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An 'off–on' fluorescent chemosensor of selectivity to Cr^{3+} and its application to MCF-7 cells

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ABSTRACT

A 'switching-on' fluorescent chemosensor for the selective and sensitive signaling of intraceullar Cr^{3+} has been designed and synthesized exploiting the guest-induced prohibition of the photoinduced electron transfer process between naphthyridine moiety and 7,10-diphenylfluoranthene moiety, the system shows a Cr^{3+}-selective chelation-enhanced fluorescence response not only in ethanol but in cell.

1. Introduction

The development of fluorescent chemical sensors is a promising field due to their simplicity, high sensitivity, and instantaneous response.[1] Within this field, the design of fluorescent chemosensors for monitoring metal ions, especially heavy and transition-metal ions such as zinc,[2] mercury,[3] copper,[4] and cadmium[5] is an important area because of their fundamental role in medical, environmental, and biological applications. Trivalent chromium, Cr^{3+}, is one of the most important heavy metal elements and its deficiency causes disturbance in the glucose levels and lipid metabolism.[6] On the other hand, Cr^{3+} adversely affects cellular structures and plays an important role in the metabolism of carbohydrates, lipids, proteins and nucleic acids, therefore, there is an urgent need to develop fluorescent chemical sensors for Cr^{3+}. But because paramagnetic chromium ions usually quench fluorescence emission via the electron transfer and intersystem crossing (isc) processes and lack of proper selective fluorescent chemosensors for Cr^{3+}, fluorescent sensors for Cr^{3+} in solution, especially in cell is rare up to now. Several examples of Cr^{3+}-selective fluorescent chemosensors in organic solvents have been reported.[7] Samanta et al. reported di(2-ethylsulfanylethyl)amine as Cr^{3+}-selective receptor moieties.[8] Liu et al. reported two rhodamine-based Cr^{3+}-selective fluorescent chemosensors.[9] Only Li et al. and Duan et al. reported sensor monitoring Cr^{3+} in living cells till now.[10]

This work is aimed at the design and construction of a fluorescent Cr^{3+}-chemosensor to highly effectively detect Cr^{3+} both in solution and cell. In general, a fluorescent probe contains two units: detection and fluorescence parts. For short metal···metal distance formed in their building blocks,[11] 1,8-naphthyridine (napy) and its derivatives have widely been used as bidentate ligands.[12] Therefore, 1,8-naphthyridine group could be used as the detection unit.[13] As for the fluorescence unit, rigid and conjugate organic structure will be the ideal fluorescent group. Considering the above, (*E*)-*N*-(7-((4-(7,10-diphenylfluoranthen-8-yl)phenylimino)methyl)-5-methyl-1,8-naphthyridin-2-yl)acetamide (**1**) was designed, in which, 4-methy-7-acetamide-1,8-naphthyridyl group as the detection unit and 4-(7,10-diphenylfluoranthenyl)benzenamine as the fluorescent unit (Scheme 1). Both parts are linked by a C=N bond to form a potential fluorescent-sensing molecule (**1**) for metal cations. Compound **1** possesses an efficient Cr^{3+}-selective OFF–ON behavior in ethanol. Furthermore, **1** can also detect intracellar Cr^{3+}.

2. Results and discussion

The optical properties of compound **1**, featuring naphthyridine Schiff base binding sites were studied. The titration experiments

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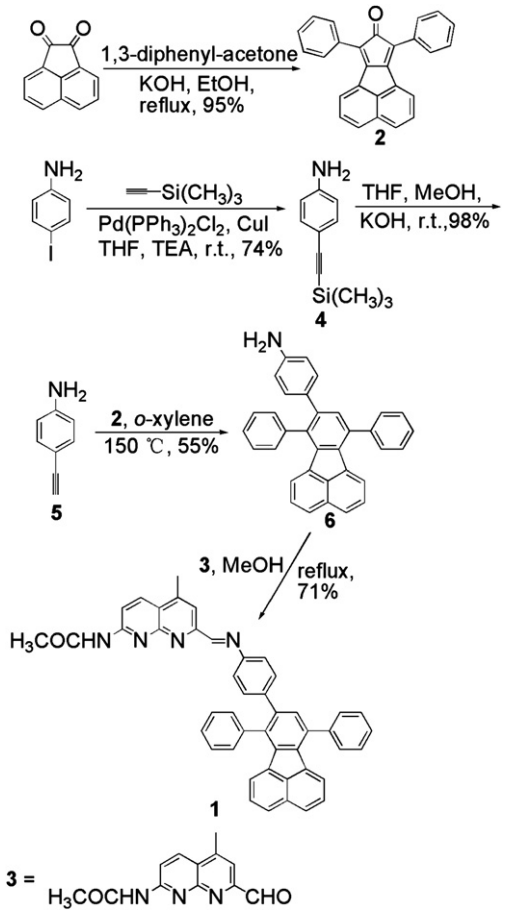


Scheme 1. Synthetic route for compound **1**.

were carried out in ethanol. The UV–vis spectrum of **1** reveals the typical naphthyridine Schiff base absorption bands at 208, 236, 297 and 375 nm (molar extinction coefficient $\varepsilon_{208}=9.59\times10^4$ M^{-1} cm^{-1}, $\varepsilon_{236}=9.21\times10^4$ M^{-1} cm^{-1}, $\varepsilon_{297}=3.97\times10^4$ M^{-1} cm^{-1}, and $\varepsilon_{375}=3.55\times10^4$ M^{-1} cm^{-1}) (Fig. 1). These bands may be assigned to electron transition from π to π^*. The addition of 9 equiv of $Cr(NO_3)_3$ (Cr^{3+}, 9.0×10^{-5} M), led to change of the original absorbance ($\varepsilon_{208}=1.67\times10^5$ M^{-1} cm^{-1}, $\varepsilon_{236}=1.13\times10^5$ M^{-1} cm^{-1}, $\varepsilon_{297}=3.84\times10^4$ M^{-1} cm^{-1}, and $\varepsilon_{375}=2.21\times10^4$ M^{-1} cm^{-1}) (Fig. 1), demonstrating interaction between compound **1** and Cr^{3+} ion.

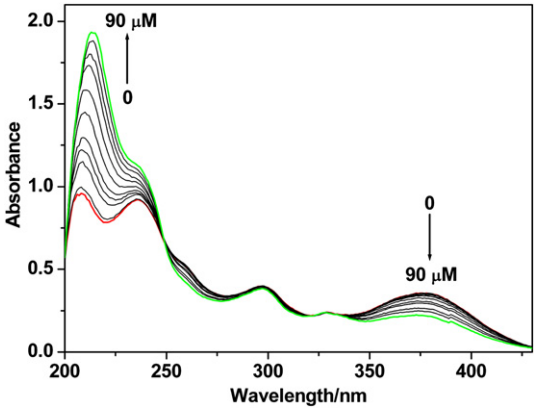


Fig. 1. UV–vis spectra of compound **1** (1.0×10^{-5} M) on addition of $Cr(NO_3)_3$ (0–9 equiv) in ethanol. The first trace is compound **1** alone, and each subsequent trace represents addition of 0.9 equiv of $Cr(NO_3)_3$.

Compound **1** hardly exhibits fluorescence emission in ethanol upon excitation at 310 nm (Fig. 2). Upon titration of Cr^{3+}, a new fluorescent emission peak at about 447 nm appeared and the intensity dramatically enhanced, indicating a Cr^{3+}-selective fluorescent signaling behavior. Because of the great enhancement of emission intensity at 447 nm ($I/I_0=10$) upon addition of trivalent chromium ion, compound **1** indicates an efficient Cr^{3+}-selective OFF–ON fluorescent behavior, all the other environmentally and biologically relevant metal ions except Fe^{3+} did not show such significant response (Fig. 3). Different from that of in literature,[14] the increased emission intensity and blue shift in emission band (Fig. 3 and inset Figure to Fig. 3) is probably due to the prohibition of the photoinduced electron transfer process between naphthyridine moiety and 7,10-diphenylfluoranthene moiety upon metal binding. The possible process of **1** in sensing of Cr^{3+} is depicted in Scheme 2, After Cr^{3+} was added into the ethanol solution of **1**, the fluorescence decay curve is fitted to one-exponential decay (Fig. 4) and the lifetime is 12 ns.

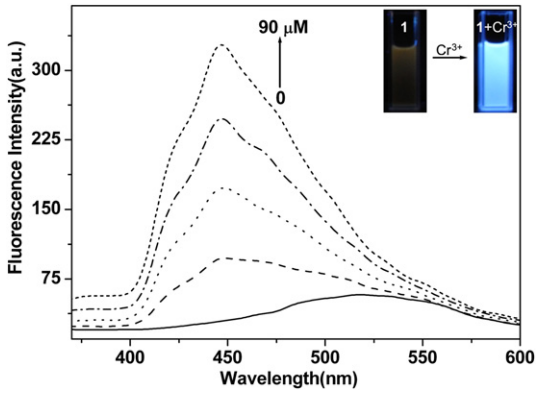


Fig. 2. Changes in fluorescence emission spectra of **1** (1.0×10^{-5} M) in ethanol upon addition of $Cr(NO_3)_3$ (the final concentration is 9.0×10^{-5} M) and the excitation wavelength is 310 nm. The first trace is compound **1** alone, and each subsequent trace represents addition of 2.25 equiv of $Cr(NO_3)_3$. Inset: change in fluorescence of **1** (1.0×10^{-5} M) upon addition of $Cr(NO_3)_3$ (9.0×10^{-5} M) under the irradiation at 365 nm (left: **1** only, right: after addition of Cr^{3+}).

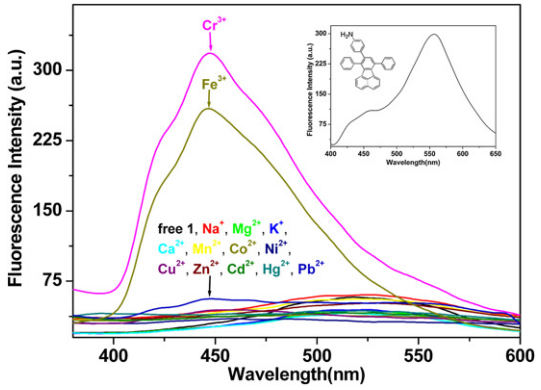
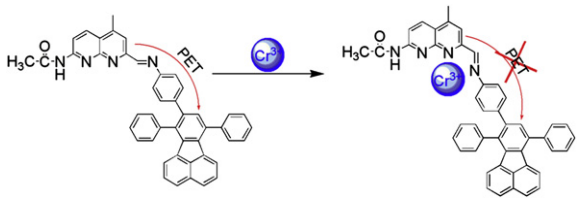


Fig. 3. Fluorescence spectra changes of **1** (1.0×10^{-5} M) upon addition of different metal ions ($Cr(NO_3)_3$, $FeCl_3$, NaCl, $MgCl_2$, KCl, $CaCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $PbCl_2$, 9.0×10^{-5} M) in ethanol. Inset: Fluorescence spectra of 4-(7,10-diphenylfluoranthen-8-yl)benzenamine. The position of fluorescent emission peak is 557 nm.

It is important for metal ion sensors that they are able to detect metal ion selectively over other cations. The selectivity of **1** for Cr^{3+} was investigated and the results are depicted in Fig. 5. Cr^{3+} elicited a great fluorescence intensity enhancement while the other metal



Scheme 2. Possible process of **1** in sensing of Cr^{3+}.

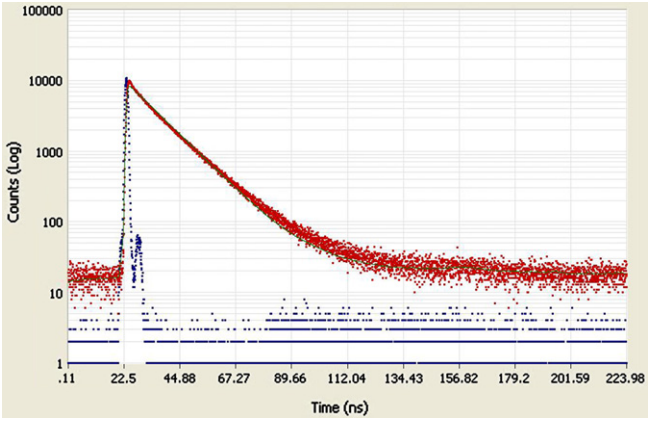


Fig. 4. The fluorescence decay curve of **1**–Cr^{3+} complex.

ions did not show significant response. The experiments of the counter ion effect on the selective properties of Cr^{3+} (Fig. 6) were also measured. Addition of chromium acetate made the fluorescence of compound **1** change very little, and chromium chloride had similar influence as that of chromium nitrate. Such fluorescence change may be resulted from the different acidity of cobalt salts (1.85 ($CrCl_3$), 2.92 ($Cr(NO)_3$), and 4.66 ($Cr(CHCOO)_3$)).

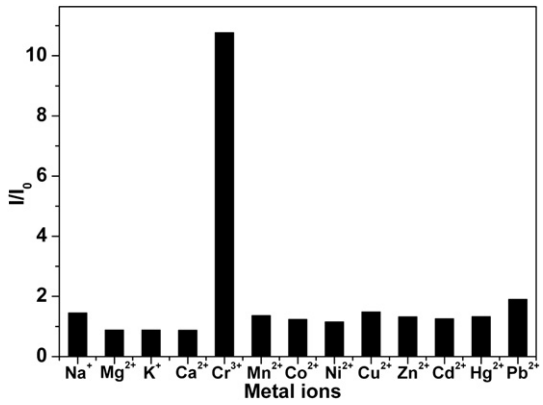


Fig. 5. Fluorescence spectra of a solution of the ion ($Cr(NO_3)_3$, NaCl, $MgCl_2$, KCl, $CaCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $PbCl_2$, 9.0×10^{-5} M) of interest and **1** (1.0×10^{-5} M). Bars represent the ratio of I to I_0. I and I_0 represent the emission intensity upon addition of different metal ions and that of compound **1** in ethanol at 447 nm, respectively. The overall emission spectra were measured at excitation of 310 nm.

The sensitivity of **1** to Cr^{3+} was examined in living cells by using confocal microscopy. Fluorescence images were recorded with excitation at 408 nm by a diode laser, Spinhole aperture, 100% gain of detector, and an oil objective with 60× magnification and 1.40 NA. The qualitatively in vitro results are exhibited in Fig. 7. After MCF-7 cells were incubated with 10^{-3} μmol **1** and 1 mL PBS for 30 min at 37 °C, no obvious fluorescence can be imaged (Fig. 7a). At the same experimental conditions, 10 min after 2×10^{-2} μmol of Cr^{3+} was introduced into the same MCF-7 cells, the strong fluorescence was imaged (Fig. 7b), which resulted from the reaction of **1** and Cr^{3+}. The bright field transmission images of these MCF-7 cells in Fig. 7c is exactly the same as the fluorescence image in Fig. 7b, confirming an intracellular fluorescence imaged.

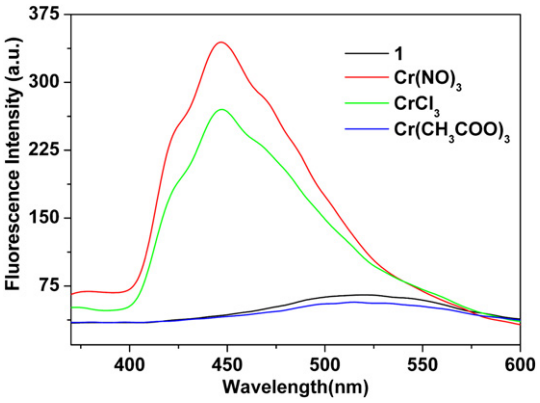


Fig. 6. Fluorescence spectra of of compound **1** (1.0×10^{-5} M) in ethanol upon addition of different Cr^{3+} salts with excitation at 310 nm.

3. Conclusion

In conclusion, we have utilized the guest-induced prohibition effect of the photoinduced electron transfer process between two moieties in chemical sensor to develop a novel probe for detecting the transition-metal ion Cr^{3+}. The new fluorescent sensor showed an excellent selectivity for Cr^{3+} over other metal ions examined in similar solutions. Confocal laser scanning microscopy experiments have proven that **1** can be used to monitor intraceullar Cr^{3+} and to map its subcellular distribution.

4. Experimental section

4.1. General instruments

For chromatography, 160–200 mesh silica gel (Qingdao, China) was employed. The ^1H and ^{13}C spectra were recorded at a Varian Mercury Bruker 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained on a VG ZAB-HS mass spectrometer or a Finnigan LCQ mass spectrometer. High resolution mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 T FTMS-MALDI/DHB). All spectral measurements were taken at 20 °C. UV–vis absorption spectra were measured with a Hitachi UV-3100 spectrophotometer and fluorescence spectra were determined on a Hitachi F-4500 spectrophotometer.

4.2. Synthetic procedure and characterization data

*4.2.1. 7,9-Diphenyl-8H-cyclopenta[l]acenaphthylen-8-one (**2**).* Compound **2** was synthesized from acenaphthenequinone and 1,3-diphenylpropane-2-one according literature method.[15] Yield: 95%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): δ (ppm) 8.08 (d, J=6.8 Hz, 2H), 7.86 (m, 6H), 7.61 (dd, ^3J(H,H), J=7.6 Hz, ^3J(H,H), J=8.0 Hz, 2H), 7.54 (dd, ^3J(H,H), J=7.6 Hz, ^3J(H,H), J=8.0 Hz, 4H), 7.42 (t, ^3J(H,H), J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.2, 132.1, 131.5, 131.4, 129.0, 128.6, 128.3, 127.8, 121.7, 120.9.

*4.2.2. 4-(Trimethylsilylethynyl)aniline (**4**).* 4-(Trimethylsilylethynyl) aniline was performed according to the literature.[16]

To a three-neck round bottomed flask was added 4-iodoaniline (1.10 g, 5.0 mmol), bistriphenylphosphine palladium(II) chloride

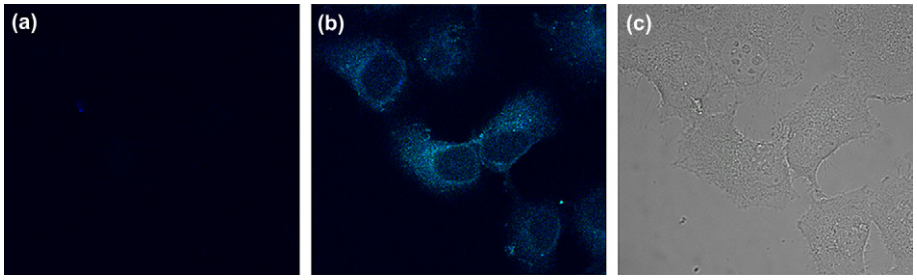


Fig. 7. The intracellular Cr^{3+} was imaged in living cells at 37 °C with use of confocal microscopy. (a) MCF-7 cells incubated with 10 μM of compound **1** solution (the volume ratio of ethanol and water is 4–6) for 30 min. (b) MCF-7 cells in part a 10 min after being treated with 2×10^{-2} μmol of $Cr(NO_3)_3$ aqueous solution. (c) Bright field image of living MCF-7 cells in parts a and b.

(702 mg, 0.200 mmol), and CuI (5 mg, 0.027 mmol). The mixture was purged with Ar gas and dry THF (10 mL) and TEA (3 mL) was added via syringe. The trimethylsilyl acetylene (0.85 mL, 6.0 mmol) was subsequently added via syringe and the reaction mixture was stirred for 2 h at room temperature. The solvent and TEA were removed under vacuum. Dried by anhydrous $MgSO_4$, the crude product was separated by column chromatography with a solvent system of 1:1 dichloromethane/petroleum ether (40–60 °C) to afford a light yellow solid (0.756 g, 74% yield).

To a stirred solution of potassium hydroxide (1.34 g, 23.8 mmol) in 6 mL methanol, 4-(Trimethylsilylethynyl)aniline (1.10 g, 0.86 mmol) in tetrahydrofuran (5 mL) was added, and the solution was refluxed overnight. Upon cooling to room temperature, the product was filtered to remove insoluble substance, and the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 (50 mL), filtered, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure providing the product as a yellow solid. Yield: 98%. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ (ppm) 7.32 (d, J=2.4 Hz, 2H), 6.61 (d, J=2.4 Hz, 2H), 3.83 (s, 2H), 2.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.0, 133.5, 114.6, 111.3, 84.4, 77.4, 77.1, 76.7, 74.9.

*4.2.3. 4-(7,10-Diphenylfluoranthen-8-yl)benzenamine (**6**).* A stirred mixture of 4-ethynylaniline (0.70 g, 6 mmol) and 7,9-diphenyl-8*H*-cyclopenta[l]acenaphthylen-8-one (1.78 g, 5 mmol) in degassed *o*-xylene (20 mL) was refluxed for 15 h. The solvent was removed under vacuum. A pale yellow powder was purified by column chromatography (200–300 mesh), using a CH_2Cl_2/hexane mixture as eluent (1.23 g, 55%). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ (ppm) 7.73 (d, ^3J(H,H), J=6.8 Hz, 4H), 7.54 (m, 2H), 7.43 (m, 6H), 7.30 (m, 4H), 7.03 (d, J=8.4 Hz, 2H), 6.67 (d, J=7.2 Hz, 1H), 6.52 (d, J=8.0 Hz, 2H), 3.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.5, 140.9, 138.2, 135.1, 133.1, 130.4, 129.1, 127.2, 126.5, 123.3, 122.7, 114.5, 77.3. ESI-MS $[M+1]^+$ 446 (100). HRMS (EI) calcd for $C_{34}H_{23}N$ [M], 445.1830; found 445.1824.

*4.2.4. (E)-N-(7-((4-(7,10-Diphenylfluoranthen-8-yl)phenylimino) methyl)-5-methyl-1,8-naphthyridin-2-yl)acetamide (**1**).* A mixture of aniline (97 mg) and 1,8-naphthyridine aldehydes (50 mg) in methanol (15 mL) was refluxed for 5 h under an argon atmosphere. After cooling to room temperature, the crude product was dried in vacuum. Subsequently, the solid was purified by column chromatography (200–300 mesh) on silica gel with dichloromethane to afford yellow **1** (107 mg, yield: 71%). ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ (ppm) 8.71 (s, 1H, NH), 8.57 (d, J=9.2 Hz, 1H), 8.57 (d, J=9.2 Hz, 1H), 8.18 (s, 1H), 7.79 (m, 5H), 7.56 (m, 3H), 7.40 (m, 7H), 7.30 (m, 4H), 7.19 (d, J=8.4 Hz, 2H), 6.73 (d, J=7.2 Hz, 1H), 2.78 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.45, 160.44, 157.39, 146.38, 140.69, 138.01, 131.04, 128.50, 127.43, 123.41, 120.67, 22.99, 18.39. ESI-MS $[M+1]^+$ 657 (100). HRMS calcd for $C_{46}H_{32}N_4O$ (m/z): 656.2576; found: 657.2649.

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