Inorganic Chemistry

Article

pubs.acs.org/IC

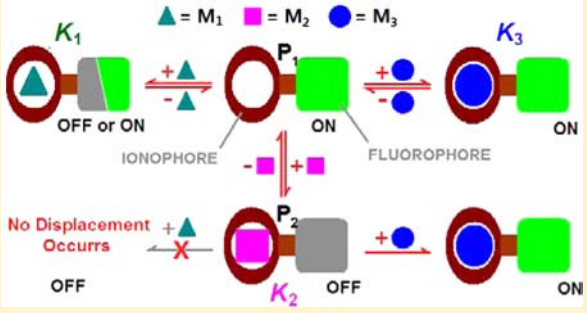
Turn-On Luminescent Sensing of Metal Cations via Quencher Displacement: Rational Design of a Highly Selective Chemosensor for Chromium(III)

Jia-Ni Wang, Qiong Qi, Lei Zhang, and Shun-Hua Li*

College of Chemistry and Chemical Engineering and Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China

Supporting Information

ABSTRACT: A highly selective luminescent chemosensor for Cr^{3+} in aqueous solution was assembled by a low-selectivity luminogenic receptor with Cu^{2+} as a metal quencher. Three tetranitrogen chelating sites were integrated into the multichannel receptor with a tris(1,10-phenanthroline)ruthenium(II) luminophore at the core. This receptor (**2**) exhibits chelating affinity for many transition-metal cations, among which Cu^{2+} efficiently quenches the emission. The further addition of Cr^{3+} into the Cu^{2+}-titrated solution of **2** results in a metal-exchange reaction and a sensitive turn-on luminescence response highly selective over other metal cations. The quencher displacement sensing strategy in this design can be a simple but efficient approach for OFF−ON luminescent sensing of metal cations that inherently lack selective ligands.



INTRODUCTION

Fluorescence response offers distinct advantages for molecular sensing in terms of simplicity, high sensitivity, and visual observation. The development of fluorescent chemosensors (FCSs) for transition-metal cations has been a subject of intensive interest because of the diverse biological or environmental relevance of these metal species.[1] However, for many transition-metal cations, the rational design of efficient FCSs remains challenging because it is not straightforward to achieve high selectivity of the designed receptor. It is a major way to base high selectivity on a tailored receptor/ligand, which usually causes the most labor in the design of these FCSs. Different from most of the developed sensing systems operating via the direct metal−ligand interaction between the receptor and target cation, some recent examples of FCSs for transition-metal cations have been designed through a metal displacement approach.[2−4] Sensing via metal displacement usually results in a distinct improvement in the selectivity at the expense of sensitivity due to the shielding function of the fill-in metal. It is theoretically possible to design a highly selective FCS on the basis of a less selective fluorogenic ligand, on the condition that a suitable templating cation is available. Many transition-metal cations are usually known as efficient fluorescence quenchers, whereas a turn-on fluorescent sensing mode is in general preferred. This problem can be well settled in FCSs based on metal displacement because a turn-on fluorescent response is easily obtained by displacement of the metal quencher on a fluorogenic ligand.[3] It is therefore possible to realize both highly selective and turn-on fluorescent sensing of transition-metal cations by a quencher displacement approach, as illustrated in Figure 1. Following this outlined principle, a highly selective FCS can be designed by the sophisticated combination of an untailored fluorogenic ligand with a suitable metal quencher. Most desirably, this may be an efficient approach for turn-on fluorescent sensing of those transition metals lacking selective ligands.

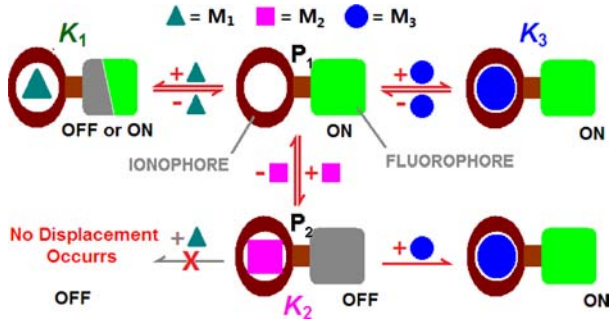
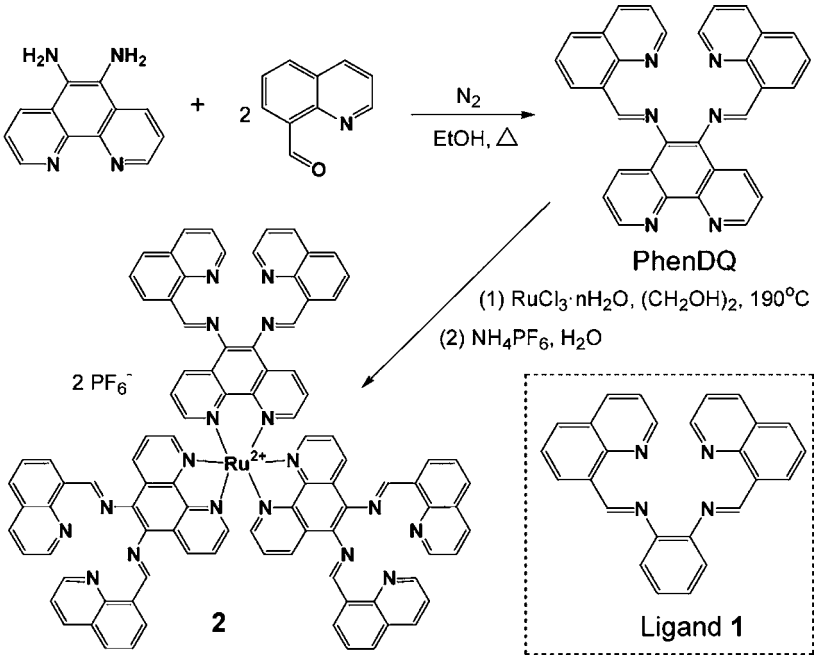


Figure 1. Illustration of the transformation from a nonselective fluorogenic receptor (P_1) to a selective OFF−ON FCS (P_2) for metal cations through quencher displacement. K_1, K_2, and K_3 represent the binding constants for the interference (M_1), quencher (M_2), and target (M_3) metal cations, respectively; $K_1 < K_2 < K_3$.

Cr^{3+} plays an essential role in human nutrition[5] but is also an environmental pollutant related to various industrial and

Received: May 6, 2012
Published: November 14, 2012

Scheme 1. Fluorogenic Ligands Investigated



agricultural concern.[6] Because Cr^{3+} is a paramagnetic cation lacking selective chelands, the design of highly selective OFF−ON FCSs for Cr^{3+} has long been a challenging task. Among the reported OFF−ON fluorescent Cr^{3+} sensing systems,[7,8] only a very few rhodamine-based chemodosimeters,[8] which utilize a spirolactam ring-opening reaction for sensing, display high selectivity toward Cr^{3+} in aqueous solution. As a proof-of-the-principle of the proposed sensing strategy based on quencher displacement, a highly selective turn-on luminescent chemosensor for Cr^{3+} in aqueous solution is designed in this study.

MATERIALS AND METHODS

General Remarks. 8-Quinolinecarbaldehyde, *o*-phenylenediamine, piperidine, $RuCl_3{\cdot}nH_2O$, and NH_4PF_6 were purchased from Sigma-Aldrich Co., Ltd. 5,6-Diamino-1,10-phenanthroline was purchased from Tokyo Chemical Industry Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and were used without further purification. Stock solutions (1.0×10^{-2} mol/L) of the sulfate salt of Ni^{2+}, the nitrate salts of Mg^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Ag^{+}, and Cr^{3+}, and the chloride salts of other investigated metal ions were prepared in aqueous solutions. Stock solutions (1.0×10^{-4} M) of **1** and **2** were prepared in aqueous solutions in amber volumetric flasks. Stock solutions (1.0×10^{-3} M) of L-cysteine, glutathione, L-cystine, and L-homocysteine in redistilled water were kept at +4 °C and used within 48 h.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the residual dimethyl sulfoxide (DMSO) peak (2.50 ppm in ^1H NMR and 39.43 ppm in ^{13}C NMR), and coupling constants (*J*) are reported in hertz (Hz). Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Bruker ESQUIRE-3000$^+$ mass spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG ESCA LAB MK-2 instrument. Absorption and fluorescence spectra were recorded on a Hitachi U-3900 ultraviolet−visible spectrophotometer and a Hitachi F-7000 fluorophotometer, respectively. The emission decay lifetimes were acquired with a Horiba Jobin Yvon FluoroMax-4 TCSPC time-resolved fluorophotometer.

Compound 1. A mixture of 8-quinolinecarbaldehyde (392 mg, 2.5 mmol), *o*-phenylenediamine (108 mg, 1.0 mmol), and piperidine (1.0 mL) in ethanol (30 mL) was refluxed under an N_2 atmosphere for about 8 h to give a red solution. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 1.5% $MeOH/CH_2Cl_2$) to give **1** as an orange solid. Yield: 228 mg, 59%. The selected spectroscopic data of **1** are as follows. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 8.89 (d, 1H, J = 4.4 Hz), 8.73 (d, 1H, J = 4.4 Hz), 8.46 (d, 1H, J = 8.4 Hz), 8.30 (d, 1H, J = 8.0 Hz), 8.11 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 7.2 Hz), 7.80 (t, 2H, J = 8.0 Hz), 7.66−7.58 (m, 2H), 7.44−7.45 (m, 2H), 7.39 (t, 1H, J = 8.0 Hz), 7.29−7.20 (m, 2H), 6.95 (d, 1H, J = 7.2 Hz), 5.87 (s, 1H, N=C*H*), 5.76 (s, 1H, N=C*H*). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 153.59, 151.61, 150.20, 146.29, 145.22, 143.51, 137.08, 136.79, 136.01, 134.71, 133.07, 130.82, 130.46, 128.23, 127.99, 127.89, 127.08, 126.59, 126.56, 122.89, 122.44, 122.18, 122.05, 119.67, 111.22. ESI-MS: m/z 387.3 ($[M + H]^+$). It should be noted that the structure of **1** is unsymmetric because of the formation of an intramolecular hydrogen bond (C−H···N) in DMSO-d_6.

Compound PhenDQ. A mixture of 8-quinolinecarbaldehyde (392 mg, 2.5 mmol) and 5,6-diamino-1,10-phenanthroline (219 mg, 1.0 mmol) in ethanol (30 mL) was refluxed under an N_2 atmosphere for about 8 h to give a red solution. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 10% $MeOH/CH_2Cl_2$) to give **PhenDQ** as a yellow solid. Yield: 263 mg, 54%. The selected spectroscopic data of **PhenDQ** are as follows. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.25 (d, 2H, J = 7.6 Hz), 9.19 (d, 4H, J = 4.2 Hz), 9.13 (d, 2H, J = 4.0 Hz), 8.36 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz), 7.80−7.72 (m, 6H), 7.61 (q, 2H, J = 4.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 116.08, 122.55, 123.18, 123.81, 126.97, 127.30, 128.92, 130.47, 130.50, 130.68, 138.01, 143.94, 144.82, 148.31, 150.09, 151.47. ESI-MS: m/z 489.1 ($[M + H]^+$).

Compound 2. A mixture of $RuCl_3{\cdot}nH_2O$ (12 mg, 0.056 mmol) and **PhenDQ** (77 mg, 0.158 mmol) in ethylene glycol (30 mL) was refluxed under an N_2 atmosphere for about 4 h. After the addition of saturated aqueous NH_4PF_6 (75 mL) with stirring at room temperature, the mixture was stirred at the same temperature for 5 min. The obtained brown precipitate was collected by filtration, dried under reduced pressure for 1 h, and purified by recrystallization from $MeOH/CH_2Cl_2$ to give **2** (86 mg, 82%). The selected spectroscopic data of **2** are as follows. XPS: Ru (3d, 280.6 eV, $3P_3$, 461.0 eV), C (1s, 284.5 eV), N (1s, 398.4 eV), F (1s, 684.5 eV), P (2p, 134.5 eV). ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 9.26 (d, 6H, J = 4.4 Hz), 8.90 (d, 6H, J = 7.2 Hz), 8.68 (d, 6H, J = 8.4 Hz), 8.30 (d, 6H, J = 8.4 Hz),

dx.doi.org/10.1021/ic3009267 | *Inorg. Chem.* 2012, 51, 13103−13107

8.14 (d, 12H, J = 4.4 Hz), 7.95 (d, 6H, J = 8.0 Hz), 7.87−7.81 (m, 18H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 151.95, 151.69, 150.90, 146.03, 144.75, 138.29, 131.29, 128.96, 127.41, 126.73, 126.69, 122.81, 63.25. ESI-MS: m/z 571.63 [Frag/2] (Figure S1 in the Supporting Information, SI).

Investigation on the Binding Affinity of 2 toward Cu^{2+} and Cr^{3+}. To evaluate the binding affinity of **2** toward Cu^{2+} and Cr^{3+}, continuous titrations of **2** with Cu^{2+} and Cr^{3+} were investigated by fluorophotometry, respectively. On the basis of the assumption that only the 1:3 binding adducts were yielded in the titration of **2** with excess Cu^{2+} or Cr^{3+}, the dissociation degree (α) could be calculated via plots of the titration curves (Figure S2 in the SI). The cumulative formation constant (β_3) for the complexes of **2** with Cu^{2+} or Cr^{3+} is calculated using eq 1,

$$\beta_3 = \frac{(1-\alpha)C_L}{\alpha C_L(C_M - 3C_L + 3\alpha C_L)^3} \quad (1)$$

where α is the dissociation degree calculated and C_L and C_M are the initial concentrations of compound **2** and the investigated metal cations, respectively. However, because multiple products are involved in the metal-binding reactions of the trifurcate receptor **2** and calculations based on the luminescence signals of larger error bands are possible, considerable deviations might be involved in the calculation results. Accordingly, the computed values of the cumulative formation constants were reported in a semiquantitative manner.

RESULTS AND DISCUSSION

Design of the Luminogenic Receptors. A simple tetranitrogen ligand **1** (Scheme 1), obtained by the reaction of 8-quinolinecarbaldehyde with *o*-phenylenediamine, was investigated at first. Ligand **1** shows its chelating affinity for a variety of metal cations, among which Cu^{2+}, Hg^{2+}, Fe^{3+}, and Ag^{+} quench the fluorescence of **1** (Figure 2). Job plots confirm

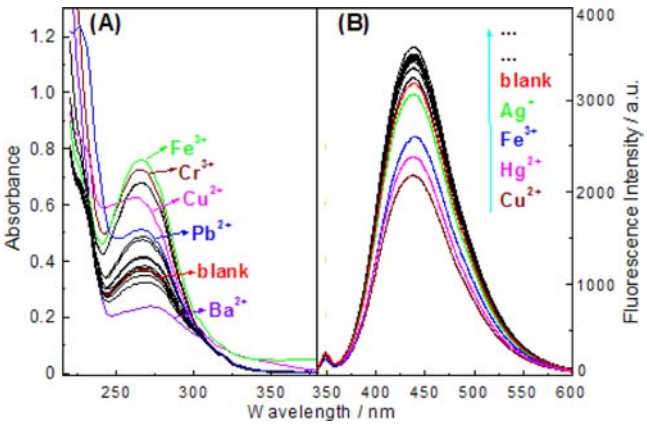


Figure 2. Absorption (A) and fluorescence (B) responses of **1** (10 μM) upon the addition of different metal cations (10.0 equiv) in aqueous solution. The investigated cations include K^{+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}, Pb^{2+}, Ag^{+}, and Hg^{2+} (pH 5.6; buffered by 0.02 M NaOAc/HOAc; excitation wavelength = 310 nm).

the 1:1 binding stoichiometry between ligand **1** and most of the tested transition-metal cations such as Fe^{3+}, Cr^{3+}, Cu^{2+}, and Hg^{2+}. In order to increase the quenching ability of Cu^{2+}, ligand **1** was fused with tris(1,10-phenanthroline)ruthenium(II), $Ru(phen)_3^{2+}$, to create a multichannel luminogenic receptor **2** (Scheme 1). $Ru(phen)_3^{2+}$ is a suitable acceptor for the quinoline-dominated fluorescence, and its emission was reported to be efficiently quenched by chelation of Cu^{2+}.[3b] **2** was expected to act as a sensitive platform for quencher-displaced luminescent sensing based on the following reasons: (1) Emission of the $Ru(phen)_3^{2+}$ core can be sensitized by the six quinoline antennae through fluorescence resonance energy transfer (FRET) and efficiently quenched by three quenchers. This will result in a sensitive luminescence response upon switching between its OFF and ON states when it is excited in the ultraviolet region. (2) The integration of three binding sites into the receptor molecule will substantially enhance its binding efficiency for the target cations.

Quenching Effect of Cu^{2+} on the Luminescence of 2. Similar to **1**, **2** also exhibits a chelating ability for many transition-metal cations, as indicated by its absorption responses (Figure S3 in the SI). The absorption band of the $Ru(phen)_3^{2+}$ moiety appears at around 473 nm, which shows a high degree of overlap with the emission band of the quinoline group. Because of efficient FRET from the quinoline groups to the $Ru(phen)_3^{2+}$ luminophore, emission of **2** (λ_{max} = 590 nm) can be excited within a broad wavelength region from 250 to 480 nm. Figures 3A and 4A show the luminescent response of **2**

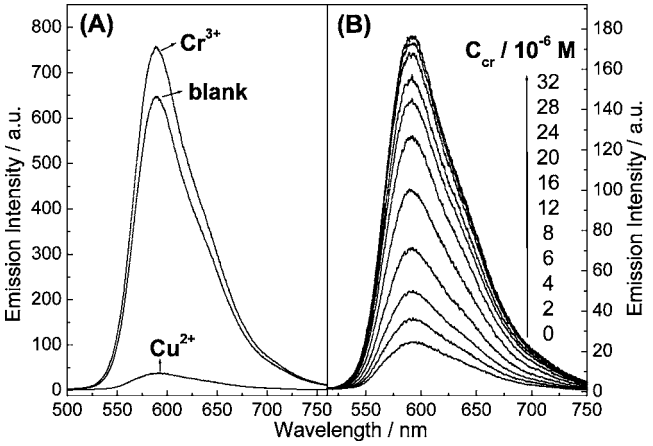


Figure 3. (A) Emission spectra of **2** (10 μM) in the presence of 10.0 equiv of metal cations in aqueous solution. (B) Traces of the emission spectrum of the Cu^{2+}-titrated solution of **2** (**2**, 4.0 μM; Cu^{2+}, 40 μM) upon the addition of different amounts of Cr^{3+} (pH 5.6; buffered by 0.02 M NaOAc/HOAc; λ_{ex} = 473 nm).

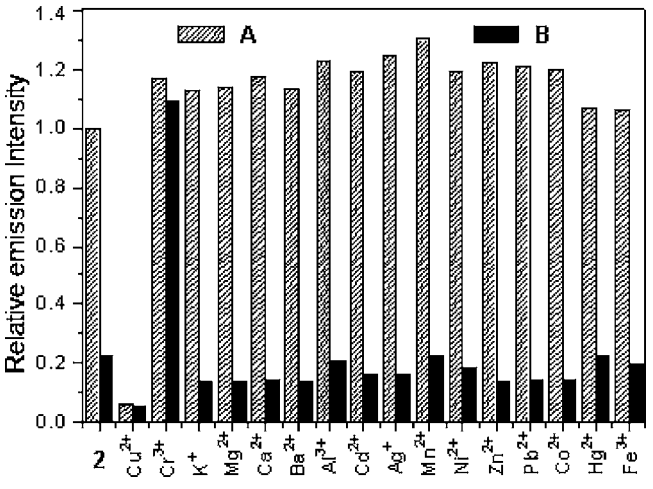


Figure 4. Luminescence responses of **2** (10 μM) toward different metal cations (10.0 equiv) before (A) and after (B) reaction with 3.0 equiv of Cu^{2+} in aqueous solution (pH 5.6; buffered by 0.02 M NaOAc/HOAc; $\lambda_{ex}/\lambda_{em}$ = 473 nm/590 nm).

dx.doi.org/10.1021/ic3009267 | Inorg. Chem. 2012, 51, 13103−13107

upon the addition of various metal cations. Indeed, the emission of **2** in aqueous solution is dramatically quenched by Cu^{2+} at a low concentration level of 10^{-5} M.

Phenomena and Mechanism of Cr^{3+} Sensing. The quenching effect of Cu^{2+} is not susceptible to the coexistence of other metal cations except for Cr^{3+} (Figure 4B). Continuous titration experiments indicate the 1:3 binding stoichiometry for both complexes of **2** with Cu^{2+} and **2** with Cr^{3+} (Figure S2 in the SI). The cumulative formation constants (β_3) for Cu^{2+} and Cr^{3+} were computed to be at the 10^{15} and 10^{18} M^{-3} levels, respectively, which reveals that Cr^{3+} has a stronger binding preference for **2** than Cu^{2+}. Indeed, the stoichiometric addition of Cr^{3+} into the Cu^{2+}-titrated solution of **2** rapidly restores the luminescence of **2**, while no similar response is observed upon the addition of $K_2Cr_2O_7$ or K_2CrO_4 (Figure S5 in the SI). The final emission spectrum is exactly the same as that of the direct Cr^{3+}-titrated product of **2**. The mass spectrum shows that a 1:3 complex of **2** with Cr^{3+} is formed after the addition of Cr^{3+} (Figure S6 in the SI). The resulting luminescence recovery is, hence, explained in terms of displacement of the Cu^{2+} quencher. The quencher displacement mechanism was further supported by titration of the Cu^{2+}-chelated sensing ensemble (Cu_3-**2**) with excess cysteine. Because of the high binding affinity of Cu^{2+} with cysteine, the reaction of Cu_3-**2** with cysteine also leads to a gradual recovery of the emission of **2** (Figure 5).

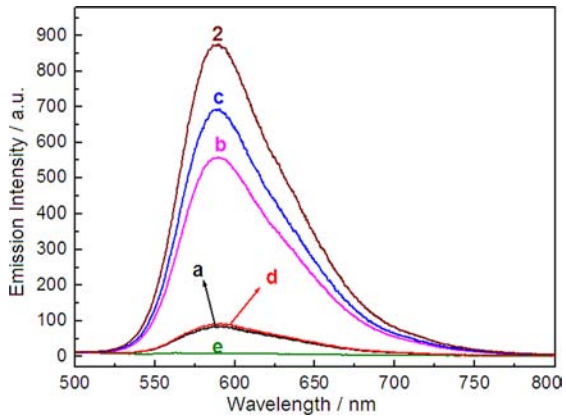


Figure 5. Emission spectra of Cu_3-**2** (**2**, 10 μM; Cu^{2+}, 50 μM) in the absence (a) and presence of bioactive sulfur-containing species (0.10 mM) including L-cysteine (b), glutathione (c), L-cystine (d), and L-homocysteine (e) in aqueous solution buffered at pH 7.0 by 0.02 M K_2HPO_4/KH_2PO_4 (excitation wavelength: 473 nm).

Luminescent Detection of Cr^{3+}. The developed sensing system was successfully applied to the detection of Cr^{3+} in aqueous media. Solution emission of Cu_3-**2** increases rapidly and substantially upon the addition of Cr^{3+}. A stable emission response can be achieved within 10 min at near-neutral pH (Figure S8 in the SI). Figure 3B shows the spectral evolution of Cu_3-**2** upon the addition of $Cr(NO_3)_3$ at pH 5.6. Under the metal displacement mechanism, the range of linear correlation between the relative emission intensity and Cr^{3+} concentration is affected by the amount of Cu^{2+} added. In general, an increase in the amount of Cu^{2+} results in a larger linear range but a lower sensitivity for Cr^{3+}. Nevertheless, Cr^{3+} can be easily detected at the micromolar level on a fluorospectrometer. For example, luminescent titration of Cr^{3+} in aqueous solution under 473 nm excitation could establish detection with a limit down to 66 nM, which is comparable to the physiologically relevant concentration of Cr^{3+} (120 nM).[5] A lower detection limit can be obtained when excited in the ultraviolet region because of a more sensitive response. Compared with the recommended permissible limit of chromium at 10^{-5} M,[6] high sensitivity of this Cr^{3+} sensing system ensures its potential applications.

The performance of the developed Cr^{3+} sensing system was further evaluated in the presence of other coexisting metal species. The presence of 0.10 mM K^+, Ca^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Pb^{2+}, or Zn^{2+} causes no obvious interference (Figure 6). Remarkably high selectivity is shown in

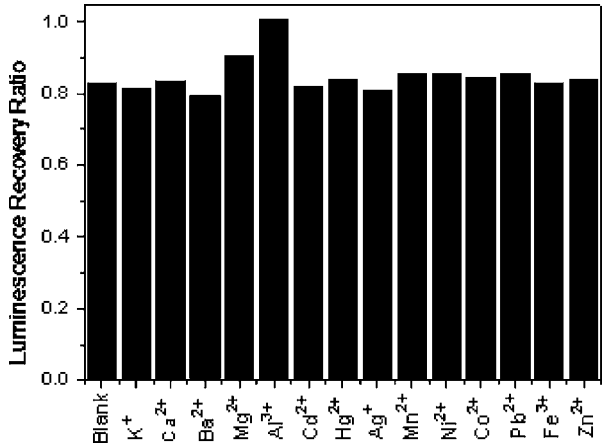


Figure 6. Influence of coexisting metal cations (100 μM) on the luminescence response of Cu_3-**2** (**2**, 4.0 μM; Cu^{2+}, 40 μM) to Cr^{3+} (20 μM) in aqueous solution (pH 5.6, buffered by 0.02 M NaOAc/HOAc; $\lambda_{ex}/\lambda_{em}$ = 473 nm/590 nm). The luminescence recovery ratio was defined as the ratio of the Cr^{3+}-caused emission enhancement to the Cu^{2+}-induced emission decrease.

luminescent sensing of Cr^{3+}. It is interesting that the coexistence of Al^{3+} or Mg^{2+} induces a slight enhancement of the sensing response, although the direct addition of Al^{3+} or Mg^{2+} into the solution of Cu_3-**2** does not result in a turn-on luminescence response (Figure 4B). Because the emission of the direct adduct of **2** with Cr^{3+} is not affected by the further addition of Al^{3+} or Mg^{2+} (Figure S10 in the SI), the coexistence of Al^{3+} or Mg^{2+} was suggested to facilitate the quencher displacement process at a low concentration of Cr^{3+}. Standard addition experiments confirmed that Cr^{3+} in synthetic samples could be determined with satisfactory recoveries (96−105%) at the micromolar level (Table S3 in the SI).

CONCLUSION

In summary, we have developed a highly selective luminescent chemosensor for Cr^{3+} based on a quencher displacement mechanism. The chemosensor was assembled by a less selective luminogenic compound with Cu^{2+} as the metal quencher, and it displays sensitive emission enhancement upon the addition of Cr^{3+} in aqueous solution. Our research exemplifies that quencher displacement can be an efficient approach for selective OFF−ON fluorescent sensing of transition-metal cations that inherently lack selective ligands. The $Ru(phen)_3^{2+}$-centered luminophore is demonstrated as a versatile and sensitive platform for this sensing mode because of its easy integration of multiple binding sites and the high quenching effect by Cu^{2+}.

dx.doi.org/10.1021/ic3009267 | Inorg. Chem. 2012, 51, 13103−13107

■ ASSOCIATED CONTENT

Supporting Information

Additional spectral data and sensing performances of the chemosensor. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lishua@xmu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Basic Research Program of China (Grant 2011CB910403), National Natural Science Foundation of China (Grants 21175113 and 20835005), and Fundamental Research Funds for the Central Universities (Grant 2011121015).

■ REFERENCES

(1) For recent reviews, see: (a) Kim, H. M.; Cho, B. R. *Chem.—Asian J.* **2011**, *6*, 58−69. (b) Leray, I.; Valeur, B. *Eur. J. Inorg. Chem.* **2009**, 3525−3535. (c) Nolan, E. M.; Lippard, S. J. *Acc. Chem. Res.* **2009**, *42*, 193−203. (d) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465−1472. (e) Que, E. L.; Domaille, D. W.; Chang, C. J. *Chem. Rev.* **2008**, *108*, 1517−1549. (f) Domaille, D. W.; Que, E. L.; Chang, C. J. *Nat. Chem. Biol.* **2008**, *4*, 168−175. (g) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780−3799. (h) Ajayaghosh, A. *Acc. Chem. Res.* **2005**, *38*, 449−459.

(2) Royzen, M.; Dai, Z.; Canary, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1612−1613.

(3) (a) He, G.; Zhao, Y.; He, C.; Liu, Y.; Duan, C. *Inorg. Chem.* **2008**, *47*, 5169−5176. (b) Schmittel, M.; Lin, H. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1595−1598. (c) You, Y.; Tomat, E.; Hwang, K.; Atanasijevic, T.; Nam, W.; Jasanoff, A. P.; Lippard, S. J. *Chem. Commun.* **2010**, *46*, 4139−4141.

(4) (a) Khatua, S.; Choi, S. H.; Lee, J.; Huh, J. O.; Do, Y.; Churchill, D. G. *Inorg. Chem.* **2009**, *48*, 1799−1801. (b) Xue, L.; Liu, Q.; Jiang, H. *Org. Lett.* **2009**, *11*, 3454−3457. (c) Xu, Z.; Baek, K.-H.; Kim, H. N.; Cui, J.; Qian, X.; Spring, D. R.; Shin, I.; Yoon, J. *J. Am. Chem. Soc.* **2010**, *132*, 601−610. (d) Atanasijevic, T.; Zhang, X.; Lippard, S. J.; Jasanoff, A. *Inorg. Chem.* **2010**, *49*, 2589−2591. (e) Khatua, S.; Kang, J.; Churchill, D. G. *New J. Chem.* **2010**, *34*, 1163−1169. (f) Li, Z.; Zhang, L.; Wang, L.; Guo, Y.; Cai, L.; Yu, M.; Wei, L. *Chem. Commun.* **2011**, *47*, 5798−5800.

(5) Vincent, J. B. *Nutr. Rev.* **2000**, *58*, 67−72.

(6) Zayed, A. M.; Terry, N. *Plant Soil* **2003**, *249*, 139−156.

(7) (a) Sarkar, M.; Banthia, S.; Samanta, A. *Tetrahedron Lett.* **2006**, *47*, 7575−7578. (b) Wu, H.; Zhou, P.; Wang, J.; Zhao, L.; Duan, C. *New J. Chem.* **2009**, *33*, 653−658. (c) Weerasinghe, A. J.; Schmiesing, C.; Sinn, E. *Tetrahedron Lett.* **2009**, *50*, 6407−6410. (d) Zheng, X.; Zhang, W.; Mu, L.; Zeng, X.; Xue, S.; Tao, Z.; Yamatob, T. *J. Incl. Phenom. Macrocycl. Chem.* **2010**, *68*, 139−146. (e) Wang, D.; Shiraishi, Y.; Hirai, T. *Tetrahedron Lett.* **2010**, *51*, 2545−2549. (f) Hu, X.; Zhang, X.; He, G.; He, C.; Duan, C. *Tetrahedron* **2011**, *67*, 1091−1095. (g) Liu, P. S.; Jiang, D.; Cui, S.; Liu, G.; Fan, C. *Microchim. Acta* **2011**, *174*, 329−336. (h) Panda, S.; Pati, P. B.; Zade, S. S. *Chem. Commun.* **2011**, *47*, 4174−4176. (i) Guha, S.; Lohar, S.; Banerjee, A.; Sahana, A.; Hauli, I.; Mukherjee, S. K.; Matalobos, J. S.; Das, D. *Talanta* **2012**, *91*, 18−25. (j) Mahato, P.; Saha, S.; Suresh, E.; Liddo, R. D.; Parnigotto, P. P.; Conconi, M. T.; Kesharwani, M. K.; Ganguly, B.; Das, A. *Inorg. Chem.* **2012**, *51*, 1769−1777. (k) Saluja, P.; Sharma, H.; Kaur, N.; Singh, N.; Jang, D. O. *Tetrahedron* **2012**, *68*, 2289−2293.

(8) (a) Mao, J.; Wang, L.; Dou, W.; Tang, X.; Yan, Y.; Liu, W. *Org. Lett.* **2007**, *9*, 4567−4570. (b) Zhou, Z.; Yu, M.; Yang, H.; Huang, K.; Li, F.; Yi, T.; Huang, C. *Chem. Commun.* **2008**, 3387−3389. (c) Wan, Y.; Guo, Q.; Wang, X.; Xia, A. *Anal. Chim. Acta* **2010**, *665*, 215−220. (d) Mao, J.; He, Q.; Liu, W. *Anal. Bioanal. Chem.* **2010**, *396*, 1197−1203.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on November 14, 2012, with the emission of receptor 2 defined incorrectly throughout the paper and Supporting Information. The corrected version was reposted on November 21, 2012.