



Highly sensitive sensing of volatile organic compound ethylamine



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ABSTRACT

Two new hemicyanine dyes with dihydroxybenzene moiety as a donor group have been investigated in terms of interacting with volatile organic compounds (VOCs) EtNH₂. The sensing behavior of the hemicyanines toward EtNH₂ was studied by UV–vis absorption spectroscopy. Different sensing mechanism of the dyes to EtNH₂ was confirmed by ¹NMR studies, together with theoretical calculations based on DFT and PPP-MO methods. We have also investigated the fast EtNH₂ gas sensing of these dyes loaded poly(acrylonitrile) nanofiber. Reversible response and recovery were achieved using alternating gas exposure. This system shows a fast EtNH₂ gas sensing within 5 s.

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1. Introduction

Recently there is an increased awareness of the importance to detect specific volatile organic compounds (VOCs) especially for indoor air quality control but also in food processing industry [1]. Determination of VOCs discharged from industries, vehicles, homes, and living organisms is of particular concern, because they can cause serious impacts on the environment and public health. A wide range of amines are pollutants in industrial and manufacturing areas because they are extensively used in the preparation of fertilizer, herbicides, pharmaceuticals, surfactants, rubber latex, biological buffer substances and colorants. Turner et al. investigated the ability of a hemithioacetal-based polymer to react with primary amines and to form a fluorescent isoindole complex [2]. They are toxic both in the gas phase and dissolved in liquid. Because of their extensive use in industries, it is necessary to develop new and effective sensors for amines. Amine compounds have been found at trace levels in the atmosphere. Many analytical methods have been developed for the separation and determination of amines such as isotachopheresis [3], ion chromatography [4], thin-layer chromatography, gas chromatography [5,6], high-performance liquid chromatography [7], and capillary electrophoresis [8]. Recently, various optical-sensing methods are also widely used for the detection of amines [9–11]. Mono-, di- and tri-

ethylamines have especially been postulated to be involved in atmospheric nucleation, i.e. the natural process whereby new particles are generated [12]. Among various types of amines, EtNH₂ is a colorless, flammable liquid and an ammonia-like odor. It has an air odor threshold concentration of 0.95 ppm of air. Inhalation exposure to EtNH₂ may cause eye irritation, tearing, conjunctivitis, and corneal edema. Qiu et al. worked with a supramolecular metal-organic framework (MOF) constructed by two-dimensional infinite coordination polymers, [Zn(1,4-benzenedicarboxylate)(H₂O)]_m, and they evaluated the fluorescence response of the MOF nano-sheets in the presence of EtNH₂ solution [13]. We have previously reported the colorimetric signaling of mono-, di-, and tri-ethylamine based on intermolecular charge-transfer interaction [14] and have also described the ultrafast EtNH₂ gas sensing of 2-chloro-3,5-dinitrobenzotrifluoride loaded poly(acrylonitrile) nanofiber based on an intermolecular charge-transfer complexation [15]. This system showed a fast EtNH₂ gas sensing with 0.4 s. We report herein the synthesis and highly sensitive EtNH₂ sensing properties of hemicyanine dyes.

2. Experimental

2.1. Materials and methods

2-Methylbenzothiazole, 2,3,3-trimethylindolenine, 2,5-dihydroxybenzaldehyde, were purchased from Sigma–Aldrich. The rest of chemicals were commercially available with high grade and were used without further purification. 2,3-

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Dimethylbenzothiazolium iodide **2** and 1,2,3,3-tetramethylindolenium iodide **3** were obtained by synthesis according to the literature methods [16].

2.2. Instruments

Melting points were determined using an Electrothermal IA900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Erba Model 1106 analyzer. Mass spectra were recorded on a JMS-700 high resolution mass spectrometer using an FAB ion source. ^1H NMR spectra were recorded on Varian Unity Inova 400 MHz FT-NMR spectrophotometer with TMS as internal standard. The UV–Vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Calculation of the HOMO and LUMO energy levels and electron densities were carried with PiSystems XTE ver. 6.2 package and Material Studio 4.3 program.

2.3. Synthesis of dye **1** and **2**

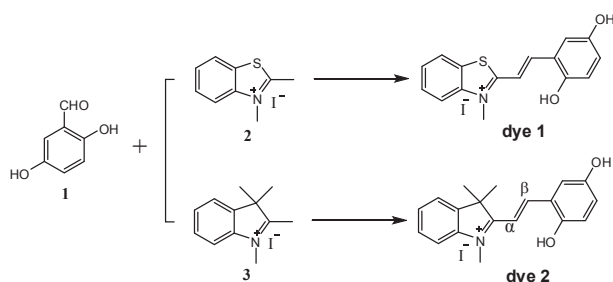
A mixture of 2,5-dihydroxybenzaldehyde **1** (0.3 g, 2.17 mmol), 2,3-dimethylbenzothiazolium iodide **2** (0.6 g, 2.12 mmol), and absolute ethanol (20 mL) was refluxed for 4 h under a nitrogen atmosphere. After cooling, the crude product was filtered and recrystallized from ethanol. Yield: 10%.

^1H NMR (400 MHz, DMSO- d_6): δ 4.30 (s, 3H, N^+-CH_3), 6.86 (d, $J = 8.8$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 1H), 7.37 (d, $J = 2.84$, 1H), 7.91–7.76 (m, 3H), 8.25–8.19 (m, 2H), 8.38 (d, $J = 7.44$ Hz, 1H), 9.18 (s, 1H, –OH), 10.24 (s, 1H, –OH). EA: anal. calcd. $\text{C}_{16}\text{H}_{14}\text{INO}_2$: C 46.73, H 3.43, N 3.41, S 7.80, Found C 46.39, H 3.42, N 3.70, S 7.77%. $[\text{M}]^{+1} = 284.3$. mp: 281–282 °C.

Dye **2** was obtained using similar procedure. Yield 16%. ^1H NMR (400 MHz, DMSO- d_6): δ 1.74 (s, 6H, $-(\text{CH}_3)_2$), 4.08 (s, 3H, $-\text{N}^+-\text{CH}_3$) 6.87 (d, $J = 8.84$ Hz, 1H), 6.99 (d, $J = 8.84$ Hz, 1H), 7.47 (s, 1H), 7.57–7.65 (m, 3H), 7.86–7.89 (m, 2H), 8.48 (d, $J = 16.36$ Hz, 1H), 9.23 (s, 1H, –OH), 10.42 (s, 1H, –OH). EA: anal. calcd. $\text{C}_{19}\text{H}_{20}\text{INO}_2$: C 54.17, H 4.79, N 3.32, Found C 53.94, H 4.83, N 3.29%. $[\text{M}]^{+1} = 294.3$. mp: 266–268 °C.

3. Results and discussion

Hemicyanine dyes are widely applied in different areas of technology due to their diversified properties. Because of their excellent spectroscopic properties of large molecular extinction coefficient ($\epsilon = 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and good fluorescence quantum yield, they are commonly used as laser dyes and fluorescence probes. We have developed new hemicyanine dye **1** and **2** in which dihydroxybenzene moiety was connected through a conjugated system with the acceptor moiety. Aromatic aldehydes react with compounds possessing active methylene groups giving the hemicyanine dyes [17]. The synthesis of dye **1** and **2** was performed by condensation reaction as shown in Scheme 1, the key intermediates



Scheme 1. Synthesis of dye **1** and dye **2**.

2,3-dimethylbenzothiazolium iodide **2** and 1,2,3,3-tetramethylindolenium iodide **3** were synthesized by the reaction of methyl iodide with 2-methylbenzothiazole and 2,3,3-trimethylindolenine, respectively.

The analytical characterizations were conducted by ^1H NMR, MS and elemental analysis to the obtained dyes. For the interpretation of the ICT process of dye **1** and dye **2**, the quantum chemical DMol³ approach was used. All the theoretical calculations were performed by DMol³ program in the Materials Studio 4.4 package [18,19] which is the quantum mechanical code using density functional theory. Perdew–Burke–Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [20] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital.

Fig. 1 displays the calculated and optimized electron density distribution and HOMO/LUMO energy levels of dye **1** and **2**. Comparison of the electron distribution in the frontier MOs reveals that the HOMO–LUMO excitation moves the electron distribution from the dihydroxybenzene moiety to the acceptor, which showed an electron density migration of ICT character of these dyes. Upon addition of EtNH₂ to the solution of dye **1**, the absorption band at 359 and 442 nm progressively decreased in intensity and a new peak at 589 nm appeared; an isobestic point at 497 nm also developed. The appearance of this isobestic point suggests that at least one stable dye **1**-EtNH₂ species is present in solution (Fig. 2(a)). Analysis of the adduct formation, studied by the changes in absorption spectra on addition of EtNH₂, indicated a 1:2 dye to EtNH₂ stoichiometry (Fig. 2(a) inset).

This finding can be supported by Fig. 1(a). In Fig. 1, the resulting energy gap between HOMO and LUMO with EtNH₂ addition was decreased from $\Delta E = 1.526$ eV to $\Delta E = 1.349$ eV that of the dye **1**-EtNH₂ is smaller than that of dye **1**. This means that the dye **1**-EtNH₂ is expected to exhibit the bathochromic absorption compared with that for dye **1**. The dihydroxybenzene part of dye **1** has two OH fragments that can be form intermolecular proton transfer complexes with the EtNH₂. The large changes in the absorption spectrum by the addition of EtNH₂ implied that the electron-donor O[−] promote the ICT process. The bathochromic changes in absorption spectra associated with the formation of dye **1**-EtNH₂ species is due to the delocalization of π -electrons on the entire molecule. To confirm the nature of the intermolecular proton transfer between dye **1** and EtNH₂, the ^1H NMR spectrum of dye **1** was recorded in the absence and presence of EtNH₂ (Fig. 3).

As shown in Fig. 3, original OH protons of dye **1** appear at 9.18 and 10.24 ppm; however, EtNH₂ addition leads to an upfield shift. With addition of EtNH₂, the olefinic and aromatic protons showed an upfield shift due to the OH–N bond formation which increased the electron density of the olefinic and phenyl ring. These results indicate that an intermolecular proton transfer between dye **1** and EtNH₂ is formed. The olefinic H_b proton of the dye **1**-EtNH₂ adduct shows a large upfield shift, indicating that the interaction of H_b with C=O produces an intermolecular hydrogen bonding.

Fig. 2(b) shows the changes in the absorption spectra of the originally yellow colored solution of 5×10^{-5} M dye **2** in 1:1 DMSO:water imparted by the addition of 0–1.5 equivalents of EtNH₂, from which it is apparent that the absorbance of the dye **2** at 373 and 462 nm gradually decreased with increasing concentration of EtNH₂ and the color of the solution changed from yellow to colorless. The detection limits of dye **1** and **2** for EtNH₂ were found to be 1×10^{-4} M and 7.5×10^{-5} M, respectively. The absorption spectral change of dye **2** upon EtNH₂ addition is due to the nucleophilic addition between EtNH₂ and C _{α} =C _{β} (in Scheme 1) of dye **2**. To explain this finding, it is approached to consider EtNH₂ addition behavior toward dye **2** molecule, namely nucleophilic addition effect. The nucleophile of EtNH₂ can react to the α position, where α

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