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Photochromism of Schiff base compounds derived from N,N'-bis(2-aminophenyl)isophthalamide: Structure and photosensitivity

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ABSTRACT

The photochromic behaviors of four Schiff bases derived from N,N'-bis(2-aminophenyl)isophthalamide were studied to reveal the substituent effect on the photosensitivity. On UV radiation, all of compounds **1–4** exhibit photochromic behavior in solution through intramolecular hydrogen atom transfer, and the tautomerism equilibrium moved toward the keto-form. The solution and solid state fluorescence were also studied. After irradiated by 254 nm UV light, the solution fluorescence emission of compounds **1** and **4** went down, but the fluorescence emission intensified for compound **3**. The solid state fluorescence (ss-FL) emission of compound **1** went down after UV irradiation. However, the ss-FL emission of **3** and **4** did not show any observable difference before and after UV irradiation. The influences of solvent, wavelength of irradiation and acidity on the adsorption spectra of the title compounds were also investigated. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.

1. Introduction

Photochromic compounds, which can switch reversibly between two forms by light excitation at certain wavelength, have great potential for optoelectronic applications such as optical memory and switches [1–9]. During the past decades, many types of photochromic compounds have been synthesized and characterized, such as diarylethenes, fulgides and azobenzene. Among these, the Schiff bases are one of the most important categories. The typical photochromic behavior of Schiff bases is the photo-induced alteration of molecular structure based on inherent enol-keto tautomerism (Scheme 1) [10–14]. In general, the ortha-hydroxyl imine unit in molecular structure is a prerequisite for the tautomerism of Schiff bases [15]. However, Herzfeld pointed out that the enol-keto tautomerism may also exist in para-hydroxyl imine type Schiff bases through solvent-conducted proton transfer [16]. Many photochromic products of Schiff bases are unstable in solution and only transient adsorption spectra can be detected by laser flash photolysis technique [17]. To investigate the substituent effect on the photosensitivity, four Schiff bases were synthesized and their photochromic behaviors were studied. Schiff base compounds 1-**4** were prepared by the usual condensation of aldehyde with N,N'-bis(2-aminophenyl)isophthalamide (Scheme 2).

2. Experimental method

2.1. Reagents and apparatus

Chemicals were purchased from ACROS and used without further purification, except for chloroform was distilled before use. The ¹H NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer, with DMSO-d₆ as solvent. ESI-MS or APCI-MS spectra were recorded on a ThermoFinnigan Decax-30000 machine. Elemental analyses were performed on a Elementar Vario-III elemental analyzer. IR spectra were measured on Nicolet Avatar 360 spectrometer as KBr discs. The UV–vis adsorption spectra were recorded on a XinMao UV-750PC spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-55 luminescence spectrophotometer.

2.2. Material and preparation

2.2.1. Synthesis of N,N'-bis(2-aminophenyl)isophthalamide (5)

Compound **5** has been reported in previous paper [18], here it was synthesized by a different route. Isophthalic acid (0.33 g, 2 mmol) and o-phenylenediamine (1.73 g, 16 mmol) were dissolved in a mixed solvent of 10 ml of DMF and 10 ml of CH_2Cl_2 . The mixture was placed in an ice bath and then NMM (1.1 ml, 10 mmol), HOBt (0.65 g, 4.8 mmol) and EDC (0.92 g, 4.8 mmol) were added successively. The mixture was stirred under ice bath for one more hour, and then stirred under room temperature for 24 h. To the mixture 10 ml of CH_2Cl_2 was added, and then the

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Scheme 1.

solution was washed with water for three times. The organic layer was collected and the CH₂Cl₂ was removed by vacuum. The residue was washed by 5% NaHCO₃, water and 30% ethanol successively to give the pure 5. Yield 71%; mp: 201–202 °C. ESI-MS (-): m/ $z = 345.1 ([M-H]^{-}).$

2.2.2. General procedure for the synthesis of compounds 1-4

Compound 5 (0.069 g, 0.2 mmol) and a corresponding aldehyde (0.4 mmol) were dissolved in 15 mL of ethanol and the mixture was refluxed for 6 h, the precipitate was filtered and washed by ethanol.

Experimental data for 1: compound 1 was prepared from 5 and 2-hydroxybenzaldehyde in 59% yield. mp: 213–215 °C; IR(KBr, cm⁻¹): 3276, 1664, 1653, 1613, 1521, 1447, 756; ¹H NMR (400 MHz, DMSO-d₆) δ: 12.85 (s, 2H, -OH), 10.23 (s, 2H, -NH), 8.93 (s, 2H, -CH=N), 8.53 (s, 1H, ArH), 8.16 (d, J = 7.6 Hz, 2H, ArH), 7.72-7.66 (m, 5H, ArH), 7.50-7.48 (m, 2H, ArH), 7.38-7.34 (m, 6H, ArH), 6.94 (t, *J* = 7.2 Hz, 2H, ArH), 6.85 (d, 2H, *J* = 8.4 Hz, ArH); ESI-MS (+): m/z = 555.1 ([M + H]⁺). Anal. Calcd.% for C₃₄H₂₆N₄O₄: C, 73.63; H, 4.73; N, 10.10. Found C, 73.51; H, 4.90; N, 10.19.

Experimental data for 2: compound 2 was prepared from 5 and Vanillin in 65% yield. mp: 215–216 °C; IR(KBr, cm⁻¹): 3373, 1666, 1590, 1516, 1448, 1290; ¹H NMR (400 MHz, DMSO-d₆) δ : 10.07 (s, 2H, -OH), 9.83 (s, 2H, -NH), 8.65 (s, 2H, -CH=N), 8.58 (s, 1H, ArH), 8.28-8.20 (m, 4H, ArH), 7.72-7.66 (m, 3H, ArH), 7.44-7.39 (m, 4H, ArH), 7.31 (t, J = 7.2 Hz, 2H, ArH), 7.23 (t, J = 7.2 Hz, 2H, ArH), 6.88 (d, J = 8.0 Hz, 2H, ArH), 3.79 (s, 6H, -OCH₃); APCI-MS (+): m/z = 615.3 ([M + H]⁺). Anal. Calcd.% for C₃₆H₃₀N₄O₆: C, 70.35; H, 4.92; N, 9.12. Found C, 70.46; H, 4.81; N, 9.30.

Experimental data for 3: 3 was prepared from 5 and 2-hydroxy-3-methoxybenzaldehyde in 70% yield. mp: 221–223 °C; ¹H NMR (400 MHz, CDCl₃) δ: 14.47 (s, 2H, -OH), 9.27 (s, 2H, -NH), 8.84 (s, 1H, ArH), 8.44 (d, 2H, CH=N), 8.25 (d, 2H, ArH), 7.92(s, 2H, ArH), 7.74-7.70 (t, 1H, ArH), 7.44-7.40 (t, 2H, ArH), 7.27-7.19 (m, 4H, ArH), 6.76-6.72(t, 2H, ArH), 6.53 (d, 4H, ArH), 2.95 (s, 6H, $-OCH_3$; APCI-MS (-): m/z = 613.4 ([M-H]⁻). Anal. Calcd.% for C₃₆H₃₀N₄O₆: C, 70.35; H, 4.92; N, 9.12. Found C, 70.21; H, 4.83; N. 9.26.

Experimental data for 4: compound 4 was prepared from 5 and 2-hydroxy-1-naphthaldehyde in 63% yield. mp: 283–284 °C; ¹H NMR (400 MHz, DMSO-d₆) δ: 10.40 (s, 1H, -OH), 9.77 (s, 2H, --NH), 9.56 (d, 1H, --OH), 8.76(s, 1H, CH=N), 8.59 (s, 1H, CH=N), 8.43–6.60 (m, 24H, ArH); ESI-MS (–): m/z = 653.7 ([M–H][–]). Anal. Calcd.% for C₄₂H₃₀N₄O₄: C, 77.05; H, 4.62; N, 8.56. Found C, 77.46; H, 4.53; N, 8.43.

3. Results and discussion

3.1. Spectral studies of the compounds under light irradiation

The irradiation time-dependent adsorption spectra of compounds 1-4 were shown in Fig. 1. The irradiation to the solution of 1 with 254 nm UV light turned the colorless solution into yellow, and a new adsorption band appeared near 400 nm and intensified with irradiation time (Fig. 1a). This adsorption band was attributed to the trans-keto-form. Concurrently, the adsorption band around 275 nm aroused from the $\pi \rightarrow \pi^*$ transition of imine unit of enolform went down with irradiation time [19]. The four clear isosbestic points at 254, 309, 359 and 368 nm, respectively indicated the presence of a two-component equilibrium system in the solution. When irradiated by 365 nm UV light, the solution of compound **1** turned into light-yellow in color, and then changed back to colorless as soon as the light was off. The adsorption spectra after irradiation did not have any changes. The 365 nm light may have induced compound 1 to switch from enol to cis-keto-form, which was unstable and readily switched back to enol-form through intramolecular proton transfer. For compound 2, irradiation with 254 nm light also generated a new adsorption peak at 384 nm. Yet, this adsorption peak intensified within 15 s of irradiation time, and then diminished with time (Fig. 1b). This indicated that the keto-form of compound 2 was unstable in the chloroform solution. We thought this to be caused by the -OH presence on the para-site of the imine unit. Therefore compound 2 was unable to take the trans-keto-form (Scheme 2). Furthermore, the hydrogen bond between the hydroxyl H and the methoxyl O in enol-form of compound **2** may have made the tautomerism equilibrium moved toward the enol-imine direction. There was no isosbestic point for compound **2**, indicating the existence of a multi-components equilibrium system in the solution. The keto-form of both 1 and 2 would switch back to enol-form after reflux in chloroform.

On irradiation with UV light, the solution of **3** produced a new adsorption band around 430 nm which may be attributed to the



Scheme 2.



Fig. 1. UV-vis adsorption spectral changes for compounds 1-4 in CHCl₃ solution (5×10^{-5} mol/l) with 254 nm UV light irradiation. Curve 0, before irradiation. (a) Compound 1, irradiation time gap is 10 s; (b) compound 2, the time gap is 5 s; (c) compound 3, the time gap is 20 s; (d) compound 4, the time gap is 10 s;

 $n \rightarrow \pi^*$ transition of keto-form (Fig. 1c) [19], however the intensity of the new generated band is much more weak than that of compound **1**. In compound **3** the hydroxy H atoms formed hydrogen

bonds with the adjacent methoxyl, so it is much more difficult for the intramolecular proton transfer to take place in **3** than in compound **1**.



Fig. 2. Solution fluorescence spectra with 254 nm UV light irradiation ($5 \times 10^{-5} \text{ mol/l}$ in CHCl₃) (a) compound **1**. Left, excitation spectra; right, emission spectra; 1 a and 1a' are before UV irradiation; 1b and 1b' are after UV irradiation for 1 min; (b) compound **3**. λ_{ex} = 346 nm. 1, before irradiation; 2, 3, after UV irradiation for 1 and 2 min, respectively; (c) compound **4**. λ_{ex} = 484 nm. 1, before irradiation; 2, 3, 4, after the irradiation of UV light for 1, 2 and 5 min, respectively.

For compound **4**, there are four adsorption bands around 319, 371, 442 and 476 nm. The adsorptions at 319 and 476 nm may be assigned to the enol-form, while the adsorptions at 371 and 442 nm may be assigned to the keto-form. The absorption bands of the keto-form can be detected before UV irradiation, which may be due to the large dissociation constant of the naphthol hydroxyl. When irradiated by UV light, the enol-adsorption bands around 319 and 476 nm diminished, while the keto-adsorption bands around 371 and 436 nm intensified with irradiation time (Fig. 1d). There are three clear isosbestic points at 294, 350 and 470 nm. The UV light caused the enol-keto tautomerism equilibrium moved toward the keto-form.

The UV-vis spectral studies of the title compounds under UV light irradiation were also conducted in ethanol. The results indicated that all of the compounds were non-photochromic in ethanol. We supposed that the keto-form of the title Schiff bases



Fig. 3. Solid state fluorescence emission spectra of compound **1** (λ_{ex} = 412 nm). 1a' is before irradiation and 1b' is after UV irradiation for 3 min.

were unstable in ethanol and the tautomerism equilibrium readily moved toward the enol-imine form.

The solution and solid state fluorescence spectra of the title compounds were also taken and studied (Figs. 2 and 3). Compound 1 was firstly excited at 362 nm and it had an intense emission at 534 nm. Then the solution was irradiated by a 254 nm UV lamp (20 W) for one minute and the fluorescence spectrum was taken again. The emission at 534 nm went down and blue-shifted to 530 nm. At the same time, the excitation spectra split into two peaks (Fig. 2a). We thought the O–H…N hydrogen bond would no longer be retained in the trans-keto-form (Scheme 1) and the rigidity of the molecular conjugated plane decreased. Therefore the emission intensity decreased. Similar to compound 1, the fluorescence emission of compound **4** in solution also went down after being irradiated with UV light (Fig. 2c). However, for compound **3**, the solution fluorescence emission intensity increased upon UV irradiation, at the same time the maximum emission wavelength blue-shifted to 540 nm (Fig. 2b). In compound 3, the electron pushing methoxyl adjacent to the hydroxyl might stabilize the excited state of the keto-form and resulted in the increase of fluorescence emission.

Compared with **1**, **3** and **4**, the fluorescence emission of compound **2** was very weak (not show here). We believed that the prerequisite for strong fluorescence emission was that the hydroxyl on the ortho-site of the imine unit, which might help in retaining the rigidity of the molecular structure through intramolecular $O-H\cdots N$ hydrogen bond.

The solid state fluorescence emission of compound **1** went down after being irradiated with UV light (Fig. 3). However, the solid state fluorescence spectra of **3** and **4** did not show any observable change upon UV irradiation. We believed that in **3**, the methoxyl involved in intermolecular hydrogen bonding, while in



Fig. 4. UV-vis adsorption spectral changes with titration by base or acid (a) compound 1; (b) compound 2; (c) compound 3; (d) compound 4; 1, Schiff base; 2, 1 + NaOH; 3, 1 + HCl.

4 the naphthyl group involved in the intermolecular π - π stacking interaction. Thus, the strong intermolecular interaction in **3** and **4** prohibited the molecular conformation change upon UV irradiation. So the solid state fluorescence spectra did not change after UV irradiation.

3.2. Deprotonation-protonation

The phenolic group and imine unit are quite sensitive to base and acid. So, the influences of acidity on the UV–vis adsorption spectra of the title Schiff bases were also studied (Fig. 4). When titrated with NaOH, all of the four compounds generated a new adsorption band at longer wavelength (**1** at 405 nm, **2** at 391 nm, **3** at 413 nm and **4** at 430 nm), and these new generated adsorption bands are assigned to the deprotonated forms of the title Schiff bases. The maximum wavelength adsorption bands of the deprotonated forms are quite similar to that of keto-forms induced by UV irradiation (also see Fig. 1). On the other hand, when titrated with HCl, for all the compounds the adsorption bands moved to shorter wavelength with the absorbance diminished. The striking adsorption spectral changes may be caused by the protonation of the imine unit (–CH=NH⁺–).

4. Conclusions

In this paper four Schiff bases have been synthesized and their photochromic behaviors were studied to reveal the substituent effect on the photosensitivity. The influences of the wavelength of UV irradiation, solvent and acidity on the photochromic properties were also investigated. The results indicated that all of the compounds were photochromic in chloroform on irradiation with 254 nm UV light. However, upon 365 nm UV irradiation, none of the compounds displayed photochromic property. The solvent also played a pivotal role on the photochromic behavior; all the title compounds were photochromic in chloroform but non-photochromic in ethanol. The substituent group closed to the imine unit also controlled the shift of the enol-keto tautomerism equilibrium. The results indicated that when the naphthol hydroxyl was presented in the molecular structure of **4**, keto-form could be detected even before UV irradiation; however when methoxyl was presented in compound **3**, the enol-form was much more favored. Furthermore, the methoxyl present in meta-position will enhance the fluorescence emission of keto-form. The influences of acidity on the adsorption spectra were also studied. The results indicated that when titrated by base, the anionic forms of the Schiff bases generated new adsorption bands at longer wavelength, which are quite similar to that of keto-forms induced by UV irradiation.

Acknowledgements

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