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Fluorescence Sensors for Bismuth (III) ion from Pyreno[4,5-*d*]imidazole Derivatives

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Abstract

Three pyreno[4,5-*d*]imidazole derivatives are synthesized and evaluated as fluorescent sensors for bismuth (III) ion. The target compounds are prepared in 55 to 86 % yields from a condensation reaction between pyrene-4,5-dione and aromatic aldehydes. The compound bearing a phenolic group can selectively detect bismuth (III) ion via fluorescence enhancement with a detection limit of 1.20 μ M in CH₃CN-DMSO mixture and 3.40 μ M in 10% pH5 aqueous in CH₃CN-DMSO mixture. The sensing mechanism involving a formation of coordination complex is investigated by UV-VIS and fluorescence titrations, ¹H-NMR, and the decomplexation of the bismuth complex by sulfide ion. The application of this sensor for quantitative analysis of spiked bismuth (III) ion in real water samples from 2 different sources is demonstrated.

Introduction

Bismuth and its compounds have been used in the field of material chemistry as semi-conductor gas sensor,¹ alloy,² cosmetic ingredient,³ optoelectronic,⁴⁻⁶ and pharmaceutical materials.⁷⁻¹⁰ Moreover, some complexes of bismuth have been used as anti-cancer¹¹ and for CT imaging.¹² Even though bismuth (III) ion has low toxicity, the prolong use of bismuth-containing drugs can lead to negative effects on the kidney and nervous systems.¹³⁻¹⁴ Besides, the use of household products that contain bismuth compounds can lead to water contamination and pollutions.¹⁵ Conventional methods for Bi³⁺ detection and quantification are inductively coupled plasma atomic emission spectrometry (ICP-AES),¹⁶ inductively coupled plasma mass spectrometer (ICP-MS),¹⁷ resonance light scattering,¹⁸⁻¹⁹ atomic fluorescence spectrometry,²⁰ and electrochemical techniques.²¹⁻²³ However, these methods require high-cost instruments and complicated equipment set up, which makes it impossible to use these techniques for real-time monitoring. In contrast, the fluorescence technique is more user-friendly and still can provide high sensitivity and selectivity. There have been several reports on the design and application of bismuth fluorescent sensors based on a metal-organic framework,²⁴ and functionalized naphthalimide,²⁵ rhodamine,²⁶⁻²⁷ hydroxyquinoline²⁸ and pyrene.²⁹

Pyreno[4,5-*d*]imidazole derivatives were used as the material in solar cells,³⁰ OLEDs,³¹⁻³² and anion sensors.³³⁻³⁴ They possess a rigid planar geometry and remarkable photophysical properties. More interestingly, the imidazole moiety can function as both proton and electron donors that can facilitate the interaction with the metal ion. To this end, we designed three pyreno[4,5-*d*]imidazole derivatives (**P1-P3**, Fig. 1) and aim to use them as specific fluorescent sensors for bismuth (III) ion. The three compounds contain different substituents on the phenyl ring that can provide information on the mechanism of sensing such as the Excited State Intramolecular Proton Transfer (ESIPT) and photo-induced electron transfer (PET).

<Figure 1>

Materials and Methods Chemicals and Instruments. All reagents used in reactions were analytical grade purchased from Sigma-Aldrich, Merck, or Fluka. Solvents for extraction and chromatography such as dichloromethane (CH₂Cl₂), hexane, ethyl acetate (EtOAc), and methanol (CH₃OH) were commercial grade and used without further purification. Solvents for UV-Vis and fluorescence experiments such as acetonitrile (MeCN), tetrahydrofuran (THF), ethanol (EtOH), and dimethylsulfoxide (DMSO) were spectrophotometric grade. Column chromatography was operated using Merck silica gel 60 (70–230 mesh) and Thinlayer chromatography (TLC) was performed on silica gel plates (Merck F245). The target molecules were characterized by MALDI-TOF mass spectrometer (Bruker Daltonics) using α -cyano-4-hydroxycinnamic acid (CCA) as a matrix. All ¹H- spectra were acquired using Varian 400 MHz and Jeol 400 MHz, while the ¹³C-NMR spectra were acquired using Bruker at 100 MHz. The UV-Vis absorption spectra were obtained from a Varian Cary 50 UV-vis spectrophotometer and the fluorescence emission spectra were recorded on a Varian Cary Eclipse spectrofluorometer.

Synthesis and characterization.

Pyrene-4,5-diones (1). his reaction was performed per a literature procedure reported by J. Hu.³⁵ In short, pyrene (10 mmol) was mixed with RuCl₃.xH₂O (0.96 mmol) in a 1:1 mixture of CH₂Cl₂ and CH₃CN (80 mL), then NaIO₄ (46.8 mmol) and H₂O (50 mL) were added. The reaction was stirred overnight at room temperature before the mixture was poured into H₂O (500 mL). The organic phased was separated and the aqueous phase was extracted with CH₂Cl₂ (50 ml) 3 times. The combined organic phases were washed with H₂O (200 ml) 3 times and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to give a dark orange solid which was purified by column chromatography using CH₂Cl₂. The product was obtained as an orange crystal in 47%. ¹H-NMR (400 MHz, CDCl₃) δ ppm 8.47 (d, J = 6.3 Hz, 2H), 8.16 (dd, J = 1.2, 8.0 Hz, 2H), 7.84 (s, 2H), 7.74 (t, J = 7.7 Hz, 2H).

Pyreno[4,5-d]imidazole derivatives (P1-P3). This reaction was performed according to a literature procedure reported by S. Sinha.³⁶ To a mixture of dione **1** (1 mmol) and an aromatic aldehyde (1 mmol) in CH₃COOH (10 ml) was added ammonium acetate (7.5 mmol). The reaction was refluxed for 4 to 6 h to form a yellow precipitate. The mixture was allowed to cool and poured into an ice-H₂O mixture (10 mL) to remove soluble salt and facilitate a complete precipitate. The solid

crude product was filtrated, washed with water, and dried by suction. The yellow solid was purified by column chromatography using 20-25% ethyl acetate in hexane.

10-Phenyl-9H-pyreno[*4*,*5-d*]*imidazole* (**P1**) was obtained as a yellow solid in 75% yield. ¹H-NMR (400 MHz, DMSO-d6) δ ppm 13.84 (s, br, NH), 8.85 (d, J = 7.5 Hz, 2H), 8.40 (d, J = 7.5 Hz, 2H), 8.27 (d, J = 7.4 Hz, 2H), 8.21 (s, 2H), 8.17 (t, J = 7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H); ¹³C-NMR (400 MHz, DMSO-d6) δ 149.41, 133.5, 130.35, 129.32, 128.96, 126.22, 124.13, 121.77, 118.97; MS (MALDI-TOF) calcd C₂₃H₁₄N₂ [M+] 318.116 found 318.027.

2-(9*H*-Pyreno[4,5-d]imidazol-10-yl)phenol (**P2**) was obtained as yellow solid in 55% yield. ¹H-NMR (400 MHz, DMSO-d6) δ ppm 13.99(s, OH), 13.21 (s, NH), 8.87 (d, J = 7.6 Hz, 2H), 8.78 (d, J = 7.6 Hz, 2H), 8.32 (d, 1H), 8.23 (s, 2H), 8.19 (t, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.16-7.11 (m, 2H); ¹³C-NMR (400 MHz, DMSO-d6) δ 157.44, 149.56, 131.51, 131.18, 127.67, 126.46, 125.89, 124.62, 121.83, 119.13, 117.22, 112.98; MS (ESI) calcd C₂₃H₁₄N₂O [M+H] 335.12 found 335.02.

10-(2-Methoxyphenyl)-9H-pyreno[*4,5-d*]*imidazole* (**P3**) was obtained as yellow solid in 86 %yield. ¹H-NMR (400 MHz, DMSO-d6) δ ppm 13.07 (s, br, NH), 8.91 (d, J = 7.5 Hz, 2H), 8.31 (d, J = 6.8 Hz, 1H), 8.25 (d, J = 7.6 Hz, 2H), 8.21 (s, 2H), 8.13 (t, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 4.08 (s, 3H); ¹³C-NMR (400 MHz, DMSO-d6) δ 156.79, 147.39, 131.65, 131.13, 130.31, 127.80, 126.33, 124.26, 121.92, 121.02, 119.41, 112.12, 56.11; MS (MALDI-TOF) calcd C₂₄H₁₆N₂O [M+] 348.126 found 348.716.

Spectrophotometric Measurement.

The stock solutions of **P1**, **P2**, and **P3** were prepared in CH_3CN and the stock solutions of metal ions were prepared in Milli-Q water. They were pipetted and diluted to the desired concentration before spectrophotometric analysis.

Results and Discussion

Synthesis

The synthesis of target compounds started with the oxidation of pyrene using NaIO₄ under catalysis of RuCl₃. The dione **1** was produced in 47% as an orange solid with consistent character according to a literature report.³⁵ An amination-condensation of this dione with aromatic aldehydes afforded that the target compound **P1**, **P2**, and **P3** in moderated to good yields.

<Scheme 1>

Photophysical properties

The photophysical properties were summarized in Table 1 and Figure S10. All target molecules showed two maximum absorption peaks around 290 and 330 nm. which resembles the characteristic peaks for pyrene derivatives. For the emission property studies, these compounds were excited at their longer maximum absorption wavelengths. The maximum emission wavelengths were observed at 407, 448, and 389 nm for compound **P1-P3**, respectively. In comparison to the other two compounds, **P2** which contains a hydroxy group on the phenyl ring exhibited a longer maximum emission wavelength and lower fluorescent quantum yield. These may cause by the Excited State Intramolecular Proton Transfer (ESIPT) initiated by the intramolecular hydrogen bonding.

<Table 1>

Solvent effect

The fluorescence spectra of **P1-P3** in solvents such as CH₃CN, THF, and C₂H₅OH are shown in Figure S11. The fluorescence properties of **P1** and **P3** are independent of the types of solvent (high polar, low polar, protic), while the fluorescence intensity of **P2** in CH₃CN was very weak. This might be the ground-state stabilization effect of the polar compound (**P2**) by the high polar solvent. Since we were interested in the turn-on sensing mode, the selectivity screening would then be conducted in CH₃CN.

Metal ion sensing studies

The selectivity of sensor **P1-P3** was tested using their CH₃CN solution at 10 μ M with various metal ions (10 eq.) such as Li⁺, Na⁺, K⁺, Ag⁺, Mg²⁺, Ca²⁺, Ba²⁺, Co²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Cu²⁺, Hg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Bi³⁺, and Cr³⁺. The result in Fig. 2 shows no exclusive selectivity for all sensors in CH₃CN. However, their maximum emission wavelengths were red-shifted to around 450 nm by the trivalent metal ions like Fe³⁺, Al³⁺, Bi³⁺, and Cr³⁺ (Figure S12). Based on the

fluorescence enhancement ratio of around 30-40 folds at 450 nm, **P2** appeared to be most sensitive towards those four metal ions. This bathochromic spectral shift may result from the complex formation between metal ions and the sensor molecules.

To improve the selectivity for **P2**, we opted to incorporate another organic solvent to the system. The ability of DMSO to coordinate with trivalent metal ions may affect the selectivity in our case.³⁷ To our delight, the use of 20% of DMSO in CH_3CN could improve the selectivity toward Bi^{3+} ion. Unfortunately, the selectivity of **P1** and **P3** could not be improved by this solvent system (Figures S13 and S14).

<Figure 2>

<Figure 3>

Fluorescence titration

The sensitivity of **P2** in the detection of Bi^{3+} was studied by fluorescence titration experiment. The fluorescence intensity gradually increased upon the addition of Bi^{3+} from 1 to 500 μ M (Figure S15a), with an apparent upper limit for signal enhancement around 500 μ M of Bi^{3+} (Figure S15b). A linear plot was constructed for the concentration range of Bi^{3+} between 0 to 20 μ M (Fig. 4). The three-time-noise detection limit was estimated to 1.20 μ M.

<Figure 4>

Interference studies

The interfering effect of other metal ions on the detection of Bi^{3+} was investigated using **P2**, Bi^{3+} , and other metal ions at a ratio of 1:10:10 molar equivalent. Figure 5 shows that only Fe³⁺ can slightly interfered to the detection of Bi^{3+} . The increasing signal may results from the competitive coordination with **P2** with Fe³⁺.

<Figure 5>

Sensing mechanism studies

The interaction between **P2** and Bi^{3+} was first investigated using UV-Vis spectroscopy. Upon the addition of 0.1 to 50 eq. of Bi^{3+} , the absorption band at 278 nm was gradually increased (Fig. 6). This new absorption band might correspond to the coordination complex between **P2** and Bi^{3+} . However, the attempt to use this technique to monitor a decomplexation process by Na₂S was unsuccessful, probably due to the formation of the insoluble Bi_2S_3 that could scatter the incident light and result in an upward absorption baseline shift (Figure S16). However, the emission spectra in Fig. 7 suggest that the fluorescence enhancement was caused by a complex formation between **P2** and Bi^{3+} , and the addition of S²⁻ ion could lead to decomplexation and a descending fluorescence signal. The binding stoichiometry of 1:1 was determined by a Job plot (Fig. 8).

The mechanistic investigation was also performed by ¹H-NMR on **P2** in deuterated methanol (Fig. 9). Upon the addition of Bi^{3+} (prepared in D_2O), most of the proton signals were shifted downfield, except for the H₁ which shifted slightly upfield. This data suggests that there is a coordination complex between **P2** and Bi^{3+} which may also lead to a deprotonation of the phenolic proton. Therefore, the enhanced fluorescence signal should also involve the inhibition of the Excited-State Intramolecular Proton Transfer (ESIPT) process.

<Figure 6>

<Figure 7>

<Figure 8>

<Figure 9>

Effect of water and pH

Before the use P2 as a sensor for Bi^{3+} in the aqueous sample, the investigation on the pH effect towards the fluorescence property was necessary since the structure of P2 contains both acidic phenol and basic imidazole groups. However, the hydrophobic nature of P2 has limited the

amount of water used in these experiments. In this study, the stock solution of **P2** was diluted with 9:1 (v/v) mixture of organic solvent (20% of DMSO in CH₃CN) and an aqueous solution of various pHs. Data in Fig. 10a showed that the fluorescent intensity of **P2** was quite persistent under the pH range from 5 to 11, while the addition of Bi³⁺ could enhance those signals at all pHs. The maximum enhancement of around 5.5 folds was observed at pH 5 (Fig. 10b). Therefore, the aqueous Bi³⁺ solution was adjusted to this pH using HCl and NaOH for the subsequent experiments. This level of acidity is also necessary since it can prevent the hydrolysis of Bi³⁺ in water.

<Figure 10>

Quantitative analysis of Bi³⁺ in real water samples

In the quantitative analysis of Bi^{3+} in water samples, a calibration curve for the system containing 10% (v/v) of pH 5 aqueous solution in mixed organic solvents (CH₃CN-DMSO (8:2, v/v)) was established (Fig. 11). The three-time-noise detection limit in this solvent system was estimated at 3.40 μ M. The water samples from two different sources were adjusted to pH 5, then spiked with Bi^{3+} at 10.00 and 15.00 μ M. The data in Table 2 showed nearly completed recovery of Bi^{3+} in each water sample. The formation of Bi^{3+} compounds with anions such as sulfate, sulfide, or phosphate in these water samples might be the cause of these incomplete recovery percentages.

<Figure 11>

<Table 2>

Conclusion

We successfully synthesized three derivatives of pyreno[4,5-*d*]imidazole (**P1-P3**) from pyrene-4,5-dione and aromatic aldehydes in moderated to good yields. In acetonitrile, all three compounds exhibit a fluorescent enhancement at 450 nm by trivalent cations such as Bi^{3+} , Fe^{3+} , Cr^{3+} , and Al^{3+} . The selectivity of the compound with a phenolic group (**P2**) could be improved towards Bi^{3+} using a CH₃CN-DMSO mixture (80:20 %v/v) as the solvent. The three-time-noise detection limit for Bi^{3+} was estimated at 1.20 μ M. The investigation by UV-Vis titration, ¹H-NMR, and the decomplexation study using Na₂S suggested that the fluorescence enhancement was involved in a complex formation between the sensor (**P2**) and Bi^{3+} .

In the system with 10% (v/v) of aqueous solution in mixed organic solvents (CH₃CN-DMSO (8:2, v/v)), the optimal condition which yielded the highest signal enhancement ratio upon addition of Bi³⁺ was at pH 5 with a detection limit at 3.40 μ M. The application of **P2** in the quantitative determination of Bi³⁺ in two real water samples resulted in acceptable recovery percentages. According to a literature survey (Table 3), the performance of **P2** is comparable to other previously reported fluorescent sensors for Bi³⁺.

<Table 3>

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article:

Figure S1. ¹H-NMR of P1 in DMSO-d6.
Figure S2. ¹³C-NMR of P1 in DMSO-d6.
Figure S3. MALDI-ToF spectrum of P1.
Figure S4. ¹H-NMR of P2 in DMSO-d6.
Figure S5. ¹³C-NMR of P2 in DMSO-d6.
Figure S6. MALDI-ToF spectrum of P2.
Figure S7. ¹H-NMR of P3 in DMSO-d6.
Figure S8. ¹³C-NMR of P3 in DMSO-d6.
Figure S9. MALDI-ToF spectrum of P3.

Figure S10. Normalized absorption and emission spectra of P1-P3 in EtOH.

Figure S11. The fluorescence spectra of P1-P3 in solvents such as CH_3CN , THF, and C_2H_5OH . Figure S12. Fluorescence spectra of a) P1, b) P2 and c) P3 (10 μ M) in CH₃CN before and after addition 10 eq of metal ions.

Figure S13. a) Fluorescence spectra and b) fluorescence enchantment ratio of P1 (10 μ M) in CH₃CNDMSO (8:2, v/v) before and after addition 10 eq of metal ions.

Figure S14. a) Fluorescence spectra and b) fluorescence enchantment ratio of P3 (10 μ M) in CH₃CNDMSO (8:2, v/v) before and after addition 10 eq of metal ions.

Figure S15. Fluorescence titration of P2 (10 μ M) by Bi³⁺ (1 to 500 μ M) in CH₃CN-DMSO (8:2, v/v).

Figure S16. UV-Vis spectra of P2 before and after the addition of Bi^{3+} , and upon a subsequent addition of Na_2S

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Figure Captions

Scheme 1. Synthesis of pyreno[4,5-*d*]imidazole derivatives

Figure 1. Target molecules P1-P3

Figure 2. Fluorescence enhancement ratio of P1, P2, and P3 (10 μ M) in CH₃CN upon addition of various metal ions (10 eq).

Figure 3. (a) Fluorescence spectra and (b) fluorescence enhancement ratio of **P2** (10 μ M) in CH₃CN-DMSO (8:2, v/v) before and after addition 10 eq of metal ions.

Figure 4. Linear Plot between the concentration of Bi^{3+} and fluorescence enhancement ratio of **P2** in CH₃CN-DMSO (8:2 v/v).

Figure 5. Interference studies of P2 (10 μ M) and Bi³⁺ (10 eq) using foreign metal ions (10 eq).

Figure 6. UV-Vis titration of P2 (10 μ M) upon the addition of various concentrations of Bi³⁺.

Figure 7. Fluorescence spectra and photographs (inset) of P2 solution before and after the addition of Bi^{3+} , and upon subsequent addition of Na_2S .

Figure 8. Job plot for determination of binding stoichiometry between P2 and Bi³⁺.

Figure 9. ¹H-NMR of P2 (in MeOH-d4) before and after the addition of Bi^{3+} (in D_2O).

Figure 10. (a) Fluorescence intensity of **P2** (10 μ M) with and without Bi³⁺ (50 μ M) and (b) fluorescence enhancement ratio in 10% (v/v) of aqueous solution at various pH in mixed organic solvents (CH₃CN-DMSO (8:2, v/v)).

Figure 11 Linear Plot between the concentration of Bi^{3+} and fluorescence enhancement ratio of **P2** in 10% (v/v) of pH 5 aqueous solution in mixed organic solvents (CH₃CN-DMSO (8:2, v/v)).

	Absorption ^a		Emission ^a		
cpd	λ _{max} (nm)	ϵ (M^{-1} c m^{-1})	λ _{ex} (nm)	λ _{max} (nm)	ϕ^{b}
P1	290 331	9900 8500	331	407	0.75
P2	289 335	13000 11300	335	448	0.41
Р3	290 333	11300 10400	333	389	0.78

 Table 1. Photophysical properties of molecules

^a solutions in ethanol; ^b Anthracene in ethanol (quantum yield 0.27) was used as the reference compound.

Water sourceSpiked (μ M)Found (μ M)Recovery (%)Tab water10.009.72 ± 0.1097.20 ± 1.0015.0013.77 ± 0.0991.80 ± 0.60Drinking water10.009.61 ± 0.0896.10 ± 0.80

Table 2. Analytical results of Bi^{3+} in water samples (n = 3).

Compound	Solvent(s)	Sensing	LOD ^a	Ref
		Mode	(µM)	
Rhodamine functionalized Zr-based	pH 6 aqueous solution	Off-on	0.008	38
MOFs				
1,8-Naphthalimide derivative	β-Cyclodextrin aqueous	Off-on	2.78	25
	solution			
Rhodamine derivative	Ethanol-MeCN	Off-on	2.69	26
Tiron	DI water	On-off	0.24	39
Pyren-1-ylmethylene-hydrazide	DMSO/water	Off-on	0.12	29
Pyreno[4,5-d]imidazole derivative	DMSO/MeCN	Off-on	1.20	This work
Pyreno[4,5-d]imidazole derivative	Water/DMSO/MeCN	Off-on	3.40	This work

Table 3. Comparison of Bi³⁺ fluorescent sensors.

^a Limit of detection.

Accel

P1 P3

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ACCE



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