

Supporting Information (SI)

A dual-model and on-off fluorescent $\text{Al}^{3+}/\text{Cu}^{2+}$ - chemosensor and the detection of $\text{F}^{-}/\text{Al}^{3+}$ with 'in situ' prepared $\text{Al}^{3+}/\text{Cu}^{2+}$ complex

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Experimental

Materials and methods

All of the chemicals were purchased from commercial suppliers and used without further purification. All of the reactions were performed under an argon atmosphere using solvents purified with standard methods.

¹H and ¹³C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 Tesla FTMS-MALDI/DHB). Melting point was measured on X-4 digital micro melting point analyzer.

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV-vis absorption spectroscopy was measured with a TU-1901 double-beam UV-vis Spectrophotometer, and fluorescence spectroscopy was determined on a Hitachi F-4500 spectrometer. The fluorescence quantum yields were measured at 20 °C with quinine bisulfate in 1 M H₂SO₄ (Φ_f = 0.546) selected as the reference.^{S1} Time-resolved fluorescence spectra were measured on a LifeSpec picosecond TRF spectrometer (Edinburgh Instruments Ltd.). The sample concentration was set to 2.5 × 10⁻⁵ M.

Synthesis of pyrido[2,3-d]pyrimidine (3)^{S2}

A mixture of nicotinamide (9.127 g, 0.075 mol) and ammonium ulfamate (13.07 g, 0.113 mol) was heated at 200 °C for 6 hours under stirring. After reaction, the above mixture was cooled to room temperature and water was added to make the product disperse. The reaction product was filtered and washed with water and ether, and the solid product was dried in vacuum and used for next reaction without structural characterization.

Synthesis and characterization of 2-aminonicotinaldehyde (2)^{S2}

A 30 mL 2 M HCl solution of **3** (used directly from the above reaction) was refluxed for 4 hours and cooled to room temperature. With 10 M NaOH solution, pH of the above reaction liquid was mediated to 7~8. The above mixture was extracted with ether and crude product was obtained from the concentration in vacuum. The final product (1.373 g) was obtained by column chromatography over silica gel column using dichloromethane/ethanol (30:1) as eluent. The yield was 30%. Characterization of compound **2**: ¹H NMR: δ_H (400 MHz; CDCl₃; Me₄Si) 6.743 (m, 3H), 7.810 (m, 1H), 8.267 (m, 1H), and 9.864 (s, 1H). ¹³C NMR: δ_C (100Hz, CDCl₃): 112.91, 113.81, 144.18, 154.75, 158.37, and 192.67. Decomposition temperature: 68~70°C.

Synthesis and characterization of 2-amino-3-(1H-benzo[d]imidazol)pyridine (1)^{41,S3}

NaHSO₃ (0.868 g, 0.083 mol), phenylenediamine (0.317 g, 0.003 mol), and 10 mL ethanol were added in a three neck flask. Under argon atmosphere, ethanol solution of compound **2** (0.369 g, 0.003 mol) was added dropwise into above solution. The mixture was refluxed for 4 hours and filtered. The solid product was washed with ethanol and the crude product was obtained from the concentration of the filtrate in vacuum. The final product (441.5 mg) was obtained by column chromatography over silica gel column using dichloromethane/ethanol (30:1) as eluent. The yield was 70%. Characterization of compound **1**: HRMS (EI) calcd. for C₁₂H₁₀N₄ [M + 1], 211.09055; found, 211.09782. ¹H NMR: δ_H (400 MHz, DMSO-*d*₆, Me₄Si): 6.73 (m, 1H), 7.24 (s, 2H), 7.62 (d, 2H), 7.89 (s, 2H), 8.10 (d, 1H), 8.22 (d, 1H), and 12.88 (s, 1H). ¹H NMR: δ_H (400 MHz, DMSO-*d*₆+D₂O, Me₄Si): 6.73 (m, 1H), 7.24 (s, 2H), 7.61 (d, 2H), 8.09 (d, 1H), and 8.19 (d, 1H). ¹³C NMR: δ_C (100 MHz, DMSO-*d*₆): 106.37, 111.47, 112.10, 118.99, 122.19, 123.33, 134.37, 135.49, 143.15, 150.15, 151.16, and 157.78. Mp = 161~163°C.

Reference

- S1 Z. X. Li, L. Y. Liao, W. Sun, C. H. Xu, C. Zhang, C. J. Fang, C. H. Yan, *J. Phys. Chem. C*, 2008, **112**, 5190–5196.
S2 Z. P. Liu, C. L. Zhang, Y. L. Li, Z. Y. Wu, F. Qian, X. L. Yang, W. J. He, X. Gao, Z. Guo, *Org. Lett.*, 2009, **11**, 795–798.
S3 Z. X. Li, L. Y. Liao, W. Sun, C. H. Xu, C. Zhang, C. J. Fang, C. H. Yan, *J. Phys. Chem. C*, 2008, **112**, 5190–5196.

Results and discussion

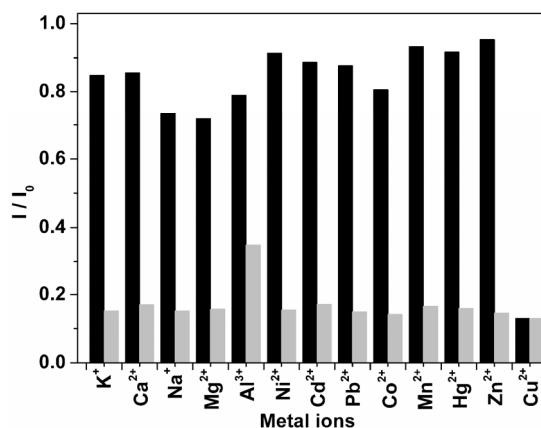


Fig. S1 Fluorescence responses of **1** (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of different metal salts (13 equiv of salt ion relative to **1**) (dark bars) and fluorescence changes of the mixture of **1** and Cu^{2+} after addition of an excess of the indicated metal ions (39 equiv relative to **1**) (light gray bars). The excitation wavelength was 356 nm. For the dark bars, I_0 and I represent the emission intensities at 528 nm in the fluorescence spectroscopy of compound **1** after addition of the metal ion to the solution of **1**; for the light gray bars, I_0 represents the emission intensity at 528 nm in the fluorescence spectrum of compound **1**, and I represents the intensity in the fluorescence spectrum of the mixture of **1** and Cu^{2+} after addition of an excess of the metal ion. The metal salts used were KCl, CaCl_2 , NaCl, MgCl_2 , $\text{Al}(\text{NO}_3)_3$, NiCl_2 , CdCl_2 , PbCl_2 , MnCl_2 , CoCl_2 , HgCl_2 , ZnSO_4 , and CuCl_2 .

Influence of solvents on the detection of Al^{3+}

We have tried other solvents such as ethanol (**Fig. S1**), DMSO (**Fig. S2**), and HEPES buffer solution (**Fig. S3**). The fluorescence in ethanol responses similar as that in H_2O -EtOH (1:9) solution, and fluorescence didn't change in DMSO and HEPES buffer solution upon addition of metal ions. Besides, we have also tried to add more proportions of water in this system, no fluorescence changed upon addition of metal ions with more proportions of water in this system.

Influence of anions on the emission spectrum of the 'in situ' prepared **1**·Al complex

We have tried other anions such as CH_3COONa , $\text{Na}_2\text{C}_2\text{O}_4$, Na_2HPO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , Na_2SO_4 , NaClO_3 , NaH_2PO_4 , NaHS, NaHSO_3 , NaHSO_4 , NaNO_2 , NaNO_3 , and Sodium citrate, and found that they could make the fluorescence spectra of **1** restore except NaHSO_4 , NaNO_3 , NaClO_3 , and NaHS (**Figures from S4 to S17**).

HRMS spectra study on the 'in situ' prepared **1**·Al and **1**·Cu complexes

We have tried to do ^1H NMR titration on this system. Because only in ethanol and H_2O -EtOH (1:9) solution, can fluorescence response was obtained upon addition of metal ions, we have selected ethanol- d_6 as solvent. Because of poor solubility of the **1** and $\text{Al}^{3+}/\text{Cu}^{2+}$ complex, no ^1H NMR data was obtained. In addition, we have also done ESI-Mass spectra of **1**·Al and **1**·Cu, but no mass data about the above complexes were obtained except that of compound **1** (**Fig. S18**).

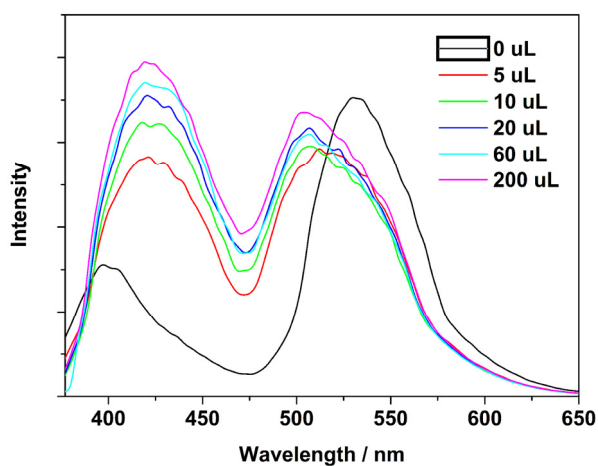


Fig. S2 Emission spectroscopy of **1** (2.5×10^{-5} M, ethanol) upon titration of Al³⁺ (the final ratio of Al³⁺ to **1** is 13.3) with excitation at 356 nm.

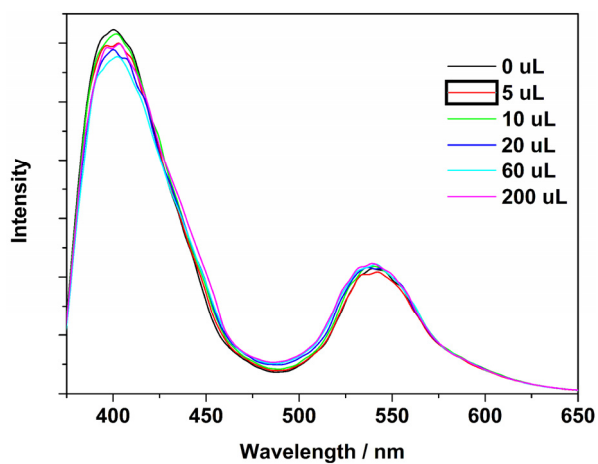


Fig. S3 Emission spectroscopy of **1** (2.5×10^{-5} M, DMSO) upon titration of Al³⁺ (the final ratio of Al³⁺ to **1** is 13.3) with excitation at 356 nm.

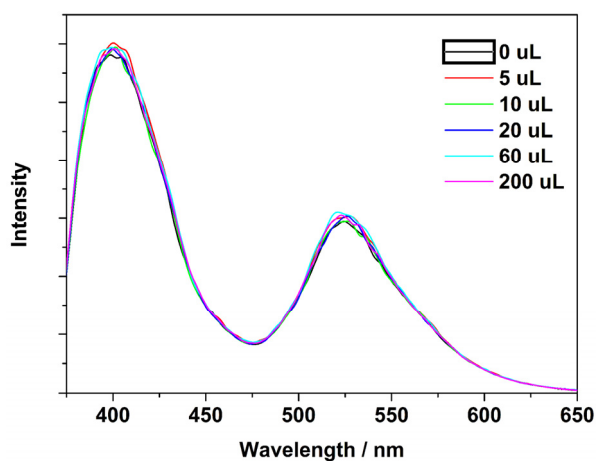


Fig. S4 Emission spectroscopy of **1** (2.5×10^{-5} M) in 0.05 M HEPES (pH 7.4) upon titration of Al³⁺ (the final ratio of Al³⁺ to **1** is 13.3) with excitation at 356 nm.

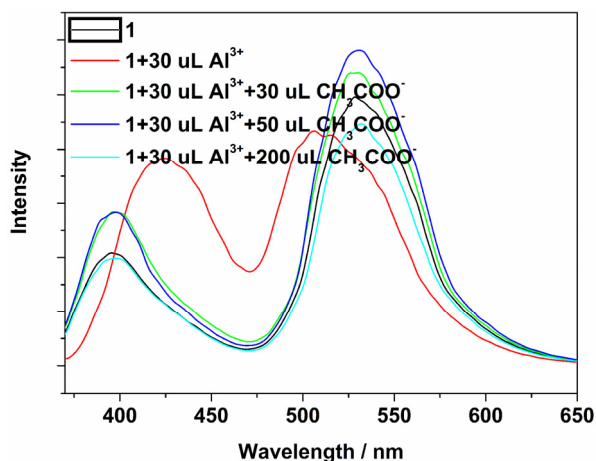


Fig. S5 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of CH₃COONa (the concentration is 10^{-2} M, water) with excitation at 356 nm.

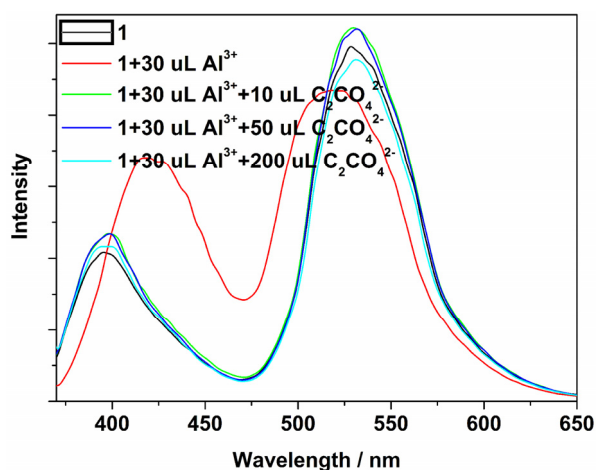


Fig. S6 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Na₂C₂CO₄ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

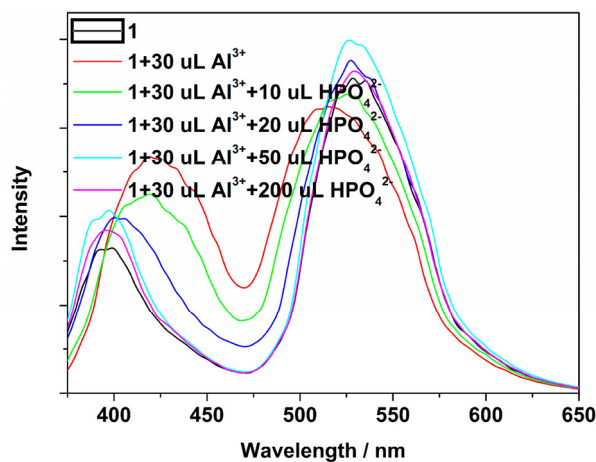


Fig. S7 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Na₂HPO₄ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

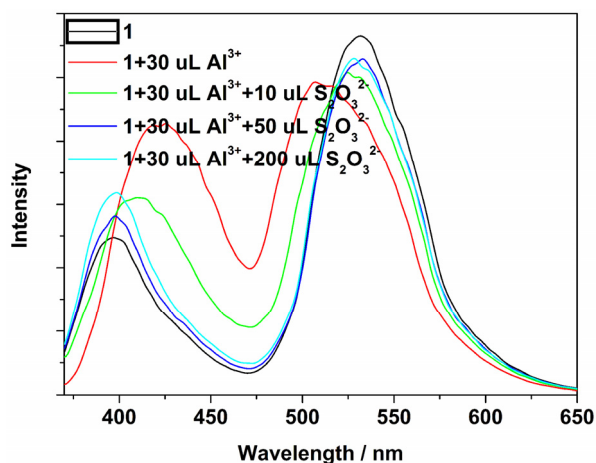


Fig. S8 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Na₂S₂O₃ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

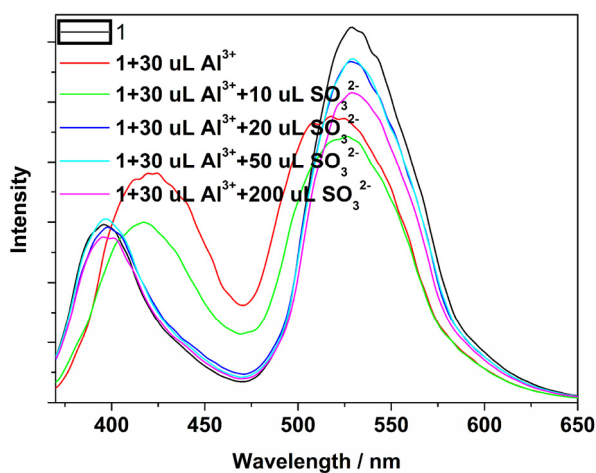


Fig. S9 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Na₂SO₃ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

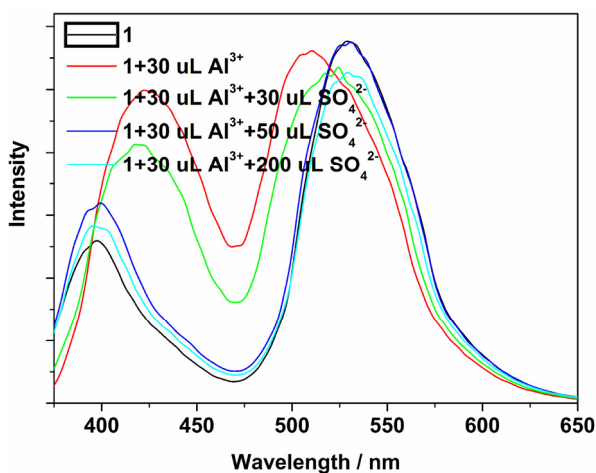


Fig. S10 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Na₂SO₄ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

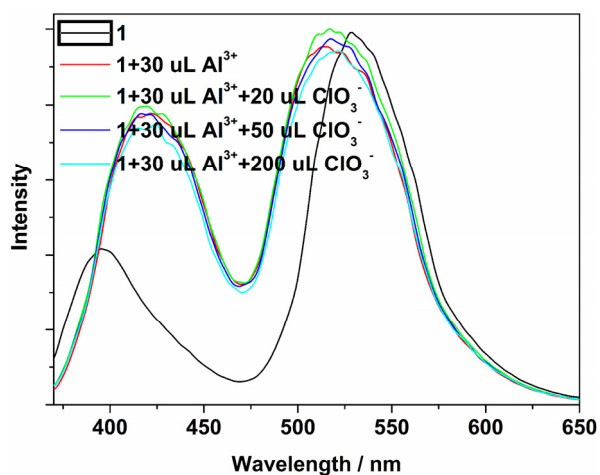


Fig. S11 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaClO₃ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

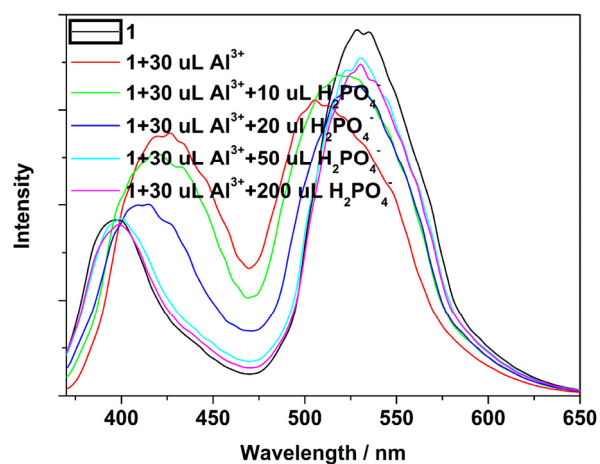


Fig. S12 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaH₂PO₄ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

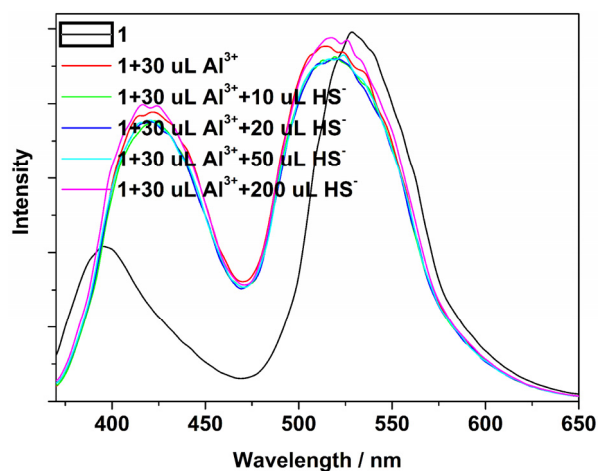


Fig. S13 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaHS (the concentration is 10^{-2} M, water) with excitation at 356 nm.

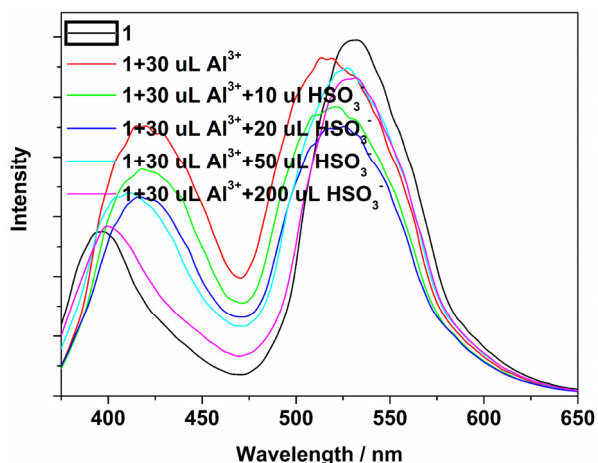


Fig. S14 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaHSO₃ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

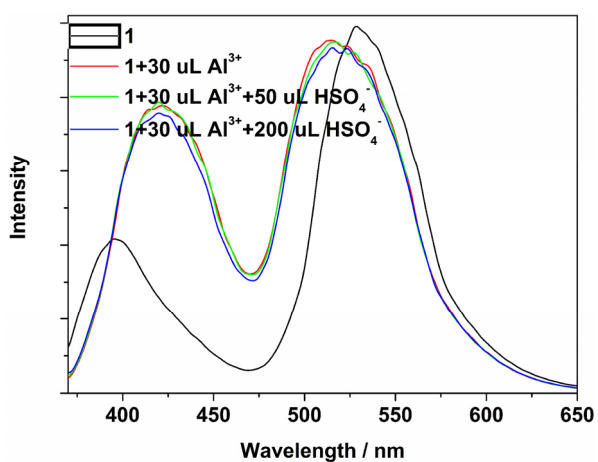


Fig. S15 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaHSO₄ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

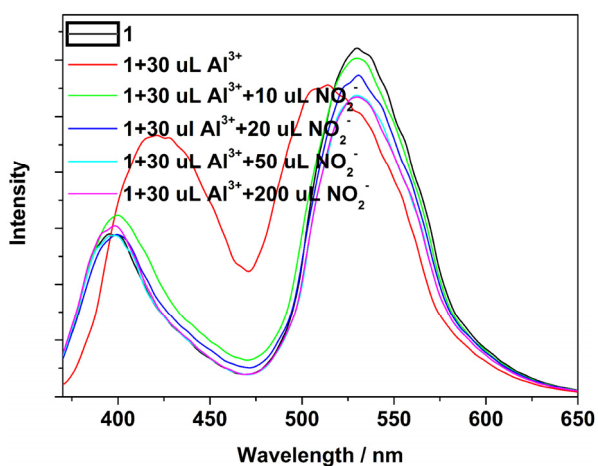


Fig. S16 Emission spectroscopy change of the 'in situ' prepared 1·Al complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaNO₂ (the concentration is 10^{-2} M, water) with excitation at 356 nm.

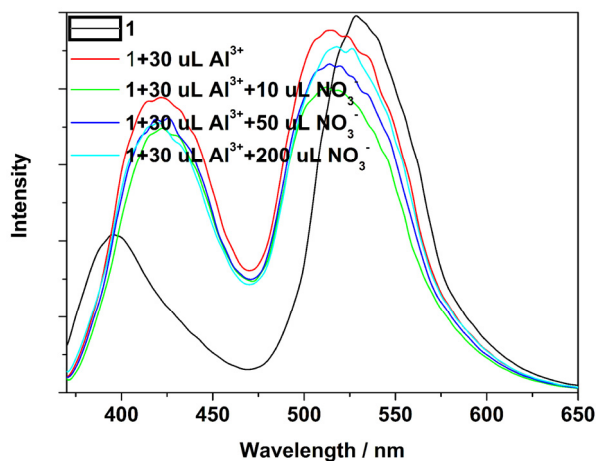


Fig. S17 Emission spectroscopy change of the 'in situ' prepared **1·Al** complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of NaNO_3 (the concentration is 10^{-2} M, water) with excitation at 356 nm.

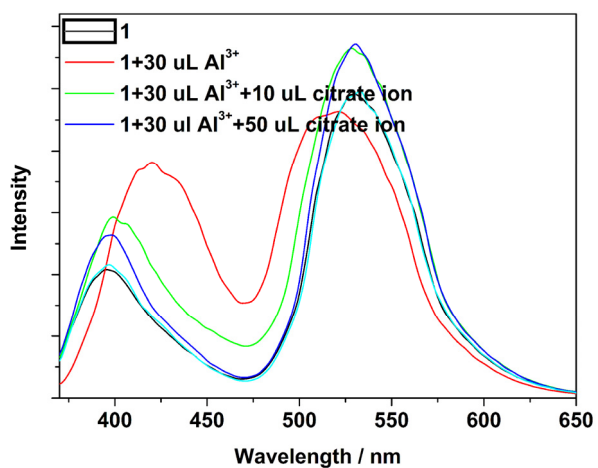


Fig. S18 Emission spectroscopy change of the 'in situ' prepared **1·Al** complex (2.5×10^{-5} M, $V_{\text{ethanol}}:V_{\text{water}} = 9:1$) upon addition of Sodium citrate (the concentration is 10^{-2} M, water) with excitation at 356 nm.

Instrument



Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS

Card Serial Number E121384
Analysis Name D:\Data\zjf\2012\20120717_000025.d
Sample Name lxy20120709
Acquisition Date 7/18/2012 6:28:27 AM
Operator: zjf
Ion Mass (Measured) 211.09740

a

| Sum Formula | Sigma | m/z | Err [ppm] | Mean Err [ppm] | Err [mDa] | rdb | N Rule | e ⁻ |
|---------------|-------|-----------|-----------|----------------|-----------|------|--------|----------------|
| C 11 H 15 O 4 | 0.018 | 211.09649 | -4.34 | -4.37 | -0.92 | 4.50 | ok | even |
| C 12 H 11 N 4 | 0.006 | 211.09782 | 1.99 | 1.61 | 0.42 | 9.50 | ok | even |

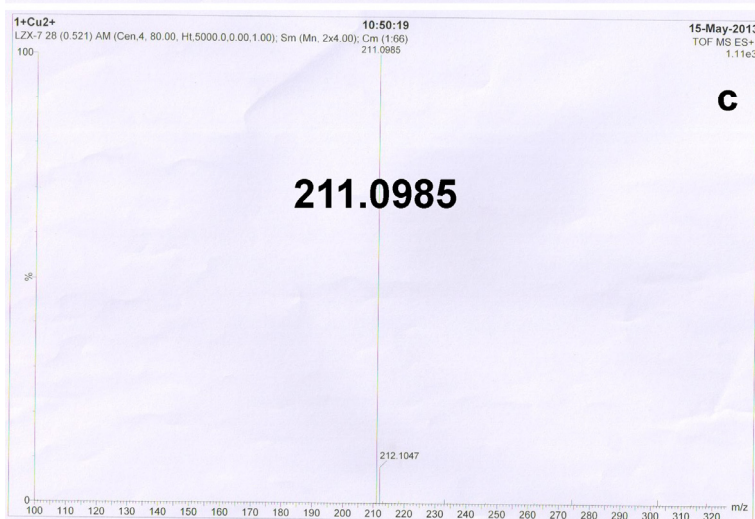
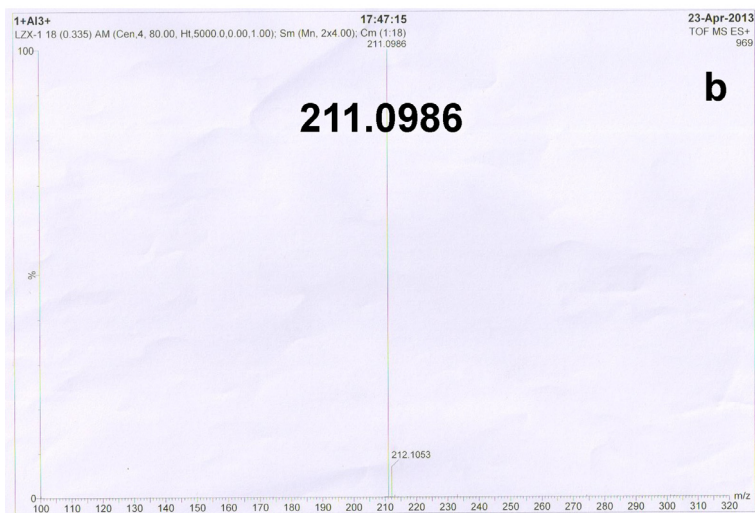


Fig. S19 HRMS spectra of **1(a)**, **1·Al (b)**, and **1·Cu (c)**.