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Triphenylamine based benzimidazole and benzothiazole: Synthesis and applications in fluorescent chemosensors and laser dyes

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ABSTRACT

Triphenylamine based fluorescent dyes TPA-benzimidazole and TPA-benzothiazole have been designed and synthesized. The TPA-benzimidazole chemosensor was tested for a number of metal ions and found to exhibit binding affinity for Fe^{3+} and Hg^{2+} in acetonitrile, and the fluorescence quenching was achieved through a PET process. The appearance of an isosbestic point in absorption titrations and Job's plot analysis supported 1:1 stoichiometries for Fe^{3+} and Hg^{2+} ions. Laser experiments showed that under transversal pumping with a Q-switched Nd:YAG (355 nm) laser in toluene, TPA-benzothiazole exhibits efficient and stable amplified spontaneous emissions (ASE) at 436 nm.

1. Introduction

Functionalized benzimidazoles and benzothiazoles are very useful N-containing heterocyclic intermediates for the development of pharmaceutical molecules [1] and drugs of biological activities [2], such as antitumor, antiviral, anticancer, antihypertensive, and antihistamines among others. They are important ligands for complexation with transition metals [3] and have also been applied in laser dyes [4], chemosensing [5], fluorescence and nonlinear organic materials [6].

As one of the most essential trace elements in biological systems, Fe^{3+} plays a major role in many biochemical processes [7]. Either its deficiency or excess can disturb cellular homeostasis or metabolism, resulting in various disease conditions [8]. Therefore, numerous efforts have been made in the development of effective Fe^{3+} fluorescent chemosensors [9,10]. A series of benzimidazole-based fluorescent probe for ratiometric detection of Fe^{3+} ions have been introduced by Jang and his co-workers [11–13]. As an environmental contaminant, Hg^{2+} is one of the most prevalent toxic metals due to its severe impact on living systems and environment [14]. During the past decades, a number of detecting strategies have been adopted in Hg^{2+} recognition [15,16], which was based on coordination of heteroatom with Hg^{2+} and the specific mercury-promoted reactions, including desulfurization reactions and oxymercuration reactions [17–19].

With above-mentioned criteria in mind, we have successfully introduced the triphenylamine moiety into benzo-heterocyclics and obtained two fluorescent dyes. TPA-benzimidazole whose fluorescence can be almost totally quenched in the presence of Fe^{3+} or Hg^{2+} cations through a photoinduced electron transfer (PET) process. The TPA-benzothiazole exhibits efficient and stable amplified spontaneous emissions (ASE) in the blue region, under transversal pumping at 355 nm in toluene.

2. Experimental

2.1. Reagents and apparatus

Solvents were dried and distilled according to standard procedures prior to use. All other compounds were commercially available and used as received. The solutions of metal ions were prepared from the corresponding nitrate salts.

^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer using the solvent residue signal as the internal standard. IR spectra were recorded in diffuse reflection with a Magna 560 FT-IR spectrophotometer. Mass spectrometric experiments were performed on Bruker micro TOF-Q mass spectrometer. All the photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The UV–vis spectra of freshly prepared solutions were performed with a Shimadzu UV-3101PC spectrophotometer. The narrow-line width laser emission and tuning ranges of dye solutions were collected using an

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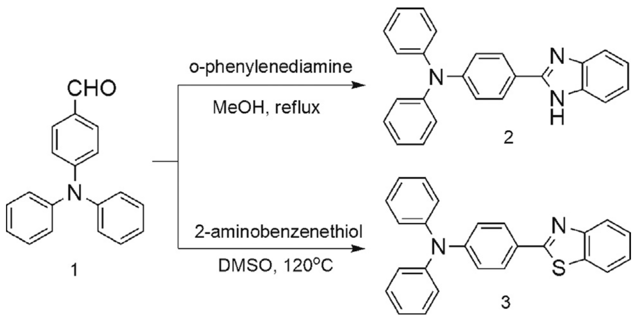
Ocean Optics Maya2000 Pro Fiber Optic Spectrometer. ASE investigations were performed using a Nd:YAG laser with a repetition rate of 10 Hz and pulse duration of about 10 ns. The laser power was detected by a Newport 2936C laser power meter.

2.2. Synthetic procedure

*2.2.1. Synthesis of compound **2***

To a stirring solution of *o*-phenylenediamine (108 mg, 1.0 mmol) in 20 mL MeOH, a solution of 4-(diphenylamino)benzaldehyde (273 mg, 1.0 mmol) was added dropwise through a dropping funnel. After that, the mixture was heated to reflux for 4 h. When the reaction was finished the mixture cooled and poured into water. The resulting precipitate was filtered, washed with water, and dried. The residue was chromatographed on silica gel (petroleum ether: CH_2Cl_2=10:1, V/V) to give the compound **2** as a milk white powder in 58% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.74 (s, 1H), 8.05 (d, J=8.7 Hz, 2H), 7.54 (s, 2H), 7.37 (t, J=7.9 Hz, 4H), 7.24–7.08 (m, 8H), 7.05 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 151.10, 148.63, 146.55, 129.59, 127.52, 125.83, 124.77, 123.78, 123.29, 121.55. IR (KBr, cm^{-1}): ν=3414, 3053, 2920, 2861, 1593, 1490, 1442, 1325, 1280, 1187, 837, 748, 697. ESI-MS: m/z=362.2.



Scheme 1. Synthesis of compounds 2 and 3.

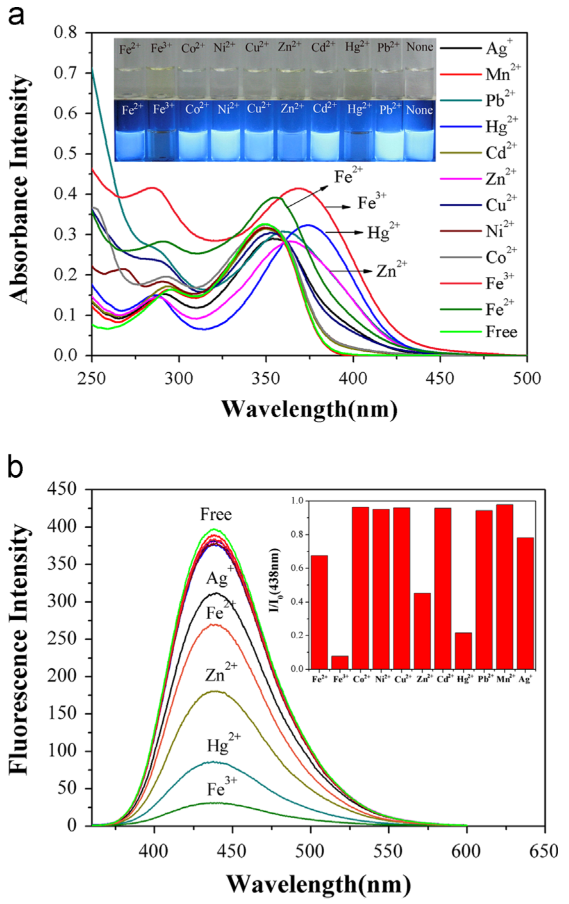


Fig. 1. (a) Absorption responses of 2 (10 μM) upon addition of 10 equiv. various cations in CH_3CN. (b) Fluorescence responses of 2 (10 μM) upon addition of 10 equiv. various cations. The inset picture shows the titration profile of I/I_0 at 438 nm.

*2.2.2. Synthesis of compound **3***

To a solution of 2-aminobenzenethiol (125 mg, 1.0 mmol) in 20 mL DMSO and 4-(diphenylamino)benzaldehyde (273 mg, 1.0 mmol) was added and the mixture was heated at 120 °C for 2 h. When the reaction was complete, the reaction mixture was cooled and poured into water and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried with $MgSO_4$ and the solvents were evaporated under vacuum. The residue was chromatographed on silica gel (petroleum ether: CH_2Cl_2=5:1, V/V) to give the compound **3** as a white powder in 70% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.05 (d, J=8.6 Hz, 2H), 7.54 (d, J=3.1 Hz, 2H), 7.37 (t, J=7.9 Hz, 4H), 7.23–7.15 (m, 3H), 7.15–7.08 (m, 5H), 7.05 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.43, 146.87, 129.49, 128.53, 126.18, 125.39, 124.71, 124.03, 122.72, 121.58; IR (KBr, cm^{-1}): ν=3433, 2922, 2856, 1598, 1478, 1324, 1278, 1180, 832, 753, 685.

3. Results and discussion

4-(diphenylamino)benzaldehyde was synthesized according to known procedures [20]. Compound **2** was obtained by a

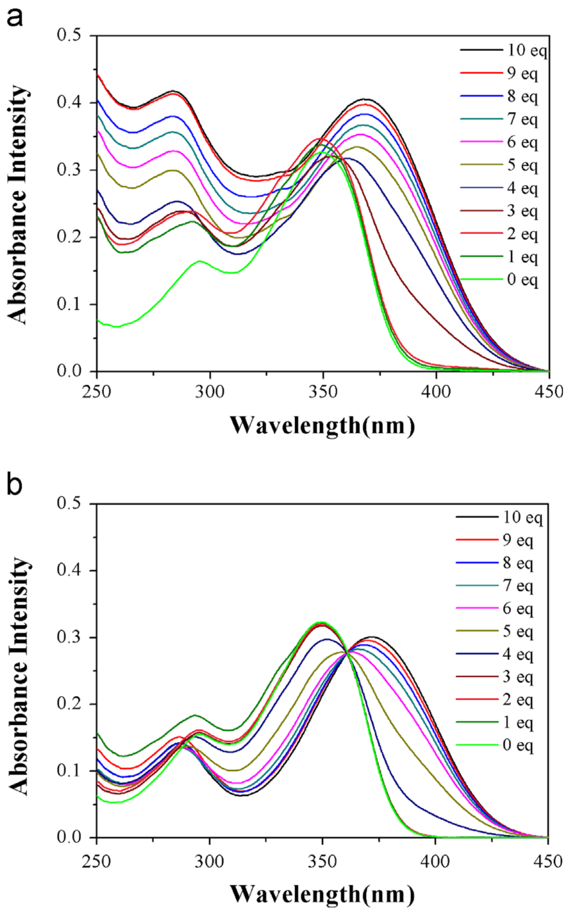


Fig. 2. Absorption titration spectra of 2 (10 μM) in CH_3CN upon addition of Fe^{3+} and Hg^{2+} (0–10 equiv.).

condensation reaction of 1 with *o*-phenylenediamine in methanol with yield of 58%. Compound **3** was obtained by a condensation reaction of 1 with 2-aminobenzenethiol in DMSO with yield of 70% (Scheme 1).

The cation binding properties of benzimidazole 2 were studied by employing the nitrate salts of various cations (Hg^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ag^{+}, and Co^{2+}) in acetonitrile (Fig. 1). After adding 10.0 equiv. of tested metal ions into the solution of 2, the absorption spectra exhibited significant changes towards Hg^{2+}, Fe^{2+}, Fe^{3+} and Zn^{2+}. The band centered at 350 nm in the spectrum of 2 moved to 372 nm upon addition of excess Hg^{2+} and Fe^{3+}, and the intensity increased upon addition of Fe^{2+} and Fe^{3+}, while other metal ions exhibited insignificant changes. Metal cations interaction for 2 was followed by emission spectral study ($\lambda_{ex}=350$ nm) in the presence of tested metal ions (10.0 equiv.). It is evident that the binding of 2 with Fe^{3+} and Hg^{2+} caused significant changes in the fluorescence bands, showing the favorable selective and unique binding manner of the two metal ions.

To gain a deep insight into the sensitivity and binding manner of 2 with the two metal ions, UV–vis absorption titrations were carried out (Fig. 2). Upon addition of increasing amount of Fe^{3+}, the absorption band of the low energy (350 nm) moved to 372 nm, and high-energy bands (295 nm) moved to 283 nm, the color of the solution turns light yellow. The enhancement of absorption intensity upon addition of Fe^{3+} reflected a change from the flexible structure of 2 to a rigid one upon metal complexation, which was most likely caused by the cancelation of PET from nitrogen donors [21]. Fig. 2b shows the absorption changes of 2 with addition of Hg^{2+} ions in the same solvent system. The absorbance of the bands associated with low (from 350 to 368 nm) energy significantly decreases upon the addition of Hg^{2+} ion, but the bands at 210 nm increases to a significantly high optical intensity. The appearance of an isosbestic point at 362 nm suggested the presence of more than two species in the medium. Similarly, the high energy π–π* transitions rationalized and blue shifted from 295 to 288 nm, which was attributed to ICT (internal charge transfer) process [22].

Next we investigated the changes in the fluorescence spectrum of 2 upon increasing concentration of Hg^{2+} and Fe^{3+} in acetonitrile under similar conditions. The results showed that, with increasing amounts of Fe^{3+} to the solution of 2, the fluorescence intensity at 438 nm (92.2%, Fig. 3a) gradually decreased. Similarly, when Hg^{2+} was added to the solution, a gradual decrease in fluorescence intensity at 438 nm (78.4%, Fig. 3b) was also observed. The quenching in the fluorescence emission was more efficient for Fe^{3+} to Hg^{2+}. The change in fluorescence intensity displayed linear behavior upon increasing the concentration of either Fe^{3+} or Hg^{2+} in acetonitrile. The mechanism of recognition of both cations is known as "on–off" by showing strong decrease of the fluorescence intensity of 2 (a chelation enhanced quenching) [23].

Using Job's method of continuous variation of mole fraction, the stoichiometries of 1:1 between 2-Fe^{3+} and 2-Hg^{2+} were found for the probe–analyte interaction (Fig. 4). However, the weak interaction of two metal ions with 1 by low complexation could be attributed to the potency of the metal ions [24,25].

In order to further confirm the coordination between 2 and the interaction metal, TPA-benzothiazole 3 was synthesized. Above mentioned experiments had been carried out by 3 with various cations. Fluorescence changes had been detected in the absorption

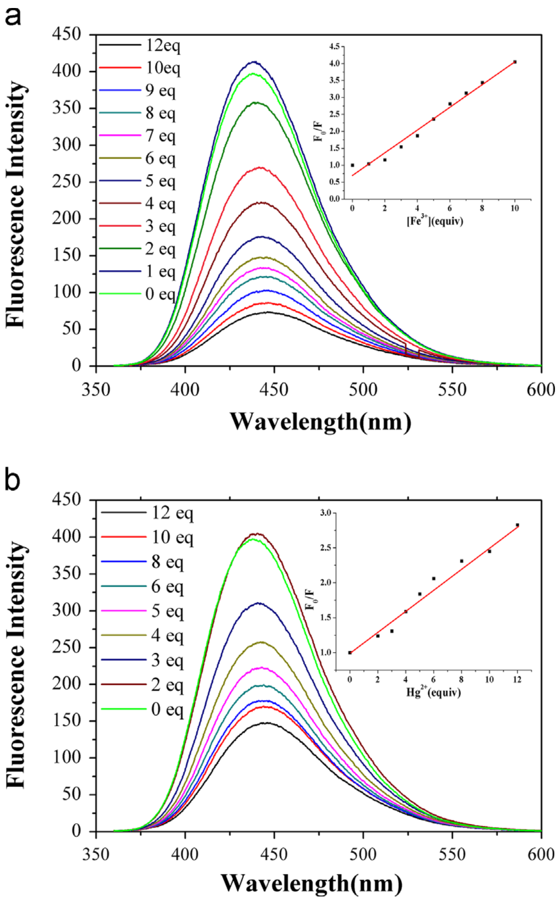


Fig. 3. Fluorescence intensity changes of compound 2 (10 μM) with continuous addition of (a) Fe^{3+} and (b) Hg^{2+} (0–10 equiv.) in CH_3CN. The inset picture shows the titration profile of F_0/F.

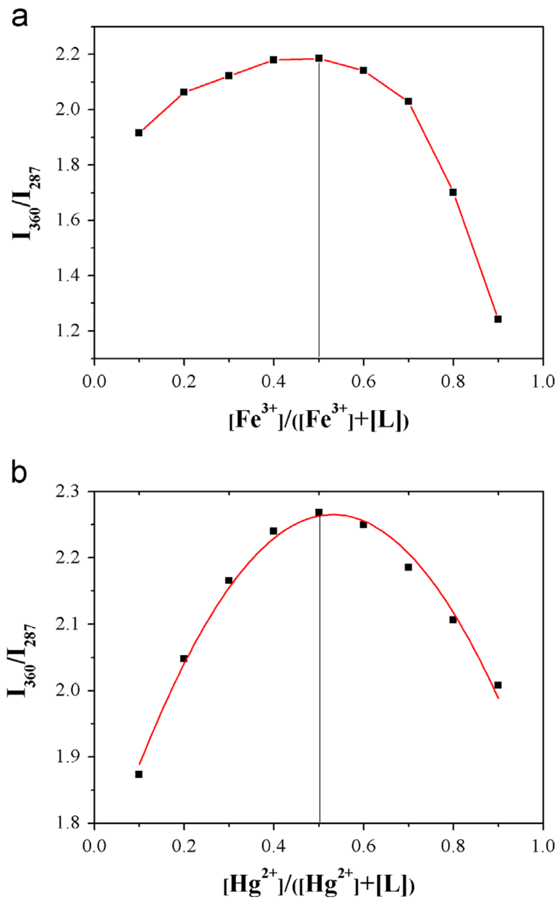


Fig. 4. Job's plot obtained from complex 2-Fe^{3+} and 2-Hg^{2+} indicate 1:1 binding mode.

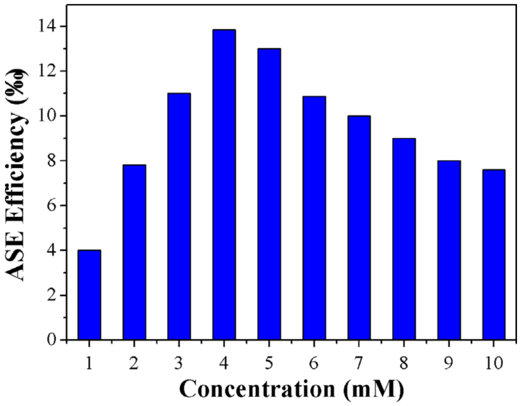


Fig. 5. ASE efficiency of 3 as a function of the dye concentration pumped by 355 nm Nd:YAG laser in toluene (~3 mJ/pulse).

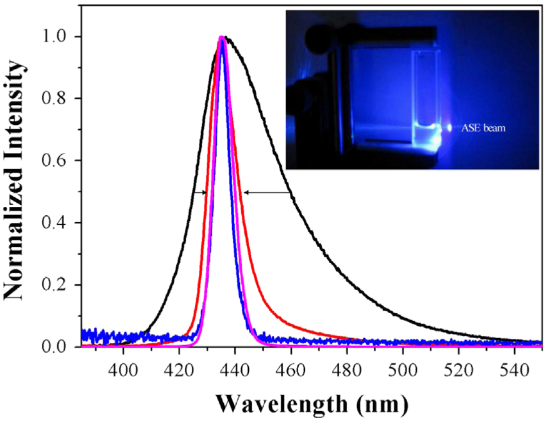


Fig. 6. Normalized emission spectra of 3 in toluene with increasing of pump energy. The inset photo shows the ASE phenomenon of 3 pumped by 355 nm Nd:YAG laser.

and fluorescence spectra after the addition of Fe^{3+}. Compared with 2, we are confident that the coordination site was C═N of the imidazole ring [26].

Due to the higher fluorescence quantum yield of 2 and 3, we took the laser experiments and the ASE phenomenon was observed by 3 in hexane and toluene [27]. The low solubility of 3 in hexane prevented us from producing highly concentrated solutions that were required for laser experiments. In medium and high polarity solvents such as ethyl acetate, chloroform and ethanol, no ASE phenomenon can be observed, no matter how strong the pump intensity is.

As expected, the highest value (1.3%) is achieved by 3 in 4 mM solution (Fig. 5). Further increasing the dye concentration compromises the ASE output efficiency. This trend can be related to the increase in re-absorption/re-emission processes with a deleterious effect in the laser action.

The transition from normal fluorescence, through threshold, to complete ASE can be clearly seen in Fig. 6. By increasing the excitation power above the threshold, the intensity of the ASE spectra is greatly increased, while the full width at half maximum of the spectra is further narrowed. At the pump energy of ~1 mJ, the FWHM of the ASE radiation is 6 nm centering at 436 nm.

4. Conclusion

In conclusion, we have synthesized two fluorescent dyes by introduction of electron-donating triphenylamine groups in benzimidazole and benzothiazole fluorescent chromophores. The TPA-benzimidazole chemosensor was tested for a number of metal ions and found to exhibit binding affinity for Fe^{3+} and Hg^{2+} in acetonitrile, and the fluorescence quenching was achieved through a PET process. The chemosensor formed a 1:1 complex with Fe^{3+} and Hg^{2+}. The coordinating site was C═N in the imidazole ring by comparing with TPA-benzothiazole. Laser experiments showed that TPA-benzothiazole exhibited efficient and stable amplified spontaneous emissions (ASE) in the blue region. Further studies focusing on developing benzo-heterocyclics sensors and devices are under investigation in our laboratory.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jlumin.2013.09.008.

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