



A highly selective optical sensor for aniline recognition

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ABSTRACT

In this paper, an optical sensor, 2,6-bis(2-benzimidazolyl)pyridine, is reported to be highly selective towards aniline. A unique spectral response of 2,6-bis(2-benzimidazolyl)pyridine towards aniline is found, and a linear relationship between the sensor's emission intensity and the aniline's concentration is observed, making 2,6-bis(2-benzimidazolyl)pyridine a promising candidate for practicable optical sensors of aniline recognition.

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1. Introduction

Aniline is one of the most important compounds in aromatic amine families, being used as a precursor to more complex chemicals. Aniline compounds, which have been classified as very toxic in humans, are well-documented human poisons and neurotoxins [1,2]. It has been found that acute inhalation exposure to high levels of aniline in humans can result in effects on the lung, such as upper respiratory tract irritation and congestion. A probable oral lethal dose in humans is at 50–500 mg/kg for a grown man. The major effect from chronic inhalation exposure to aniline in humans is the formation of methemoglobin, which can cause interference with the oxygen-carrying capacity of the blood. In addition, aniline is also considered to be a probable human carcinogen by the United States Environmental Protection Agency (EPA) and has been ranked in EPA's Group B2.

Optical sensors have been demonstrated to be attractive for the measurement of a wide variety of physical parameters because of their advantages, such as the immunity to electromagnetic interference, high resolution, non-electrically conducting and so on [3–7]. In spite of aniline's important relevance to biology, there are only a few synthetic receptors that can form supramolecular adducts with aniline. Iyer and co-workers have reported that 2,6-bis(2-benzimidazolyl)pyridine is an efficient receptor for binding urea with high affinity [8,9]. It is observed that the host–guest complex formed between 2,6-bis(2-benzimidazolyl)pyridine and urea is very stable, where 2,6-bis(2-benzimidazolyl)pyridine utilizes not only its cavity but

also the imine nitrogen located on the outer core to form a stable donor–acceptor complex with urea. Encouraged by Iyer's exciting results, in this paper, we explored the possibility of using 2,6-bis(2-benzimidazolyl)pyridine as a receptor to detect aniline and its derivatives, such as biphenylamine, triphenylamine, and benzene-1,4-diamine. It is found that 2,6-bis(2-benzimidazolyl)pyridine exhibits a unique spectral response towards aniline, making 2,6-bis(2-benzimidazolyl)pyridine a promising candidate for practicable optical sensors of aniline recognition.

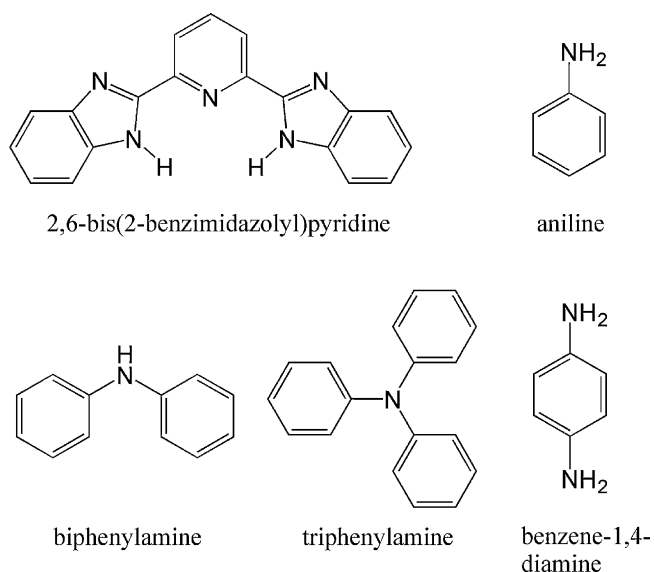
2. Experimental

Molecular structures of the host and the guests used in this paper are shown in Scheme 1.

2,6-Bis(2-benzimidazolyl)pyridine (BBP), aniline (Q1), biphenylamine (Q2), triphenylamine (Q3), and benzene-1,4-diamine (Q4) were purchased from Aldrich Chemical Co., and used without further purification. Acetonitrile was purified using the standard procedure. All the photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. UV–Vis absorption spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. All measurements were carried out in the air at room temperature without being specified.

To evaluate the solution state properties of receptor BBP, titrations were performed by careful additions of Q1, Q2, Q3, and Q4 aliquots into acetonitrile solutions of BBP. The ratios of BBP/Qn ($n=1, 2, 3, 4$) systems are given as follows: A: pure BBP (1×10^{-5} mol/L); B: 1:0.2 (1×10^{-5} mol/L: 0.2×10^{-5} mol/L); C: 1:0.4 (1×10^{-5} mol/L: 0.4×10^{-5} mol/L); D: 1:2 (1×10^{-5} mol/L: 2×10^{-5} mol/L); E: 1:4 (1×10^{-5} mol/L: 4×10^{-5} mol/L); F: 1:10 (1×10^{-5} mol/L: 10×10^{-5} mol/L); G: 1:20 (1×10^{-5} mol/L: 20×10^{-5} mol/L); H: 1:30 (1×10^{-5} mol/L: 30×10^{-5} mol/L);

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Scheme 1. Molecular structures of the host and guests.

I: 1:40 (1×10^{-5} mol/L: 40×10^{-5} mol/L); J: 1:50 (1×10^{-5} mol/L: 50×10^{-5} mol/L). The spectroscopic changes were recorded by means of UV-Vis and fluorescence spectroscopy in acetonitrile. The choice of solvents is restricted by the insolubility of BBP in nonpolar solvents.

3. Results and discussion

3.1. Absorption spectra of BBP/Qn ($n = 1, 2, 3, 4$) systems

Figs. 1–4 demonstrate the absorption spectra upon the addition of Qn ($n = 1, 2, 3, 4$) into acetonitrile solutions of BBP. It can be seen in Fig. 1 that on increasing the concentration of Q1 from 0 to 0.4×10^{-5} mol/L, a decrease of the absorption at 327 nm occurs. Concurrently, a new absorption peaking around 270 nm with higher intensity shows up. Iyer suggests that this newly generated absorption band is due to the potential formation of a stable complex between BBP and a guest molecule [8,9]. And this study shows the formation of an isobestic peaking at ~ 290 nm, indicating the presence of at least one species at equilibrium. Upon higher Q1 concentrations, the absorption spectra exhibit characters of Q1s absorption spectrum, peaking at 239 and 290 nm. Meanwhile, the

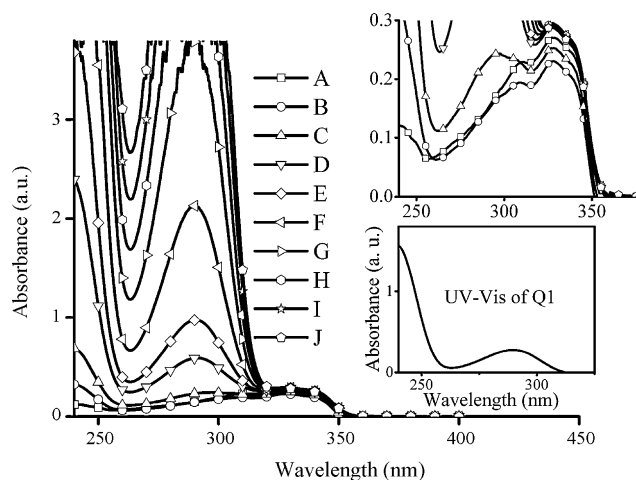


Fig. 1. UV-Vis spectra of BBP/Q1 system. The inset shows a magnified view of absorption (up) and the UV-Vis spectrum of pure Q1 (down).

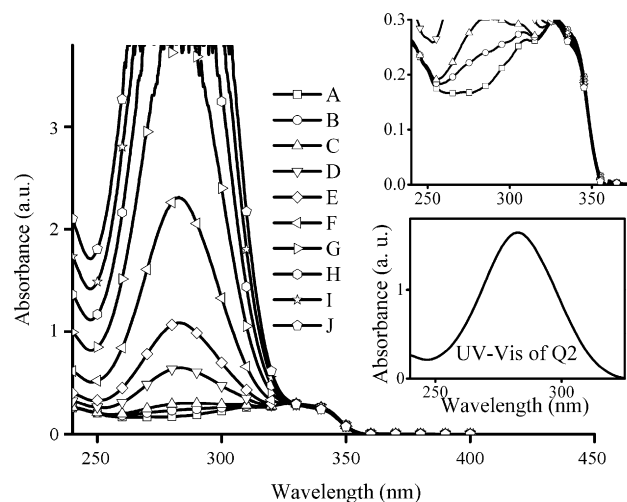


Fig. 2. UV-Vis spectra of BBP/Q2 system. The inset shows a magnified view of absorption (up) and the UV-Vis spectrum of pure Q2 (down).

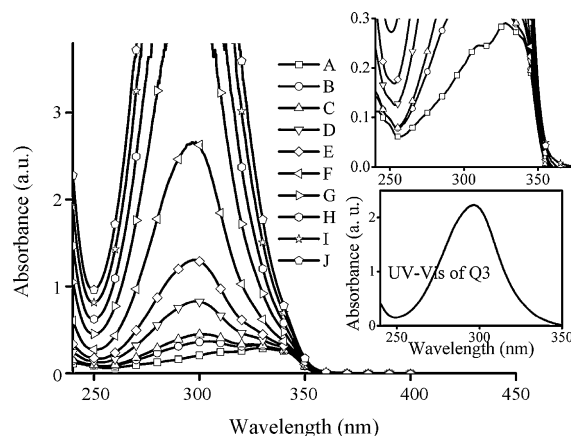


Fig. 3. UV-Vis spectra of BBP/Q3 system. The inset shows a magnified view of absorption (up) and the UV-Vis spectrum of pure Q3 (down).

absorption at 327 nm becomes constant with the increasing concentration of Q1, and we are giving an explanation as follows. Since the absorption edge of Q1 ends at 310 nm, the absorption at 327 nm is thus dominated by the concentrations of the supermolecular complex (BBP...Q1) and BBP. When Q1 is added into the BBP solution, the amount of free BBP tends to decrease and BBP...Q1

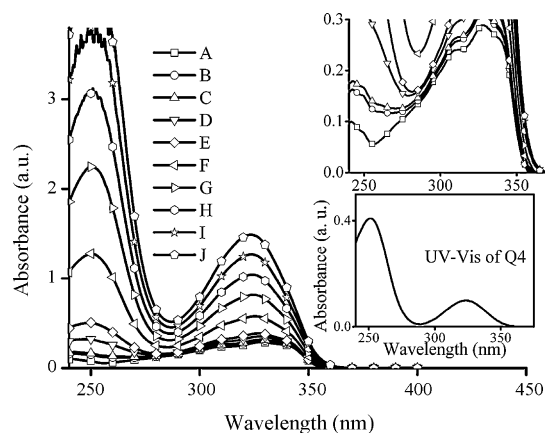


Fig. 4. UV-Vis spectra of BBP/Q4 system. The inset shows a magnified view of absorption (up) and the UV-Vis spectrum of pure Q4 (down).

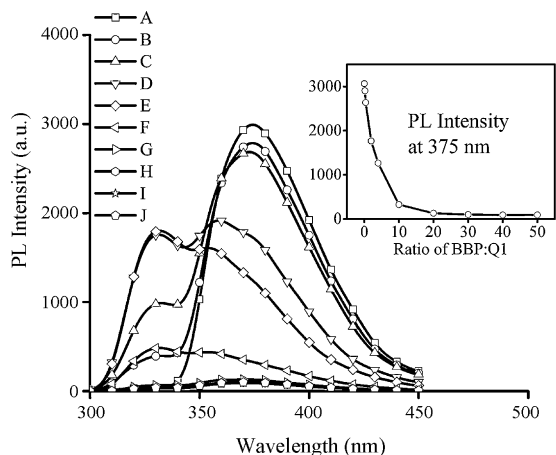


Fig. 5. PL spectra of BBP/Q1 system. Inset: PL intensity variation at 375 nm.

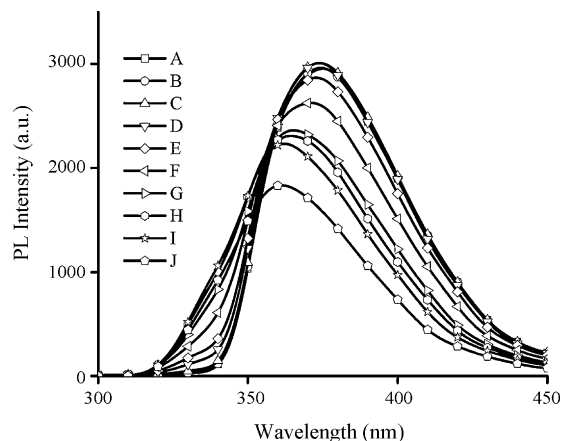


Fig. 6. PL spectra of BBP/Q2 system.

begins to form, until the BBP/Q1 system achieves a balance state. After reaching the balance, the concentrations of BBP, Q1 and BBP become constant. As a result, the absorption at 327 nm becomes constant with the increasing concentration of Q1.

On the other hand, no isosbestic is found from the absorption spectra of BBP/Q2–Q4 systems as shown in Figs. 2–4. The absorption spectra of Q2–Q4 become dominant contributions with the increasing concentrations of Q2–Q4. The absorption difference between BBP/Q1 system and BBP/Q n ($n = 2, 3$) systems suggests the absence of stable formation of supermolecular complexes between BBP and Q2/Q3, which may be explained as follows. The crystal structures of supermolecular complexes between the host (BBP) and the guest (urea) reveal that a guest molecule fits into the cavity of BBP and is bonded to the NH protons of BBP to form a stable donor–acceptor complex in a 1:1 ratio [8,9]. In this kind of complex, one host molecule donates its protons to the lone pair of the guest which is pointed inwards into BBP's cavity. Thus, stability of the supermolecular complex between BBP and a guest molecule is then determined by the amount of lone pairs offered by the guest molecule and steric hindrance of the guest. Q1–Q3 own one lone pair in each molecule. However, from Q1 to Q3, steric hindrance increases dramatically, suggesting a decreased stability of the supermolecular complexes, which explains the absence of stable supermolecular complexes between BBP and Q2/Q3.

As for BBP/Q4 system, BBP may form a stable supermolecular adduct with Q4 through the imine nitrogen located on BBP's outer core via hydrogen-bonding, leading to an enlarged conjugation system. Unfortunately, the spectral evidence of supermolecular complex formation may be covered up by the strong absorption of Q4 peaking at 324 nm which is quite close to BBP's maximum absorption ($\lambda_{\max} = 327$ nm). On the other hand, BBP/Q4 system shows an obvious red shift of absorption edge as shown in Fig. 4, which is caused by the enlarged conjugation system, suggesting the formation of adduct between BBP and Q4.

3.2. Fluorescence spectra of BBP/Q n ($n = 1, 2, 3, 4$) systems

Figs. 5–8 demonstrate the PL spectra upon the addition of Q n ($n = 1, 2, 3, 4$) into acetonitrile solutions of BBP. It can be observed that with the increasing concentration of Q n ($n = 1, 2, 3, 4$), the emission of BBP peaking at 375 nm exhibits an obvious decrease trend in all BBP/Q n ($n = 1, 2, 3, 4$) systems. As for BBP/Q1 system, a new emission band peaking at ~ 330 nm is observed, along with the gradient decrease of emission at 375 nm. The inset of Fig. 5 shows the intensity variation at 375 nm upon the addition of Q1, from which it can be seen that BBP loses 90% of its initial emission intensity

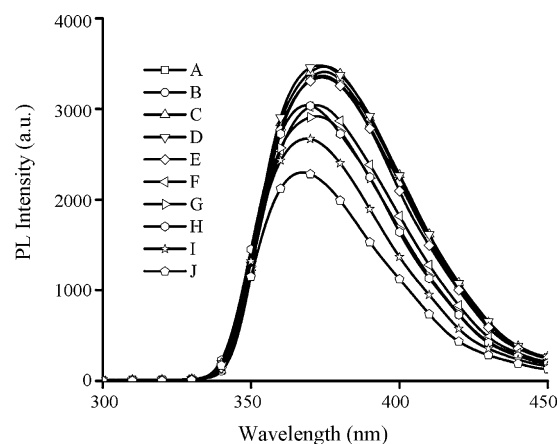


Fig. 7. PL spectra of BBP/Q3 system.

when the concentration of Q1 increases to 10×10^{-5} mol/L. Upon further addition of Q1, the emission intensity at 375 nm decreases slowly. Thus, the sensitive window of BBP towards aniline localizes in a region of 1:0.2 to 1:10 (BBP:Q1). In addition, there shows a new emission peaking at 350 nm, perhaps due to the formation of BBP...Q1. Upon higher Q1 concentrations from F to J, the emission intensity at 350 nm also decreases sharply. As above mentioned, the concentrations of BBP...Q1 and BBP become constant after reaching the balance. Upon higher Q1 concentrations, the excess

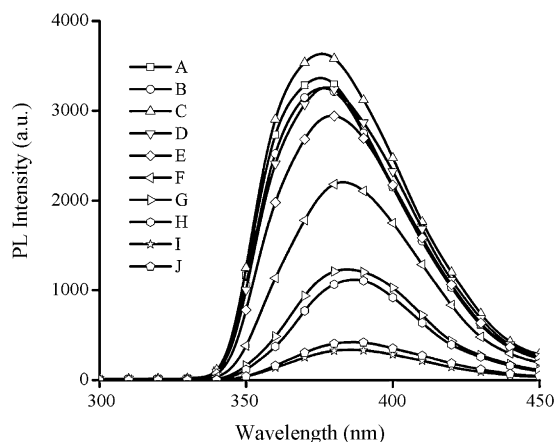


Fig. 8. PL spectra of BBP/Q4 system.

Q1 begins to quench the BBP...Q1 luminescence, leading to the decreased emission intensity of BBP...Q1.

Similarly, a new emission band ranging from 320 to 350 nm is also observed for BBP/Q2 system, but not as obvious as that in BBP/Q1 system. Emission intensity of BBP shows a decrease trend upon the increasing concentration of Q2. In addition, the emission peak of BBP exhibits an obvious blue shift from 375 to 360 nm as shown in Fig. 6. The hydrogen-bonding between BBP and Q2 may be responsible for the blue shift. Considering that the UV-Vis spectra of BBP/Q2 system deny the possibility of Q2 molecule fitting into BBPs cavity, owing to Q2s steric hindrance, it can be thus concluded that Q2 is located on the outer core of BBP via hydrogen-bonding. And this kind of adduct exerts no obvious effect on the UV-Vis absorption spectra of BBP, but an obvious effect on BBPs PL spectra. Given the identical optical band gap suggested by the UV-Vis spectra shown in Fig. 2, it is believed that the emission blue shift of BBP in BBP/Q2 system is mainly caused by the dipole effect of Q2. As for BBP/Q3 system, no newly generated emission band is detected, and the emission blue shift of BBP is much less obvious (375–367 nm). As we mentioned, the newly generated emission band and spectral blue shift are mainly caused by the hydrogen-bonding between BBP and guest molecules. Thus, not surprisingly, BBP/Q3 system, whose guest molecule owns the biggest steric hindrance among the four guest molecules, exhibits no newly generated emission band and slight emission blue shift.

A trend of emission intensity decrease of BBP is found in BBP/Q4 system as shown in Fig. 8, from which a spectral red shift from 375 to 387 nm is also observed. Compared with the optical band gap red shift as we mentioned, it is thus confirmed that the UV-Vis and PL spectral red shifts are caused by the stable superamolecular adduct between BBP and Q4 via hydrogen-bonding.

3.3. Spectral selectivity of BBP towards aniline

From the comparison of PL spectra of BBP/Qn ($n = 1, 2, 3, 4$) systems, it can be seen that the PL spectra of BBP/Q1 system are different with those of BBP/Q2–Q4 systems: the obvious newly generated emission band peaking at ~ 330 nm is only detected in BBP/Q1 system, while, in BBP/Q2–Q4 systems, no obvious newly generated emission peak is found. This provides us an easy way to differentiate aniline from its derivatives via the PL spectra of

BBP/guest systems. In addition, it can be seen from the inset of Fig. 5 that the emission intensity of BBP/Q1 system at 375 nm follows a linear decrease trend upon the increasing concentration of Q1, the most sensitive window towards Q1 is found to be the region from 1:0.2 to 1:10 (BBP:Q1) as we mentioned. By increasing the ratio of BBP:Q1 from 1:0 to 1:10, BBP loses 90% of its initial emission intensity, suggesting that BBP exhibits spectral response to Q1 in a wide range. So, the wide range identification of aniline can be easily realized by the appearance of a new emission band, and concentrations of aniline can be easily determined by measuring the emission intensities at 375 nm, suggesting that BBP is a promising optical sensor for aniline recognition.

4. Conclusion

In summary, we developed 2,6-bis(2-benzimidazolyl)pyridine as a highly selective optical sensor for aniline recognition. It exhibits a unique spectral response to aniline, while no such response is detected towards aniline's derivatives. The PL intensity follows a good linear decrease trend upon the increasing concentration of aniline, making BBP a promising candidate for optical sensor for recognition of aniline.

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