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Selective fluorescence sensing of ferric ion with novel triazolethione Schiff bases probes

Abstract: New triazolethione Schiff base derivatives **3a–f** were synthesized. The structures of the products were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR and MS. Their complexation properties to different heavy and transition metal ions were studied by UV-Vis and fluorescence spectroscopy. Compound **3a** shows selective recognition of Fe^{3+} with a 1:1 stoichiometric complex formation.

Keywords: ferric ion; fluorescence; recognition; Schiff bases; triazolethione.

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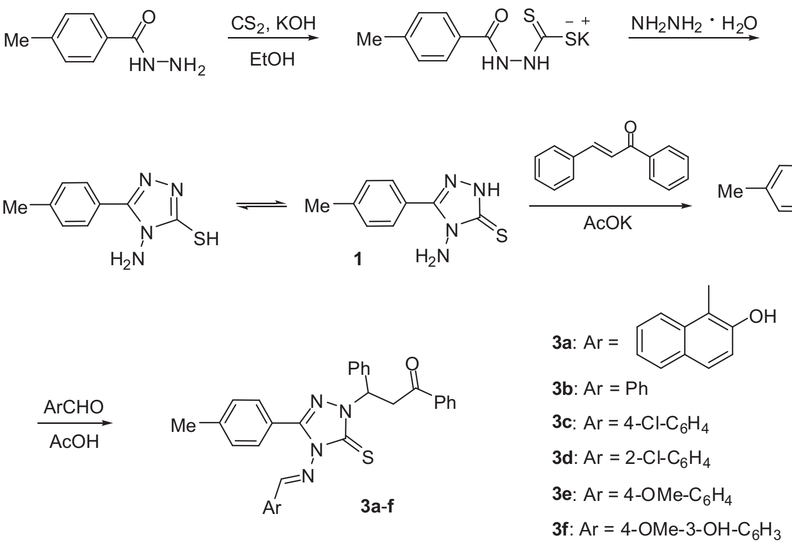
Introduction

Contamination of water by heavy metal ions is a serious environmental problem. Heavy metals can be toxic pollutants that are nonbiodegradable and have environmental, public health and economic impacts [1]. In this regard, metal-selective fluorescent probes have been widely exploited to detect biologically or environmentally relevant metal ions [2–6]. However, very few fluorescent sensors for Fe^{3+} have been reported.

Schiff base derivatives are frequently utilized as sensors for anions and alkaline earth cations [7–10]. Recently, some Schiff base-based fluorescent probes have also been utilized to detect heavy and transition metal ions [11–13]. There are few reports about the triazole Schiff base derivatives for recognition of Fe^{3+} [14, 15]. In this work, six new triazolethione Schiff base derivatives were synthesized and preliminary complexation to heavy and transition metal ions were studied. The results show that compound **3a** displays a highly selective and sensitive response towards Fe^{3+} in CH_2Cl_2/DMF media.

Results and discussion

The synthetic route to triazolethione Schiff bases derivatives **3a–f** is shown in Scheme 1. The final compounds were characterized by elemental analysis, ^{1}H NMR,



Scheme 1

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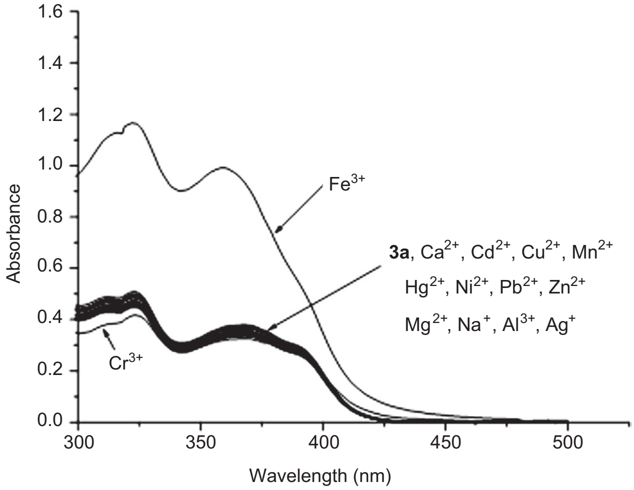

Figure 1 UV-Vis spectra of compound **3a** (10 μM) upon addition of various metal ions (20 μM) in CH_2Cl_2 and DMF (v/v = 9:1).

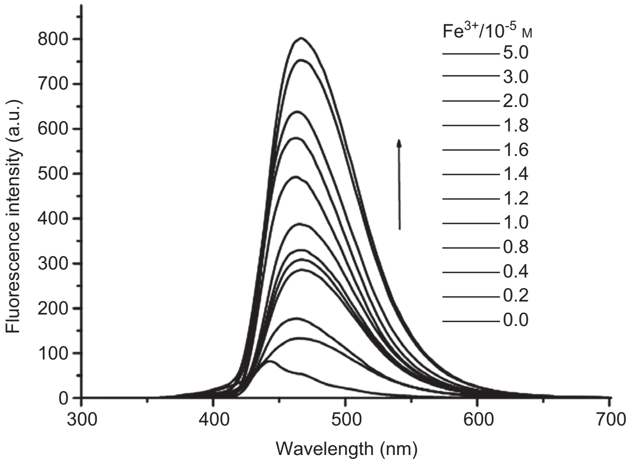

Figure 3 Fluorescene emission spectra of **3a** (10 μM) for Fe^{3+} ion titration in CH_2Cl_2 and DMF (v/v = 9:1) (λ_{ex} = 386 nm).

^{13}C NMR, IR and MS. All analytical data were in agreement with the desired structures.

Complexation properties of compounds **3a–f** towards various heavy and transition metal cations including Ca^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Na^+, Al^{3+}, Fe^{3+}, Ag^+ and Cr^{3+} were investigated by using UV-Vis and fluorescence spectroscopy. It was found that compound **3a** is the most selective agent for recognition of Fe^{3+}. As shown in Figure 1, the absorption maximum band of metal-free compound **3a** is observed at 367 nm. When Fe^{3+} is added, the absorption band is increased in intensity and blue-shifted to approximately 358 nm. The addition of Cr^{3+} causes a small change in the spectrum, and even smaller changes are observed after addition of other metal ions.

The fluorescence spectra of compound **3a** in the presence of Fe^{3+} and Cr^{3+} in CH_2Cl_2/DMF solution are shown in Figure 2. Metal-free compound **3a** exhibits weak fluorescence emission at 445 nm. Upon the addition of 2 equiv. of Fe^{3+}, the fluorescence intensity is significantly enhanced and the wavelength is red-shifted by 18 nm. Because addition of Cr^{3+} does not cause remarkable response, it may be concluded that **3a** is a selective and sensitive agent for complexation of Fe^{3+}.

The titration of probe **3a** by Fe^{3+} using excitation at λ_{ex} = 386 nm is given in Figure 3. With an increase in concentration of Fe^{3+}, the fluorescence spectra exhibit an increase in emission intensity at 463 nm. Because a single isosbestic point is observed, a single equilibrium is reached during complexation. The binding constant determined from the titrations of **3a** with Fe^{3+} is 3.21×10^6.

For the complexation ratio between compound **3a** and Fe^{3+} ion, the Job's plot experiment by varying the

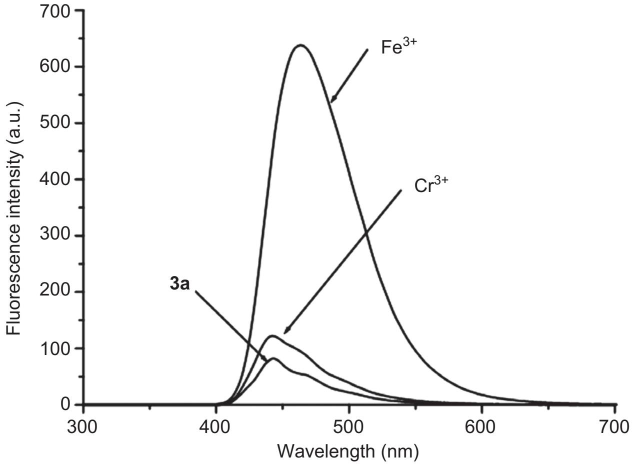

Figure 2 Fluorescence emission spectra of compound **3a** upon addition of Fe^{3+} and Cr^{3+} (20 μM) in CH_2Cl_2 and DMF (v/v = 9:1).

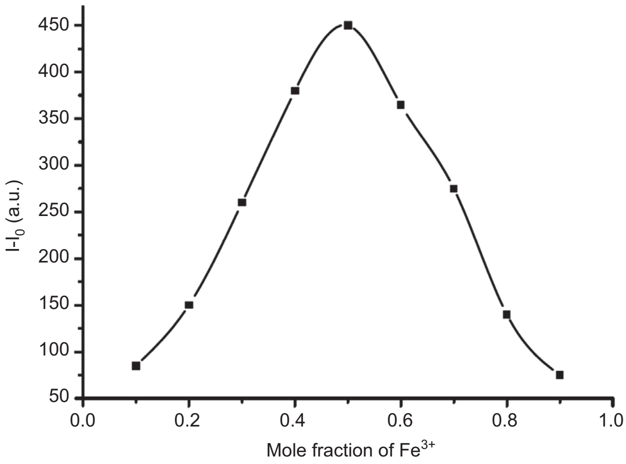

Figure 4 Job's plot for compound **3a** and Fe^{3+} (λ_{ex} = 386 nm).

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concentrations of both compound **3a** and Fe^{3+} ion was conducted. As shown in Figure 4, the maximum point at the molar fraction of 0.5 indicates the complexation ratio of 1:1.

Conclusion

Of the six new triazolethione Schiff bases, compound **3a** displays selective fluorescence change upon the addition of Fe^{3+} in the presence of other metal ions. This system provides potential fluorescent probe for Fe^{3+}.

Experimental

3-(*p*-Methylphenyl)-4-amino-5-mercapto-1,2,4-triazol **1** [16] and chalcone [17] were prepared as previously described. Other reagents were obtained from commercial sources and used without further purification. Melting points were measured on a Yanagimoto MP-500 apparatus and are uncorrected. IR spectra were obtained in KBr pellets on a Perkin Elmer spectrophotometer. Mass spectral data were obtained on an Agilent 1100 LC/MS instrument. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ at room temperature on a Bruker Avance-500 spectrometer.

General procedure for synthesis of compounds 3a–f

A magnetically stirred mixture of chalcone (0.05 mol) and K_2CO_3 (0.05 mol) in methanol (30 mL) was treated with 3-(*p*-methylphenyl)-4-amino-5-mercapto-1,2,4-triazol **1** (0.04 mol). The mixture was heated under reflux for 8 h, and then cooled. The resulting solid of **2** was filtered and crystallized from ethanol. A solution of **2** (0.02 mol) and aromatic aldehyde (0.02 mol) in glacial acetic acid (25 mL) was stirred and heated under reflux for 12 h. The insoluble impurities were then filtered out from the hot solution and the solution was concentrated under reduced pressure. The residue was crystallized from ethanol to give analytically pure product **3a–f**.

3-[3-(*p*-Methylphenyl)-4-(2-hydroxynaphthylmethyleneamino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3a) Yield 69%; mp 164–166°C (dec); IR: 3252, 3024, 2979, 2861, 1677, 1601, 1468, 1458, 1350, 1257, 1151, 747, 696 cm^{-1}; ^1H NMR: δ 11.44 (s, 1H, CH = N), 11.29 (s, 1H, OH), 8.15 (d, 1H, *J* = 8.5 Hz, Ar-H), 8.04 (d, 2H, *J* = 7.5 Hz, Ar-H), 8.01 (d, 1H, *J* = 7.5 Hz, Ar-H), 7.90 (t, 2H, *J* = 8.5 Hz, Ar-H), 7.79 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.68 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.62 (m, 4H, Ar-H), 7.49 (m, 2H, Ar-H), 7.42 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.39 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.16 (d, 1H, *J* = 9.0 Hz, Ar-H), 6.89 (dd, 1H, J_1 = 9.0 Hz, J_2 = 5.0 Hz, CH), 4.51 (dd, 1H, J_1 = 18.0 Hz, J_2 = 9.0 Hz, CH_2), 3.77 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.0 Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 162.5, 160.9, 148.3, 138.4, 136.5, 135.8, 133.4, 133.4, 129.6, 128.9, 128.8, 128.7, 128.7, 128.5, 128.4, 127.6, 124.2, 120.8, 119.0, 107.4, 58.1, 42.8, 21.0; MS: m/z 569.7 ($M+H^+$). Anal. Calcd for $C_{35}H_{28}N_4O_2S$: C, 73.85; H, 4.93; N, 9.91. Found: C, 73.92; H, 4.96; N, 9.85.

3-[3-(*p*-Methylphenyl)-4-benzylideneamino-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3b) Yield 74%; mp 179–181°C (dec); IR: 3263, 3056, 2958, 2893, 1675, 1606, 1464, 1426, 1352, 1264, 1151, 823, 751, 690 cm^{-1}; ^1H NMR: δ 10.22 (s, 1H, CH = N), 8.04 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.86 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.77 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.65 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.60 (t, 1H, *J* = 7.0 Hz, Ar-H), 7.53 (d, 1H, *J* = 7.0 Hz, Ar-H), 7.49 (m, 4H, Ar-H), 7.40 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.34 (t, 1H, *J* = 7.0 Hz, Ar-H), 7.25 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.88 (dd, 1H, J_1 = 9.0 Hz, J_2 = 5.0 Hz, CH), 4.47 (dd, 1H, J_1 = 18.0 Hz, J_2 = 9.0 Hz, CH_2), 3.78 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.0 Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 163.3, 162.2, 148.4, 140.9, 138.5, 136.6, 133.3, 132.7, 132.3, 129.1, 128.9, 128.8, 128.7, 128.7, 128.6, 128.22, 128.2, 127.7, 122.8, 57.1, 42.9, 21.5; MS: m/z 503.6 ($M+H^+$). Anal. Calcd for $C_{31}H_{26}N_4OS$: C, 74.14; H, 5.18; N, 11.19. Found: C, 74.08; H, 5.21; N, 11.15.

3-[3-(*p*-Methylphenyl)-4-(4-chlorobenzylideneamino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3c) Yield 75%; mp 164–166°C (dec); IR: 3008, 2945, 2873, 1687, 1670, 1603, 1507, 1454, 1376, 1344, 817, 747, 697 cm^{-1}; ^1H NMR: δ 10.298 (s, 1H, CH = N), 8.03 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.77 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.73 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.64 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.59 (t, 1H, *J* = 7.5 Hz, Ar-H), 7.48 (m, 4H, Ar-H), 7.39 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.33 (t, 1H, *J* = 7.5 Hz, Ar-H), 7.26 (t, 2H, *J* = 9.5 Hz, Ar-H), 6.86 (dd, 1H, J_1 = 9.5 Hz, J_2 = 5.0 Hz, CH), 4.47 (dd, 1H, J_1 = 18.0 Hz, J_2 = 9.5 Hz, CH_2), 3.75 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.0 Hz, CH_2), 2.40 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 162.1, 161.3, 148.5, 141.0, 138.4, 136.6, 133.4, 131.3, 129.9, 129.3, 129.2, 128.8, 128.7, 128.2, 128.21, 127.7, 122.7, 57.1, 42.8, 21.5; MS: m/z 538.1 ($M+H^+$). Anal. Calcd for $C_{31}H_{25}N_4OSCl$: C, 69.40; H, 4.66; N, 10.38. Found: C, 69.33; H, 4.69; N, 10.43.

3-[3-(*p*-Methylphenyl)-4-(2-chlorobenzylideneamino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3d) Yield 79%; mp 160–162°C (dec); IR: 3015, 2960, 2871, 1685, 1669, 1593, 1499, 1467, 1378, 1348, 811, 738, 699 cm^{-1}; ^1H NMR: δ_H (ppm) 10.84 (s, 1H, CH = N), 8.08 (q, 3H, *J* = 7.5 Hz, Ar-H), 7.75 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.67 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.61 (t, 1H, *J* = 7.5 Hz, Ar-H), 7.500 (m, 4H, Ar-H), 7.41 (t, 2H, *J* = 7.5 Hz, Ar-H), 7.34 (t, 2H, *J* = 7.0 Hz, Ar-H), 7.26 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.89 (dd, 1H, J_1 = 9.0 Hz, J_2 = 5.0 Hz, CH), 4.47 (dd, 1H, J_1 = 18.0 Hz, J_2 = 9.0 Hz, CH_2), 3.79 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.0 Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 162.2, 159.1, 148.6, 140.9, 138.4, 136.6, 136.6, 133.3, 132.9, 130.8, 130.2, 129.2, 128.8, 128.7, 128.7, 128.6, 128.2, 128.2, 127.9, 127.8, 127.1, 122.8, 57.1, 42.8, 21.50; MS: m/z 538.1 ($M+H^+$). Anal. Calcd for $C_{31}H_{25}N_4OSCl$: C, 69.38; H, 4.67; N, 10.48. Found: C, 69.33; H, 4.69; N, 10.43.

3-[3-(*p*-Methylphenyl)-4-(4-methoxybenzylideneamino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3e) Yield 77%; mp 146–148°C (dec); IR: 3005, 2959, 2867, 1690, 1671, 1607, 1493, 1464, 1380, 1345, 845, 741, 702 cm^{-1}; ^1H NMR: δ_H (ppm) 9.93 (s, 1H, CH = N), 8.06 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.79 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.672 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.62 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.51 (m, 1H, Ar-H), 7.41 (m, 5H, Ar-H), 7.25 (t, 2H, *J* = 8.0 Hz, Ar-H), 7.03 (d, 2H, *J* = 8.0 Hz, Ar-H), 6.914 (dd, 1H, J_1 = 9.0 Hz, J_2 = 5.0 Hz, CH), 4.4 (dd, 1H, J_1 = 18.0 Hz, J_2 = 9.0 Hz, CH_2), 3.90 (s, 3H, OCH_3), 3.78 (dd, 1H, J_1 = 18.0 Hz, J_2 = 5.0 Hz, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 164.0, 162.2, 149.9, 148.1, 146.9, 140.9, 138.6, 136.6, 133.2, 129.1, 128.7, 128.7, 128.6, 128.2, 128.1, 127.7, 125.1, 124.9, 122.9, 114.4, 57.2, 55.5, 42.9, 21.5; MS: m/z 533.7 ($M+H^+$). Anal. Calcd for $C_{32}H_{28}N_4O_2S$: C, 72.23; H, 5.27; N, 10.57. Found: C, 72.16; H, 5.30; N, 10.52.

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3-[3-(*p*-Methylphenyl)-4-(3-hydroxy-4-methoxybenzylideneamino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-1-yl]-1,3-diphenylpropan-1-one (3f) Yield 73%; mp 175–177°C (dec); IR: 3286, 3019, 2951, 2881, 1693, 1672, 1594, 1497, 1452, 1379, 1342, 885, 815, 734, 703 cm^{-1}; ^{1}H NMR: δ 9.851 (s, 1H, CH = N), 8.06 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.79 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.67 (d, 2H, $J = 7.5$ Hz, Ar-H), 7.619 (t, 1H, $J = 7.0$ Hz, Ar-H), 7.51 (m, 3H, Ar-H), 7.41 (t, 2H, $J = 7.0$ Hz, Ar-H), 7.36 (d, 2H, $J = 7.0$ Hz, Ar-H), 7.33 (t, 1H, $J = 7.5$ Hz, Ar-H), 7.25 (d, 1H, $J = 8.0$ Hz, Ar-H), 7.02 (d, 1H, $J = 8.0$ Hz, Ar-H), 6.89 (dd, 1H, $J_1 = 9.0$ Hz, $J_2 = 5.0$ Hz, CH), 6.07 (s, 1H, OH), 4.48 (dd, 1H, $J_1 = 18.0$ Hz, $J_2 = 9.0$ Hz, CH_2), 3.94 (s, 3H, OCH_3), 3.79 (dd, 1H, $J_1 = 18.0$ Hz, $J_2 = 5.0$ Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR: δ 195.8, 164.4, 162.3, 149.9, 148.1, 146.9, 140.9, 138.5, 136.6, 133.3, 129.1, 128.7, 128.7, 128.6, 128.2, 128.2, 127.7, 125.1, 124.9, 122.9, 114.6, 109.2, 57.2, 56.1, 42.9, 21.5; MS: m/z 549.7 (M+H$^+$). Anal. Calcd for $C_{32}H_{28}N_4O_3S$: C, 70.13; H, 5.11; N, 10.25. Found: C, 70.05; H, 5.14; N, 10.21.

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