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ORIGINAL PAPER

Synthesis, Crystal Structure and Photophysical Properties of Two Reduced Schiff Bases Derived from 5-Aminoisophthalic Acid

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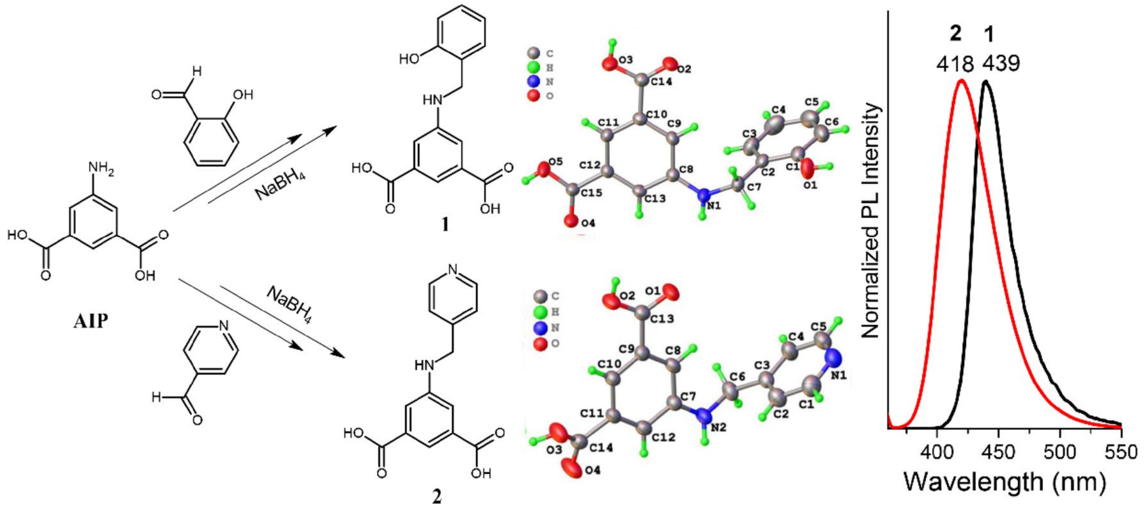
Abstract

Two reduced Schiff bases, namely 5-[(2-hydroxybenzyl)amino]isophthalic acid (**1**) and 5-[(pyridin-4-ylmethyl)amino] isophthalic acid (**2**), were synthesized in two-step method using 5-aminoisophthalic acid as the starting material, and were characterized by single-crystal X-ray diffraction, elemental analysis, infrared, ^{1}H NMR, mass, absorption and fluorescence spectra. Both **1** and **2** crystallize in monoclinic system with space groups $P2_1/c$ for **1** and $P2_1/n$ for **2**. Photophysical properties of both **1** and **2** are significantly different from those of raw material 5-aminoisophthalic acid due to stronger p → π conjugation when one amino hydrogen atom in 5-aminoisophthalic acid is substituted with electron-donor group. **1** displays a very strong narrow-band blue fluorescence with the maximum peak at 439 nm, a high quantum efficiency up to 64%, and a narrow full width at half maximum of 35 nm, while **2** has a broader and weaker fluorescence with the peak at 418 nm and FHWM of about 50 nm.

Graphical Abstract

Two reduced Schiff bases with blue fluorescence were synthesized from 5-aminoisophthalic acid in two-step method including formation of the corresponding Schiff bases and further reduction by $NaBH_4$.



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Keywords Reduced Schiff base · 5-[(2-Hydroxybenzyl)amino]isophthalic acid · 5-[(Pyridin-4-ylmethyl)amino]isophthalic acid · 5-Aminoisophthalic acid · Crystal structure · Photophysical property

Introduction

Schiff bases usually have bright colors, strong fluorescence as well as important physiological functions and have been widely applied as pH sensors, drugs, organic dyes, organic ligands for synthesizing metal complexes [1–5]. Innumerable Schiff bases have been already synthesized in the past several decades [5–7]. Compared with Schiff bases featured with rigid C=N double bond, the structure flexibility of the corresponding reduced Schiff bases obtained through the reduction of rigid C=N double bond to C–N single bond increases significantly accompanying with the change of electronic effect, which will further result in diverse structures and various properties for the formed metal complexes [8–11]. Therefore, the reduced Schiff base has received much attention recently.

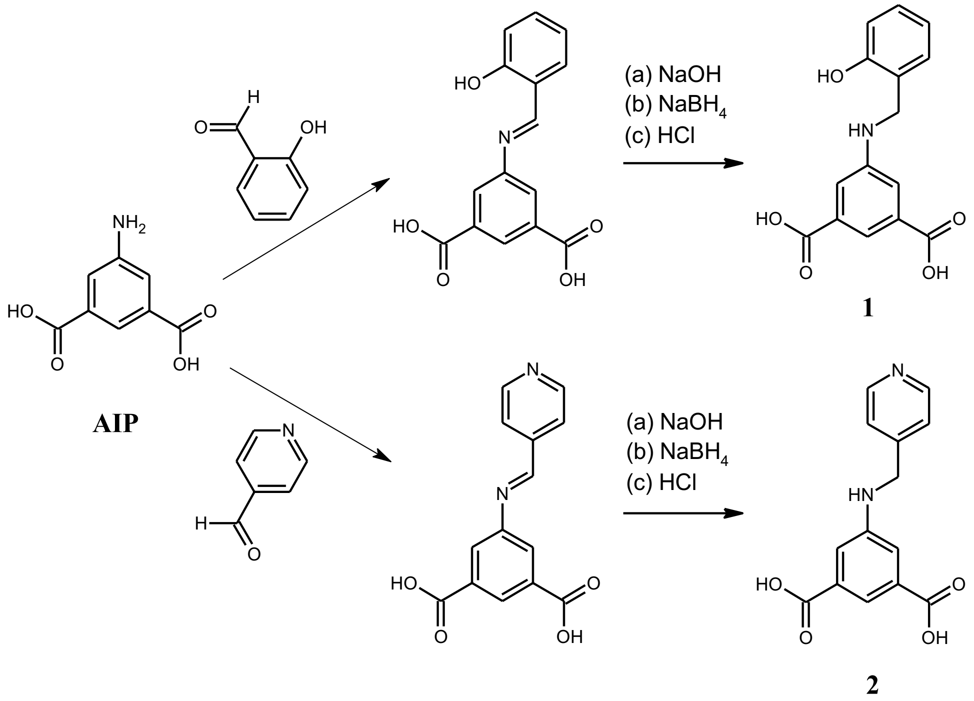
5-Aminoisophthalic acid (AIP) was an important and widely used organic compound with several functional groups including two carboxyl (–COOH) groups and one amino (–NH_2) group, which has been used as organic drug intermediates and organic ligands of metal complexes [12–14]. Due to the present of –NH_2 group, AIP can react with various aldehydes to produce diverse Schiff bases by taking off water molecules, which may further be reduced to the corresponding reduced Schiff bases by some common reducing agents such as $NaBH_4$.

In this paper, two reduced Schiff bases, 5-[(2-hydroxybenzyl)amino]isophthalic acid (**1**) and 5-[(pyridin-4-ylmethyl)amino]isophthalic acid (**2**), were synthesized by using AIP as raw materials, and their single crystals were obtained by recrystallization in *N,N*-dimethylformamide/water mixed solvents. The corresponding synthetic routes for **1** and **2** were displayed in Scheme 1. The crystal structures and photophysical properties of **1** and **2** were further characterized by single-crystal X-ray diffraction, infrared spectrum, nuclear magnetic resonance spectrum (^{1}H NMR), electrospray ion trap mass spectrum, absorption spectrum, fluorescence spectrum and elemental analysis.

Experimental

Materials and Methods

AIP, salicylaldehyde, 4-pyridinecarboxaldehyde, sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH) and hydrochloric acid (HCl, 37 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol and *N,N*-dimethylformamide (DMF) were purchased from Shantou Xilong Chemical Plant. All the commercially available chemicals were of analytical grade and were utilized without further purification.



Scheme 1 Synthetic routes for reduced Schiff bases **1** and **2**

Crystal structure determinations were performed on an Agilent Xcalibur Eos diffractometer for **1** and a Bruker SMART APEX II CCD diffractometer for **2**, respectively. Infrared (IR) spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet 6700 FT-IR infrared spectrometer using KBr pellets technique. ^1H NMR spectra were performed on a Bruker AVANCE III 400 MHz nuclear magnetic resonance spectrometer (DMSO-d_6, TMS internal standard). Mass spectra were obtained using a Bruker Esquire HCT ultra ion trap mass spectrometer, equipped with an Agilent electrospray ion source. UV–Vis absorption spectra and fluorescence spectra were conducted at room temperature on a Shanghai Mapada 3300 UV–Vis spectrophotometer and a Hitachi F-7000 fluorescence spectrometer, respectively. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C element analyzer.

Synthesis of 5-[(2-Hydroxybenzyl)amino]isophthalic Acid (1)

Reduced Schiff base **1** was synthesized from AIP through two steps including the formation of Schiff base 5-[(2-hydroxybenzylene)amino]isophthalic acid and its further reduction by $NaBH_4$, and the detailed synthesis was as follows: (1) AIP (20 mmol, 3.58 g) was first dissolved in DMF (20 mL) under magnetic stirring at room temperature, followed by successive addition of ethanol (60 mL) and salicylaldehyde (20 mmol, 2.442 g). Then a large amount of orange–red precipitation was generated after a continuous stirring of 24 h, further collected by centrifugation at 4000 rpm, washed with ethanol and dried under vacuum for 12 h at 50 °C to yield 3.3 g (58%) dried Schiff base 5-[(2-hydroxybenzylene)amino]isophthalic acid powder. (2) Under continuous magnetic stirring, NaOH (10 mmol, 0.4 g) and the above Schiff base powder (5 mmol, 1.42 g) were added into ethanol (60 mL) at time interval of 5 min, followed by the addition of $NaBH_4$ (5 mmol, 0.18 g)-containing DMF solution (60 mL). Then the resulting mixture was allowed to react for 1 h before adding H_2O (10 mL) to dissolve completely. Finally, HCl solution (20 mL, 1 M) and H_2O (40 mL) were successively added to produce a large amount of white precipitate. The precipitate was then filtered, washed with water and ethanol, and dried at 50 °C for 1 day, providing a dried powder of reduced Schiff base **1** with a yield of 1.32 g (92%). Colorless block single crystals of **1** were obtained by recrystallisation from DMF/H_2O mixed solvent with a volume ratio of 1:2. FT-IR (KBr pellet, ν/cm^{-1}): 3415 (s), 1687 (s), 756 (s). ^1H NMR (DMSO-d_6, 400 MHz) δ 12.93 (s, 2H), 9.60 (s, 1H), 7.95 (s, 1H), 7.67 (t, J = 4.0 Hz, 1H), 7.36 (s, 2H), 7.15 (d, J = 12.0 Hz, 1H), 7.08 (m, 1H). 6.83 (d, J = 8.0 Hz, 1H), 6.69(m, 1H), 4.26 (s, 1H). MS (DMF): *m/z* $[M+H]^+$ 287.82, $[M–H]^-$ 285.67 (Fig. S1, ESI). Anal. Calcd. for $C_{15}H_{13}NO_5$ (287.27): C, 62.72; H, 4.56; N, 4.88. Found: C, 62.81; H, 4.63; N, 4.82.

Synthesis of 5-[(Pyridin-4-ylmethyl)amino]isophthalic Acid (2)

Similar to **1**, reduced Schiff base **2** was also synthesized including the following two steps: (1) at room temperature, AIP (150 mmol, 27.16 g) was first dissolved in DMF (80 mL) under magnetic stirring, followed by the addition of ethanol (20 mL) and 4-pyridine formaldehyde (13 mL). The resulting mixture was stirred for 20 h to generate pale yellow precipitation which was further collected by centrifugation at a rate of 4000 rpm, washed with ethanol and dried under vacuum at 50 °C for 12 h to obtain 35.33 g (87%) pale yellow Schiff base 5-[(pyridin-4-ylmethyl)amino]isophthalic acid powder. (2) Under continuous and vigorous stirring, NaOH (150 mmol, 6.0 g), the above 5-[(pyridin-4-ylmethyl)amino]isophthalic acid powder (75 mmol, 20.32 g) and $NaBH_4$ (112.5 mmol, 4.25 g)-contain DMF solution (20 mL) were added into ethanol (300 mL) at time interval of 5 min, followed by the successive addition of 150 mL of H_2O at 2 h later for dissolving completely, the freshly prepared 1 M HCl solution (200 mL) for adjusting pH to 6, and H_2O (825 mL) promoting precipitation during 1 h. The precipitate was filtered, washed with H_2O and dried at 50 °C for 1 day to obtain 14.3 g (70.0%) colorless reduced Schiff base **2** powder. Colorless plate single crystals of **2** were obtained by recrystallisation from DMF/H_2O mixed solvent with a volume ratio of 2:1. FT-IR (KBr pellet, ν/cm^{-1}): 3318 (s), 1695 (s), 767 (s). ^1H NMR (DMSO-d_6, 400 MHz) δ 12.96 (s, 2H), 8.51 (d, J = 4.0 Hz, 2H), 7.70 (s, 1H), 7.36 (d, J = 4.0 Hz, 2H), 7.33 (s, 2H), 6.96 (t, J = 8.0 Hz, 1H). 4.42 (d, J = 8.0 Hz, 2H). MS (DMF): *m/z* $[M+H]^+$ 273.09, $[M–H]^-$ 271.08 (Fig. S2, ESI). Anal. Calcd. for $C_{14}H_{12}N_2O_4$ (**2**, 272.26): C, 61.76; H, 4.44; N, 10.29. Found: C, 61.71; H, 4.48; N, 10.33.

Crystal Structure Determination

Crystal data of **1** and **2** were collected at 293 K on an Agilent Xcalibur Eos diffractometer with SuperNova (Mo) X-ray source mirror monochromator (λ = 0.71073 Å) and a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatised Mo Kα radiation (λ = 0.71073 Å), respectively. Using Olex2, both crystal structures were solved with the ShelXS-2014 structure solution program using direct methods and refined with the ShelXL-2014 refinement package using a full-matrix least-squares method on F^2. Absorption corrections were applied by using CrysAlis PRO for **1** and SADABS for **2** based on multi-scan techniques. Anisotropic thermal parameters were employed to refine all non-hydrogen atoms. Hydrogen atoms were treated by a mixture of independent and constrained refinement. The crystallographic data and structure refinement details are listed in Table S1. Crystallographic data files of **1** and **2** have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1815474 and 994623, respectively.

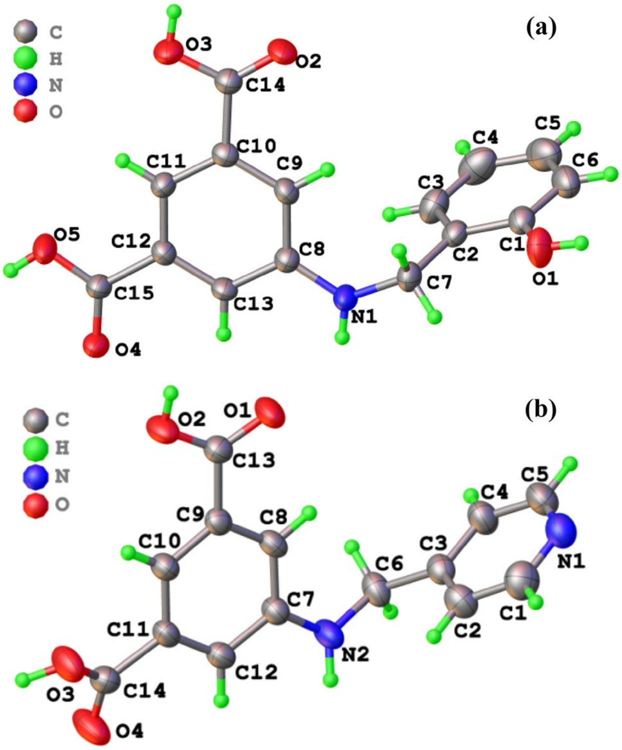


Fig. 1 ORTEP plots of **a** **1** and **b** **2**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small green spheres

Results and Discussion

Crystal Structures of 1 and 2

The single crystal structure analysis reveals that both reduced Schiff bases **1** and **2** belong to monoclinic system with space groups $P2_1/c$ for **1** and $P2_1/n$ for **2** (Table S1). Both crystal structures of **1** and **2** were herein reported for the first time although powdery **2** has been reported previously but without providing the corresponding crystal structure information and photophysical properties [10, 11, 15]. Recently, the salt form of **2** has been also obtained [11], but it can be found that the cell parameter and space group of both **2** and its salt form are obviously different from each other. From their crystal structures shown in Fig. 1, it can be found that both **1** and **2** contain isophthalate and phenol(**1**)/pyridine(**2**) units which are connected by a NH–CH_2 segment. All bond lengths and angles are in reasonable range (Tables S2, and S3, ESI). For **1**, the benzene rings from the isophthalate and phenol units are in different planes with a dihedral angle of 75.67° and the C(8)–N(1)–C(7)–C(2) torsional angle of – 86.4(2)°, while the pyridine and isophthalate units of **2** are also in different planes with a dihedral angle of 88.33° and the C(7)–N(2)–C(6)–C(3) torsional angle of 88.7(4)°. The results coincide with the formation of flexible reduced Schiff bases **1** and **2** through reducing the corresponding rigid Schiff bases.

Additionally, the infinite two-dimensional network of **1** can be formed along the $(\bar{1}01)$ plane through the intermolecular O–H···O hydrogen-bonding interactions between phenolic hydroxyl group and carboxylate group (O(1)–H(1)···O(4) hydrogen bond), and between carboxylic hydroxyl group and carboxyl group (O(3)–H(10)···O(4) and O(5)–H(12)···O(2) hydrogen bond) (Table 1; Fig. 2). For **2**, very rich intermolecular hydrogen-bonding interactions including O–H···N, N–H···O, C–H···O besides O–H···O hydrogen bonds were

Table 1 Hydrogen-bond geometry of **1** and **2**

Compound	D–H···A	D···H (Å)	H···A (Å)	D···A (Å)	<D–H···A (°)	Symmetry codes
1	O(1)–H(1)···O(4)	0.82	1.94	2.743(2)	167	1 – x, – 1/2 + y, 3/2 – z
	O(3)–H(10)···O(4)	0.82	1.87	2.687(2)	178	– x, – 1/2 + y, 1/2 – z
	O(5)–H(12)···O(2)	0.82	1.80	2.615(2)	175	– x, 1/2 + y, 1/2 – z
2	N(2)–H(7)···O(1)	0.89(3)	1.98(3)	2.850(3)	164(3)	– 1/2 + x, 3/2 – y, – 1/2 + z
	O(2)–H(9)···N(1)	0.82	1.75	2.561(3)	172	5/2 – x, 1/2 + y, 3/2 – z
	O(3)–H(11)···O(2)	0.93(4)	1.68(4)	2.606(3)	175(3)	1 – x, 2 – y, 1 – z
	C(6)–H(3)···O(3)	0.97	2.60	3.465(4)	149	1/2 + x, 3/2 – y, – 1/2 + z
	C(5)–H(5)···O(4)	0.93	2.57	3.325(4)	139	3/2 + x, 3/2 – y, 1/2 + z
	C(10)–H(10)···O(3)	0.93	2.45	3.233(4)	142	1 – x, 2 – y, 1 – z

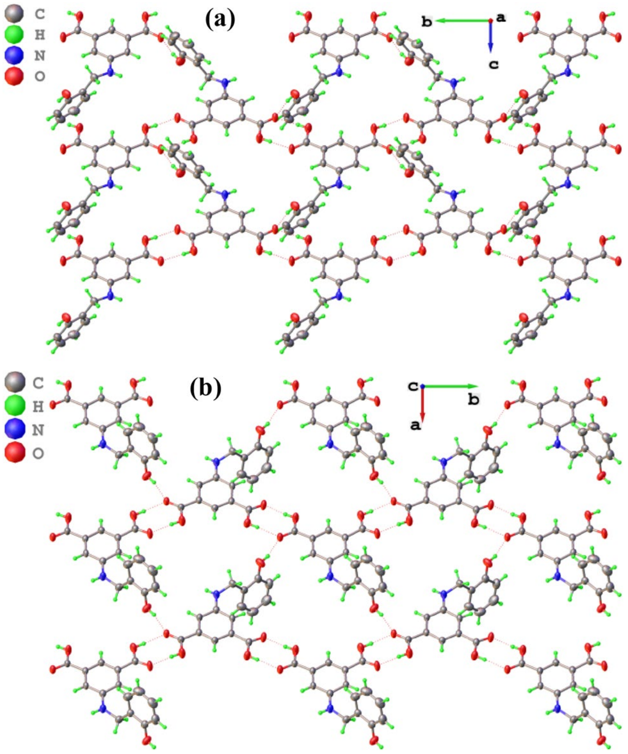


Fig. 2 Infinite two dimensional network of compound **1** viewed along the **a** [100] and **b** [001] direction

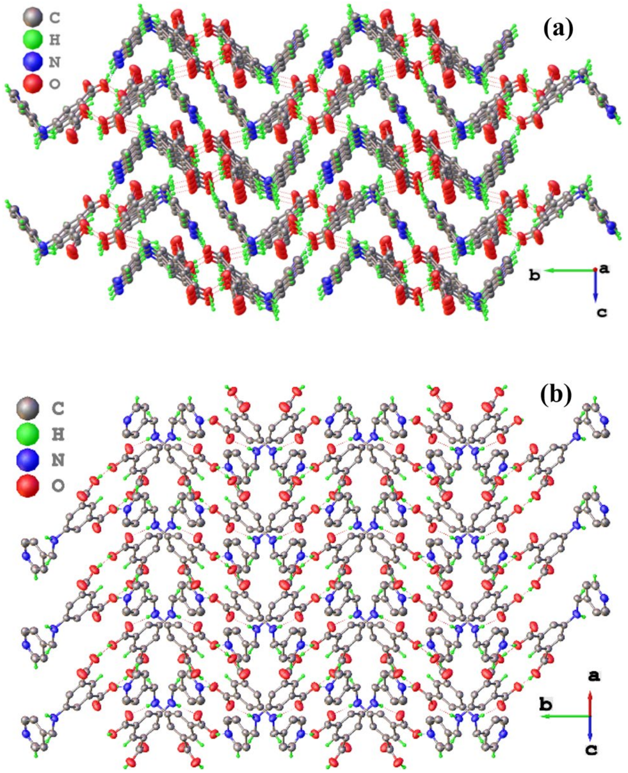


Fig. 3 Three dimensional packing of **2** viewed along the **a** [100] and **b** [101] direction

also observed, and further assembled **2** into an infinite three-dimensional supramolecular network (Table 1; Fig. 3).

IR Spectra

Figure 4 shows the IR spectra of raw material AIP, reduced Schiff bases **1** and **2**. For AIP, strong carboxylic C=O asymmetric stretch peak appears at 1698 cm^{-1}, which red-shifts slightly to 1687 cm^{-1} and 1695 cm^{-1} for the obtained reduced Schiff bases **1** and **2**, respectively. Meanwhile, the C–H vibration peak of meta-disubstituted benzene ring blue-shifts from 750 cm^{-1} for AIP to 756 cm^{-1} for **1** and to 767 cm^{-1} for **2**. The sharp, strong and single peak at 3318 cm^{-1} for **1** or at 3415 cm^{-1} for **2** is attributed to the N–H vibration peak from their imino group other than amino group. The very small shifts of both C=O asymmetric stretch peak and C–H vibration peak of meta-disubstituted benzene ring as well as significant shift of the N–H vibration peak are consistent with the facts that both **1** and **2** not only retain the isophthalic acid moiety but also contain the imino group derived from the amino group in AIP.

Absorption and Fluorescence Spectra

Different substitute groups usually result in different photophysical properties due to their electronic effect and/or steric effect [16]. The normalized absorption spectra of AIP, reduced Schiff bases **1** and **2** dissolved in DMF were shown in Fig. 5a. In the spectral range from 250 to 450 nm, two sharp characteristic absorption peaks at 293 and 356 nm for **1** or at 291 and 351 nm for **2**, respectively, were significantly red-shift as compared with those of AIP at 270 and 344 nm. The red shift of two characteristic absorption

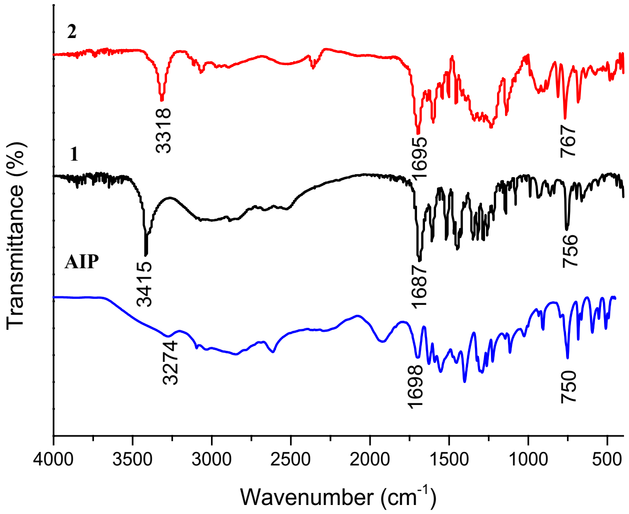


Fig. 4 IR spectra of AIP, **1** and **2**

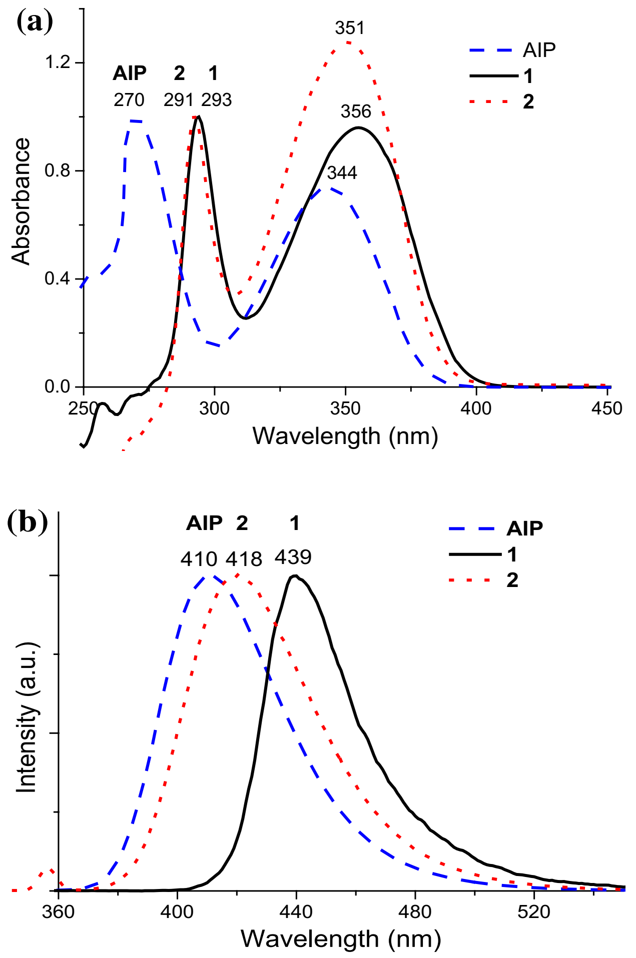


Fig. 5 **a** Absorption spectra and **b** normalized fluorescence spectra of AIP, **1** and **2**

peaks originated from the substitution of –NH_2 group with –NHR (R = 2-hydroxybenzyl for **1** or pyridin-4-ylmethyl for **2**) which lead to enhanced p → π conjugation due to stronger electron-donor effect [16, 17], especially for **1**.

The normalized fluorescence spectra of AIP, reduced Schiff bases **1** and **2** dissolved in DMF were also measured as shown in Fig. 5b. Upon the irradiation of 350 nm UV light, **1** showed a very strong deep-blue fluorescence with the maximum peak at 439 nm, a high quantum efficiency up to 64%, and a narrow full width at half maximum (FHWM) of 35 nm, while **2** showed a broader and weaker fluorescence with the peak at 418 nm and FHWM of about 50 nm. Obviously, their fluorescence is sensitive to substitute group, and the red shift of fluorescence peaks of both **1** and **2** relative to AIP can be observed. This is possibly due to stronger p → π conjugation when electron-donor–NH_2 group was substituted with electron-donor–NHR group [16], consistent with the observation shown in absorption spectra (Fig. 5a).

Conclusion

Reduced Schiff bases **1** and **2** have been synthesized by the first reaction of AIP acid with two different aldehydes (salicylaldehyde and 4-pyridinecarboxaldehyde) to form Schiff bases and their further reduction by $NaBH_4$. The crystal structures and some photophysical properties both **1** and **2** were also provided. Relatively strong narrow-band fluorescence and rich functional groups make them applicable in the fields such as fluorescent probes/labels and flexible organic ligands for synthesizing various metal complexes.

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