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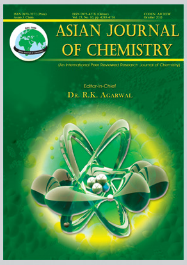

Design and Synthesis of Some 1,8-Naphthalimides as Fluorescence Probes for Transition Metal Ions

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Some 1,8-naphthalimide derivatives (**4a-4d**) were designed and synthesized from 1,8-naphthalic anhydride and their structures were characterized by ^{1}H NMR, MS and elementary analysis. Then their fluorescence probes for five transition metal ions Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} was investigated by fluorescence titration, respectively. The results showed that compound **4a** can available and selectively probe for cobalt(II) ion, with quenching constant (K_{SV}) 6.37 × 10^3 L mol^{-1} and binding constants (K_a) 3.03 × 10^3 L mol^{-1}, respectively.

Key Words: 1,8-Naphthalimides, Synthesis, Fluorescence probes.

INTRODUCTION

Fluorescence probes can selectively signal and recognize the presence of a special substance by the change of their fluorescence emission has attracted considerable interest in the past decade[1-4]. Among the multifarious fluorescence probes, the photoinduced electron transfer (PET) type fluorescent probes[5], which contain a fluorophore as the signal moiety, a receptor as the guest binding site and a spacer unit to connect the fluorophore and the receptor together, are widely used as direct fluorescent metal sensing molecules[6,7].

Recently, the probes for the detection of transition metal ions have become increasingly important because transition metal ions are essential trace elements in biological systems and a toxic pollutant in the environment[8,9]. Therefore, the design and synthesis of this kind of fluorescence probes has become hot subject in bioorganic chemistry. In the literatures[10,11], 1,8-naphthalimides were introduced as fluorophore group and showed strong fluorescence and excellent photostability. In addition, its electron deficient fluorophore could effectively weaken the photoinduced electron transfer interaction between transition metal ions and fluorophore[10,11]. In this study, 1,8-naphthalimide moiety was designed as fluorophore of some new fluorescence probes and salen group was introduced as receptor for its good metal coordinating ability[12] (**Scheme-I**).

EXPERIMENTAL

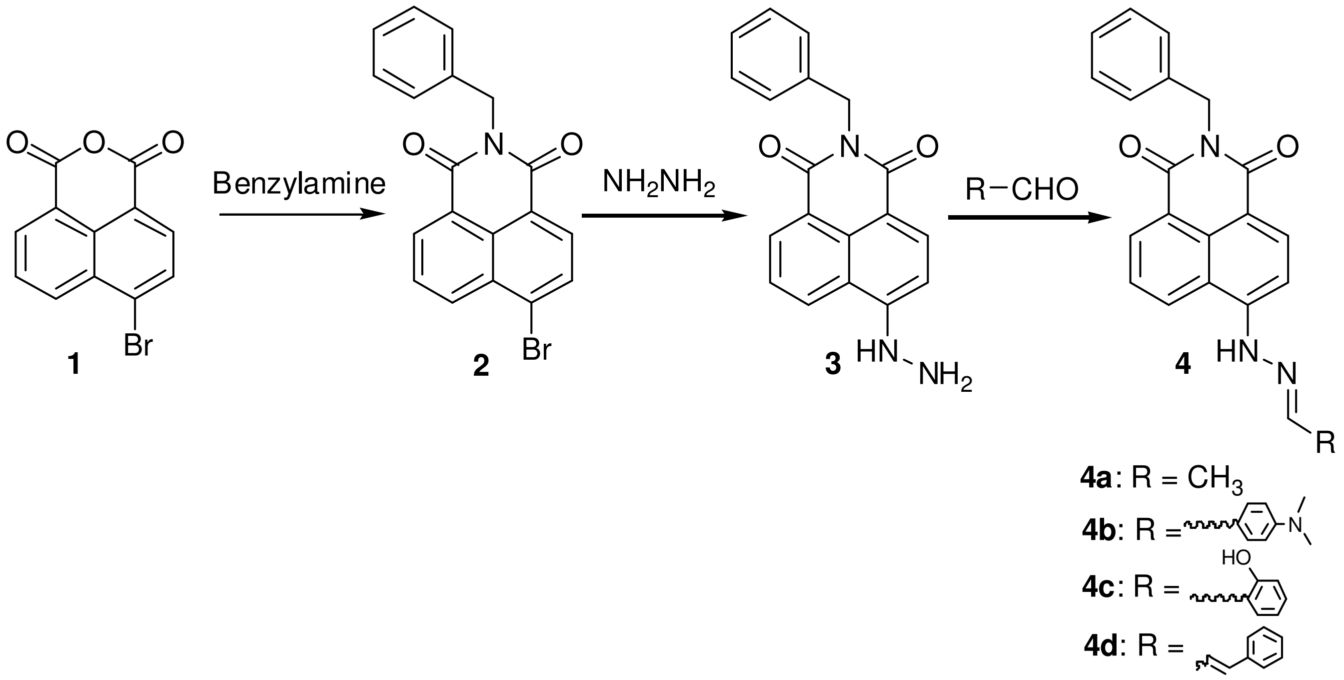
All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. The ^{1}H NMR studies were carried out by the Bruker Avance 500 instrument and the mass spectral studies were done using Bruker Esquire HCT instrument. Elemental analyses were determined in the Carlo Erba model 1106 instrument. Melting points were recorded using an electrothermal-WRS-1A melting point apparatus and are uncorrected. The fluorescence spectra were recorded in the RF-5301 fluorospectrophotometer.

General procedure

Synthesis; Synthesis of compound 2: The mixture of 4-bromo-1,8-naphthalic anhydride (100 mmol) and benzylamine (110 mmol) was refluxed in ethanol (100 mL) for 4h and then filtered to give yellow crystals of compound **2**.

Compound 2: Yield 90.2 %, m.p. 174.2-174.9 ºC. Anal. calcd. (%) for $C_{19}H_{12}NO_2Br$: C, 62.32; H, 3.30; N,3.82. Found (%): C, 62.18; H, 3.43; N,3.95. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.2 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 8.4 Hz, 1H), 5.39 (s, 2H).

Synthesis of compound 3: The mixture of compound **2** (50 mmol) and hydrazine hydrate (100 mmol) was refluxed in



Scheme-I

2-methoxyethanol (25 mL) for 4h and then filtered to give yellow powder of compound **3**.

Compound 3: Yield 80 %, m.p. 218.2-220 ºC, Anal. calcd. (%) for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N,13.24. Found (%): C, 71.68; H, 5.01; N,13.03. ^{1}H NMR (500 MHz, DMSO), δ: 11.53 (s, ^{1}H, N-H), 8.78-8.82 (m, 5H, Ar-H), 8.24 (d, 2H, Ar-H), 8.17 (d, 2H, Ar-H), 7.90 (s, 1H, Ar-H), 7.83 (d, 2H, Ar-H), 5.45(s, 2H, -CH_2-).

Synthesis of compounds 4: The mixture of compound **3** (10 mmol) and different aldehydes (12 mmol) was refluxed in ethanol (25 mL) for 4h and then filtered to give yellow powder of compound **4**.

Compound 4a: Yield 85.3 %, m.p. 198.2-200 ºC, Anal. calcd. (%) for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found (%): C, 73.71; H, 5.21; N,12.01. MS (ESI) m/z: 344[M+1]$^+$; ^{1}H NMR (500 MHz, CDCl), δ: 8.63 (s, 1H, Ar-H), 8.56 (d, 1H, Ar-H), 8.34 (s, 1H, N-H), 8.12 (d, 1H, Ar-H), 7.68 (dd, 2H, Ar-H), 7.56 (d, 2H, Ar-H), 8.45 (d, 1H, Ar-H), 7.32 (m, 2H, Ar-H), 6.55 (s, 1H, CH=C), 5.40 (s, 2H, -CH_2-), 1.58 (s, 3H, -CH_3).

Compound 4b: Yield 81.0 %, m.p. 223.4-225.1 ºC, Anal. calcd. (%) for $C_{28}H_{24}N_4O_2$: C, 74.98; H, 5.39; N, 12.49. Found (%): C, 74.71; H, 5.64; N, 12.31. MS (ESI) m/z: 449[M+1]$^+$; ^{1}H NMR (500 MHz, DMSO), δ: 8.64 (d, 1H, Ar-H), 8.59 (d, 1H, Ar-H), 8.49 (s, 1H, N-H), 8.18 (d, 1H, Ar-H), 7.99 (dd, 1H, Ar-H), 7.72 (d, 1H, Ar-H), 7.65 (d, 3H, Ar-H), 7.56 (d, 2H, Ar-H), 7.25-7.32 (m, 5H, Ar-H), 6.57 (s, 1H, CH=C), 5.40 (s, 2H, -CH_2-), 3.08 (s, 6H, 2CH_3-).

Compound 4c: Yield 85.0 %, m.p. 256-258 ºC, Anal. calcd. (%) for $C_{26}H_{19}N_3O_3$: C, 74.10; H, 4.54; N, 9.97. Found (%): C, 73.87; H, 4.33; N, 10.19. MS (ESI) m/z: 422[M+1]$^+$; ^{1}H NMR (500 MHz, DMSO), δ: 8.62-8.71 (m, 6H, Ar-H), 8.51-8.58 (m, 5H, Ar-H), 8.34 (s, 1H, N-H), 8.31 (s, 1H, N-H), 7.51-7.57(m, 3H, Ar-H), 6.66 (s, 1H, CH=C), 5.41 (s, 2H, -CH_2-).

Compound 4d: Yield 72.1 %, m.p. 178-180 ºC, Anal. calcd. (%) for $C_{28}H_{21}N_3O_2$: C, 77.94; H, 4.91; N, 9.74. Found (%): C, 77.71; H, 5.15; N, 9.98. MS (ESI) m/z: 432[M+1]$^+$; ^{1}H NMR (500 MHz, DMSO), δ: 8.64 (d, 1H, *J* = 5.0 Hz, Ar-H), 8.56 (d, 1H, *J* = 10.0 Hz, Ar-H), 8.49 (s, 1H, N-H), 8.18 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.99 (s, 1H, CH=CH), 7.68 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.45 (m, 3H, Ar-H), 7.32 (m, 2H, Ar-H), 7.27-7.31(m, 6H, Ar-H), 6.77 (d, 2H, *J* = 10.0 Hz, CH=CH), 5.42 (s, 2H, -CH_2-).

Detection method: The transition metal ions association property of the compounds **4** were investigated by fluorescence quenching spectroscopy. At room temperature, compounds **4** and transition metal ions sulfate ($CdSO_4$, $CoSO_4$, $CuSO_4$, $NiSO_4$ and $ZnSO_4$) were dissolved in DMF-water (7:3, v:v) to the proper concentration, respectively. After addition of transition metal ions (0.1 mL) solution to compounds **4** solution (3.9 mL), respectively, the reaction mixture was allowed to stand for 0.5 h (until the stable) with intermittent shaking and the fluorescence spectroscopy was scanned in the RF-5301 fluorospectrophotometer.

RESULTS AND DISCUSSION

4-Bromo-1,8-naphthalic anhydride was treated with benzylamine to offer *N*-benzyl-4-bromo-1,8-naphthalimide (**2**) in 90.2 % yields, which was then treated with hydrazine hydrate to get compound (**3**) in 80 % yields. By the condensation of compound **3** with some aldehydes, the target compounds (**4a-4d**) were obtained in 81-85.3 % yields. The structures of synthesized compounds were identified by ^{1}H NMR, MS and micro analysis. The characterized data of the synthesized compounds were given in experimental section.

In ^{1}H NMR spectra of the compounds **2-4**, the chemical shifts in the range of 7.83-8.67 and 7.25-7.57 ppm were assigned to the resonance of the hydrogen of naphthalene moiety and benzene ring, respectively. The chemical shift in about 5.40 ppm was assigned to the resonance of the hydrogens in methylene group. The resonances of all other protons were also appeared in the expected region. In addition, the mass spectra and micro analysis data were well consistent with their structure. The results adequately indicated the confirmation of their structures.

The compounds **4** displayed strong fluorescence emission in dimethyl sulphoxide-water (7:3, v:v) as shown in Fig. 1. The associations between the compounds **4** and the transition metal ions were investigated by fluorescence titration. The fluorescence change of the compounds **4** were monitored in dimethyl sulphoxide-water (7:3, v:v) and the typical spectral changes were shown in Fig. 1.

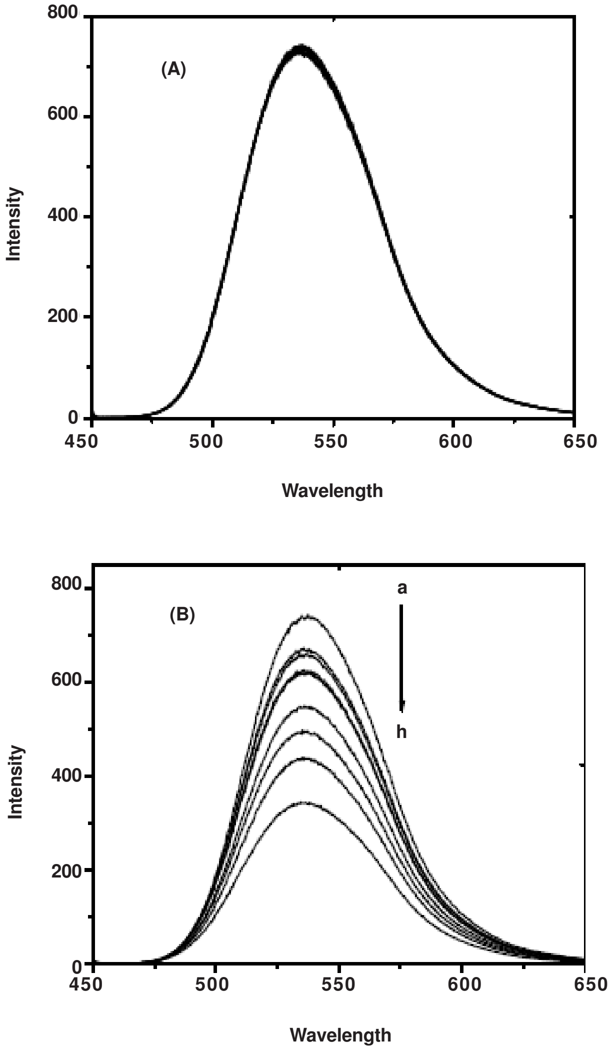


Fig. 1. Fluorescence spectra of compound **4a** quenched by Cd^{2+} (A) and Co^{2+} (B)a; a. The concentration of compound **4a** was 2.5×10^{-5} $mol \cdot L^{-1}$; The concentrations of Co^{2+} a→h were: 0, 0.1, 0.5, 1.0, 5.0, 10.0, 50.0, 100.0×10^{-5} $mol \cdot L^{-1}$, respectively

As can be seen in Fig. 1(A), the fluorescence emission intensities of compounds **4b-4d** were not quenched at all. It indicated that compounds **4b-4d** did not have any association with Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}, as well as sulfate anion. The same phenomenon happened when compound **4a** was treated with Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}, respectively, in the same condition. However, the intensity of the emission spectrum from 2.5×10^{-5} mol/L solution of the compound **4a** decreased as the concentration of Co^{2+} was increased, which indicated an association between the compound **4a** and Co^{2+}. The result strongly suggested that compound **4a** have good selective recognition with Co^{2+}. On the basis of this observation, it was suggested that the selective recognition of **4a** should be attributed to the tender receptor group ethyl-salen, since that the tender group was more sensitive to the changes of the molecular microenvironment in a vicinity of the chromophore molecules and the binding to transition metal ions.

$$\frac{F_0}{F} = 1 + k_q \tau_0 c(Q) = 1 + K_{cv} c(Q) \quad (1)$$

$$\frac{F_0}{F_0 - F} = \frac{F_0}{\Delta F} = \frac{1}{f_a K_a c(Q)} + \frac{1}{f_a} \quad (2)$$

Fluorescence quenching of compound **4a** by Co^{2+} ion was then confirmed by the Stern-Volmer equation[13,14] (1) and modified Stern-Volmer equation[13,14] (2) as that in Fig. 2 and the values of Stern-Volmer quenching constant (K_{SV}) and binding constants (K_a) were consequently determined to be 6.37×10^3 L mol^{-1} and 3.03×10^3 L mol^{-1}, respectively. All the above results implied that compound **4a** can availably and selectively probe for Co^{2+}.

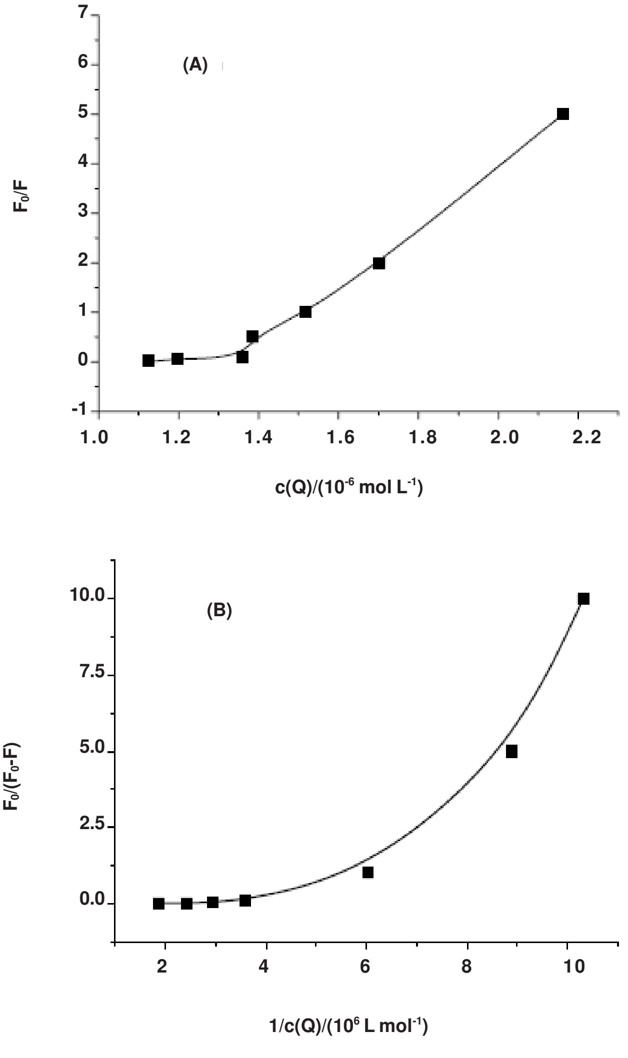


Fig. 2. Stem-Volmer (A) and Lineweaver-Burk (B) plots of the fluorescence quenching of compound **4a**

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REFERENCES

1. A.P. De Silva, B. McCaughan, B.O.F. McKinney and M. Querol, *Dalton Trans.*, 1902 (2003).
2. G.W. Gokel, W.M. Leevy and M.E. Weber, *Chem. Rev.*, **104**, 2723 (2004).
3. S.K. Wu, *Prog. Chem.*, **16**, 174 (2004).
4. K. Haupt and K. Mosbach, *Chem. Rev.*, **100**, 2495 (2000).
5. A.P. De Silva, Q.N. Hu, T. Gunnlauggson, A.J.M. Huxley, C.P. McCoy, J.T. Radmancher and T.E. Rice, *Chem. Rev.*, **97**, 1515 (1997).
6. V. Amendola, L. Fabbrizzi, F. Forti, M. Licchelli, C. Mangano, P. Pallavicini, A. Poggi, D. Sacchi and A. Taglieti, *Coord. Chem. Rev.*, **250**, 273 (2006).
7. B. Valeur and I. Leray, *Acc. Chem. Res.*, **205**, 3 (2000).
8. R. Corradini, A. Dossena, G. Galaverna, R. Marchelli, A. Panagia and G. Sartor, *J. Org. Chem.*, **62**, 6283 (1997).
9. G.K. Walkup and B. Imperiali, *J. Am. Chem. Soc.*, **118**, 3053 (1996).
10. Z.G. Li, Q. Yang and X.H. Qian, *Bioorg. Med. Chem.*, **13**, 4864 (2005).
11. T. Gunnlaugsson, P.E. Kruger, T.C. Lee, R. Parkesh, F.M. Pfeffer and G.M. Hussey, *Tetrahedron Lett.*, **44**, 6575 (2003).
12. Y. Hu, Q.Q. Li, H. Li, Q.N. Guo, Y.G. Lu and Z.Y. Li, *Dalton Trans.*, 11344 (2010).
13. M.R. Eftink, in ed.: T.G. Dewey, Fluorescence Quenching Reactions, Biophysical and Biochemical Aspects of Fluorescence Spectroscopy, Plenum Press, New York, pp. 1-44 (1991).
14. J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Plenum Press, New York, p. 698 (1999).