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The synthesis and proton-induced spectral switching of a novel azine dye and its boron complex

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ABSTRACT

An azine dye and its boron complex were synthesized and their structures were confirmed using elemental analysis, UV–Vis, fluorescence, mass and ¹H NMR spectroscopic techniques. The effects of protonation/deprotonation on the absorption and emission characteristics of the two dyes were determined. The observed effects of pH upon the colour of the dyes were interpreted in terms of electron density distribution and intramolecular charge transfer.

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PIĞMĔNTS

1. Introduction

Azine dves have attracted attention as potential coordinating ligands [1–9] and offer several biological applications, including the preparation of chemically modified electrodes (CME's) for the amperometric detection of the reduced form of the coenzyme NaDH, mono and binuclear cationic complexes as DNA probes and identification of cells using the positive myeloperoxidase reaction [1,4,10–13]. This work concerns the synthesis of a novel azine dye 5 and corresponding boron complex 6, as such boron complexes characteristically display strong absorption and sharp emission peaks in high quantum yield [2,14,15]. The color switching ability of the dyes, induced by protonation and deprotonation, was determined and interpreted in terms of the transformation of the donor-acceptor-donor (D-A-D) configuration [16-19] of the azine dye to a D-A molecular architecture (Scheme 1), as evidenced by changes in the corresponding electron density distribution within the azine dye.

2. Experimental

2.1. Characterisation

Elemental analyses were recorded using a Carlo Elba Model 1106 analyzer, mass spectra were recorded on a Shimadzu QP-1000 and FAB mass spectra were obtained using a JMS700. ¹H NMR spectra were obtained using a Varian Inova 400 MHz FT-NMR employing TMS as internal standard. UV-Vis absorption spectra were recorded on an Agilent 8453 spectrophotometer and fluorescence spectra were measured using a Shimadzu RF-5301PC spectrophotometer. Fluorescence quantum yields were determined using fluorescein ($\Phi_{\rm F}=$ 0.90, acetonitrile as the solvent) as reference. Quantum chemical calculations based on DFT were carried out using the Dmol³ module installed in a *Materials Studio* 4.4 package (Accelrys Inc.) [20,21], employing Perdew–Burke–Ernzerhof (PBE) functions of generalized gradient approximation (GGA) level [22]. Chemicals were purchased from Aldrich; all solvents were analytically pure and were used without drying or purification. The effect of protonation and deprotonation on the azine dyes was determined by the step-wise addition of a 1×10^{-5} molL⁻¹ aq solution of tetrabutyl ammonium hydroxide or 1×10^{-5} molL⁻¹ aq HCl solution.



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Scheme 1. Synthetic route used.

2.2. Synthesis (Scheme 1)

2.2.1. Compound 3

Salicylaldehyde **1** (0.9 g, 8.2 mmol) and hydrazine **2** (caution: may pose explosion hazard, especially if heated; incompatible with sources of ignition, light, shock, strong oxidizing agents, strong acids, metal oxides; 2.67 g, 53.3 mmol) were dissolved in 4 ml of methanol with stirring. After the formation of a white dispersion, the reaction mixture was filtered under reduced pressure and the ensuing white solid was washed in hexane and dried.

Yield 70%. ¹H NMR(400 MHz) DMSO-*d*₆: δ 5.42 (s, 2H, -NH₂), 6.87 (t, *J* = 7.32 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.56 Hz, 1H), 7.18 (t, *J* = 7.32 Hz, 1H), 11.09(s, 1H, -OH). M⁺ = 136.

2.2.2. Dye 5

3 (0.5 g, 3.7 mmol) and 4-dimethylamino-benzaldehyde 4 (0.55 g, 3.7 mmol) were dissolved in 60 ml of methanol and the reaction mixture was refluxed for 7 h at the end of which time, a yellow solid precipitated. The yellow solid (**5**) was filtered, dried and chromotographed on silica gel.

Yield 77%. ¹H NMR(400 MHz) DMSO-*d*₆: δ 3.00 (s, 6H), 6.76 (d, *J* = 8.32 Hz, 2H), 6.92–6.98 (m, 2H), 7.33 (t, *J* = 7.56 Hz, 1H), 7.58 (d, *J* = 7.84 Hz, 1H), 7.68 (d, *J* = 8.36 Hz, 2H), 8.60 (s, 1H), 8.85 (s, 1H), 11.53 (s, 1H, -OH). EA: anal. calcd. C₁₆H₁₇N₃O: C; 71.89, H; 6.41, N; 15.72. found C; 71.78, H; 6.55, N; 15.42%. M⁺ = 267 Quantum Yield: $\Phi_F = 0.007$.

2.2.3. Dye 6

5 (0.1 g, 0.37 mmol) was dissolved in 10 ml of toluene under N₂; 10 ml of triethylamine was added to the reaction solution at room temperature and $BF_3O(CH_2CH_3)_2$ (0.7 ml, 5.55 mmol) was then added over 10 min. The ensuing orange solid was filtered under reduced pressure, washed using distilled water, dried and chromotographed on silica gel.

Yield: 76% ¹H NMR (400 MHz, CDCl₃): δ 3.08 (s, 6H), 6.69 (d, J = 9.08 Hz, 2H), 6.99 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 8.32 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 8.6 Hz, 1H), 7.71 (d, J = 8.84 Hz, 2H), 8.61(s, 1H), 8.96 (s, 1H). EA: anal. calcd. C₁₆H₁₆BF₂N₃O: C 60.98, H 5.12, N 13.33, Found C 60.95, H 5.24, N 13.11%. FAB mass: M⁺ = 315.1. MH⁺ = 154(matrix base peak, 2-nitrobenzylalcohol) Quantum Yield: $\Phi_{\rm F} = 0.04$.

3. Results and discussion

The effects of protonation and deprotonation on the colorimetric, chemosensing properties of a 1×10^{-5} M solution of **5** in

CH₃CN were investigated. Upon the addition of acid, the main absorption peak at 380 nm decreased and a new peak at 460 nm appeared; simultaneously, fluorescence emission intensity decreased (Fig. 1). The observed acid-induced changes in the absorption and emission behavior of **5** can be attributed to protonation of the dye **5a**. The observed changes in emission and



Fig. 1. Absorption and emission changes for a 1 \times 10 $^{-5}$ M solution of 5 in CH_3CN imparted by protonation and deprotonation.

absorption (i.e., transformation of **5** to **5a**) was reversible by adjustment of pH.

Fig. 2 shows the effect of pH on the absorption and emission properties of the boron complex-azine dye chromophore **6** from which it is apparent that similar results were obtained to those secured using **5** insofar as the absorption peak at 395 nm decreased and a new absorption peak at 460 nm appeared. In the case of the boron complex **6**, the maximum absorption peak shifted from 380 nm, which was identical to that found for **5**, to 395 nm; the new absorption peak at 460 nm was also the same as that observed for dye **5**. Once again, adjustment of the pH resulted in reversible emission and absorption imparted by protonation/deprotonation.

Software was used to calculate the electron density distribution and related energy potential of the push-pull, intramolecular charge transfer operating in both the donor-acceptor-donor (D-A-D) and donor-acceptor (D-A) configurations of **5** and **5a**. From Fig. 3 it is apparent that that in the HOMO state, the electron density of **5a** is greater in the benzene ring which bears the -OHand $-N(CH_3)_2$ groups, namely the donor moieties. However, in the LUMO state of **5**, the electrons in the donor moieties are fewer and the electron density within the acceptor units is greater. Thus, D-A-D intramolecular charge transfer determines the chromogenic properties of **5**.



Fig. 2. Absorption and emission changes of a 1×10^{-5} M solution of 6 in CH_3CN with imparted by protonation and deprotonation.



Fig. 3. Electron distribution of HOMO and LUMO energy levels in 5 and 5a.

However, different characteristics were observed in the case of the protonation/deprotonation of **5**. The addition of acid to a solution of **5** converts the D–A–D configuration to a D–A molecular system. In the protonated derivative, **5a**, the protonated dimethylamine groups cannot act as a donor and, therefore, electron density is highest within the donor part of the HOMO state and within the acceptor part of the LUMO state (Fig. 3).

The energy potential values of **5** in both HOMO and LUMO states were compared. As shown in Fig. 1, protonation shifted the absorption band bathochromically in the D–A configuration, the corresponding energy levels being: HOMO (-2.349)/LUMO (-4.548) in the D–A–D configuration and HOMO (-7.345)/LUMO (-5.682) in the D–A configuration. The low excitation energy gap of 1.663 for the D–A system obtained for **5a** fitted well with the observed maximum absorption wavelengths in terms of the decrease in the peak at 380 nm and the increase in the peak at 460 nm.

4. Conclusions

A novel azine dye and its boron complex were synthesized and their effect of pH on absorption/emission character were studied and interpreted using electron density distribution software. Upon the addition of acid, the main absorption peak of **5** at 380 nm decreased and a new peak at 460 nm appeared. In the case of the born complex, **6**, the absorption peak at 395 nm decreased and a new absorption band at 460 nm appeared. The maximum absorption peak of dye **6** shifted from 380 nm, which was identical to that observed for **5**, to 395 nm. The donor–acceptor–donor (D–A–D) configuration of **5** was transformed by the addition of acid to a D–A configuration. The electron distributions of both the HOMO and LUMO energy states were computationally calculated and showed that the lower energy gap for **5a** fitted well with the observed maximum absorption wavelengths.

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