR, ^{1}H NMR spectroscopy, elemental analysis and thin layer chromatography. The data were found be in good agreement with the structure of dye. The ^{1}H NMR spectra of dye shows characteristic bands in the region of $\delta = 1.0$–9 ppm. In the region the signals characteristic for the protons in benzene ring, cyclobut-3-ene-1,2-dione ring, and the imino group are present.