Dansyl-based fluorescent chemosensors for selective responses of Cr(III)†

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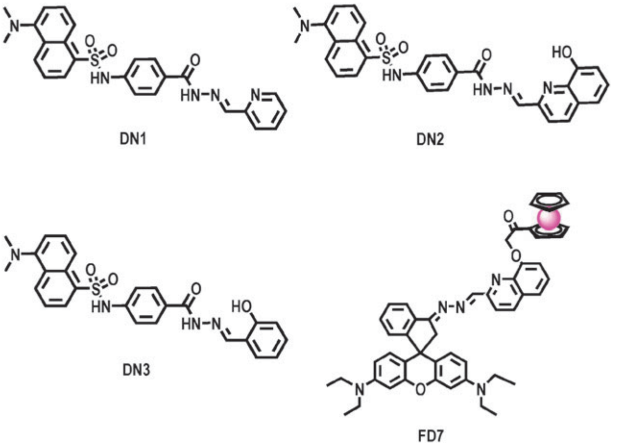
Three chemosensors **DN1**, **DN2** and **DN3**, incorporating dansyl dye as a fluorophore and various carboxhydrazones as ionophores, are reported. **DN1** contains a pyridine-carboxhydrazone tridentate coordination site, forming a 2:1 stoichiometric complexation species with Cr^{3+}, and exhibits selectivity for Cr^{3+} over alkali and alkaline earth metals and most first-row transition metals in aqueous media. **DN1** displays high quantum yield ($\Phi = 0.86$) and fluorescence enhancement following Cr^{3+} coordination within a wide pH range. **DN2** contains a 8-hydroxyquinoline-carboxhydrazone tetradentate metal-binding moiety, forming a 1:1 complex with Cr^{3+}. **DN2** also exhibits significantly fluorescence enhancement but a much lower quantum yield following Cr^{3+} binding in aqueous solution. In contrast, their congener **DN3**, having a salicyl-carboxhydrazone tridentate binding site, does not exhibit any significant fluorescence variation following Cr^{3+} binding. These results demonstrate that the hydroxyl group is an important factor influencing the fluorescence response to Cr^{3+} in aqueous media.

Introduction

On account of its simplicity and high sensitivity, fluorescence is increasingly important for trace chemical detection.[1] An important area within this field is the design of fluorescent chemosensors for selective response toward various metal ions.[2,3] Recently, the molecular design of selective fluoroionophores for alkaline and alkaline-earth metals has been well established,[4] and considerable efforts have been devoted to develop fluorescent chemosensors for heavy and transition metal ions.[5] However, very few fluorescent sensors for Cr^{3+} have been reported, owing to the lack of a proper selective ionophore for Cr^{3+}.[6] Chromium(III) is an essential trace element in human nutrition and has great impact on the metabolism of carbohydrates, fats, proteins and nucleic acids by activating certain enzymes and stabilizing proteins and nucleic acids.[7] At the same time, it is an environmental pollutant that has caused concern in industry and agriculture,[8] and so systematic investigations into the specific detection of Cr^{3+} still need to be developed, especially for aqueous systems.[9]



Scheme 1 Chemical structures of the receptors.

The sensing of metal ions by means of chelation-enhanced fluorescence (CHEF) is an active area of research.[10] Ligands bearing multidentate chelating units, which can potentially coordinate to the metal ion and contribute to the CHEF effect, have been important in the applications of ionophore design.[11,12] In this paper, we describe the design and synthesis of two carboxhydrazone derivatives for the fluorescent detection of Cr^{3+} in aqueous media, by incorporating the dansyl group into the *para* site of the benzene ring (Scheme 1). We anticipated that this coordination unit attached to the carboxhydrazone group would be beneficial for Cr^{3+} specificity, and that the presence of the dansyl group would result in high quantum efficiency and sensitivity to environmentally relevant Cr^{3+} levels (the ppm range) in aqueous media, since dansyl has been extensively used in the design of fluorescent sensors for metal ions.[13]

Experimental

Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. ^1H NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in d_6-DMSO, TMS as internal standard). Mass spectrometric data were obtained on HP1100LC/MSD and LCQ-Tof mass spectrometers. Elemental analyses of C, N and H were performed with Vario EL III analyzer. Fluorescence emission spectra were obtained using JASCO FP-6500 luminescence spectrometer. Stock solutions (0.02 M) of the aqueous salts of K^+, Na^+, Ca^{2+},

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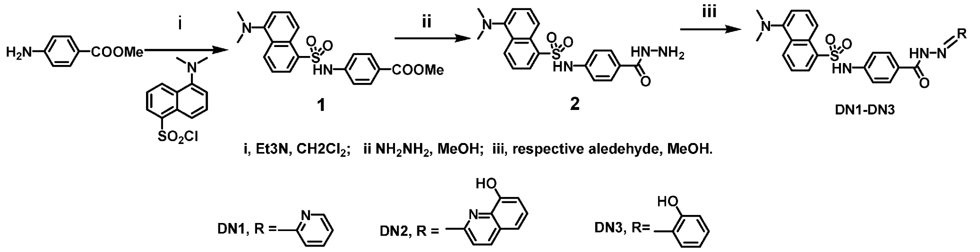

Scheme 2 Synthesis of the chemosensors.

Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Hg^{2+} and Cr^{3+} were prepared. Optical absorption spectra were measured on a HP8453 Uv/Vis spectrophotometer at room temperature. All the spectroscopic measurements were performed at least in triplicate and averaged.

For Cr^{3+}-bound **DN1**, fluorescence quantum yield was determined using optically matching solutions of Rhodamine-6G (Φ_f = 0.94 in ethanol) as standard at an excitation wavelength of 500 nm. For Cr^{3+}-bound **DN2** the reference was $Ru(2,2\text{-bpy})_3(ClO_4)_2$ (Φ_f = 0.059 in acetonitrile) at an excitation wavelength of 450 nm. The quantum yield was calculated using equation (1):

$$\Phi_{\text{sample}} = \Phi_{\text{std}} \frac{(I_{\text{sample}}/A_{\text{sample}})}{(I_{\text{std}}/A_{\text{std}})} \left(\frac{\eta_{\text{sample}}}{\eta_{\text{std}}}\right)^2 \qquad (1)$$

where Φ_{sample} and Φ_{std} are the radiative quantum yields of the sample and standard, I_{sample} and I_{std} are the integrated emission intensities of the corrected spectra for the sample and standard, A_{sample} and A_{std} are the absorbances of the sample and standard at the excitation wavelength, and η_{sample} and η_{std} are the indices of refraction of the sample and standard solutions, respectively.

Syntheses

Methyl *N*-dansyl-4-aminobenzenate 1. 5-Dimethylamino-1-naphthalenesulfonyl chloride (dansyl chloride) (3.45 g, 12.8 mmol) in 50 ml dichloromethane was added dropwise into a solution of methyl 4-aminobenzoate (1.63 g, 10.7 mmol) and triethylamine (5.41 g, 53.5 mmol) in 70 ml dichloromethane. The solution was stirred at room temperature for 24 h, and washed with 2 × 100 ml water. The organic layer was dried with $MgSO_4$. The yellow solid obtained by evaporating the solvent was recrystallized from ethyl acetate and used directly in the next step.

***N*-Dansyl-4-aminobenzene carbohydrazide 2.** Compound **1** (2.20 g, 5.72 mmol) was dissolved in 100 ml methanol containing hydrazine hydrate (5.73 g, 114.5 mmol). After refluxing for 24 h, the solvent was removed. The yellow solid obtained was used in next step.

General procedure for the syntheses of DNs (Scheme 2). Compound **2** (1.50 g, 3.90 mmol) was dissolved in 20 ml methanol with the appropriate aldehyde (4 mmol). Acetic acid (5 drops) was added to the mixture and the solution was refluxed for 24 h. The yellow solid was obtained by filtration.

Compound DN1. The crude product was recrystallized from dichloromethane/methanol (10:1) and dried under vacuum. Yield 43.5% (Calc. from methyl 4-aminobenzoate). Anal. Calc. for $C_{25}H_{23}N_5O_3S$: H, 4.90; C, 63.41; N, 14.79. Found: H, 5.21; C, 63.16; N, 14.01. ^{1}H NMR (d_6-DMSO, ppm): 11.78 (s, 1H, H_{CONH}), 11.13 (s, 1H, H_{SO2NH}), 8.54 (s, 1H, $H_{CH=N}$), 8.41 (d, 1H, H_{py}, J = 8.0 Hz), 8.31 (br, 2H, H_{np}), 8.27 (d, 1H, H_{np}, J = 7.2 Hz), 7.87 (d, 1H, H_{py}, J = 7.6 Hz), 7.80 (t, 1H, H_{py}, J = 7.6 Hz), 7.67 (d, 2H, H_{ph}, J = 7.6 Hz), 7.59 (t, 2H, H_{np}, J = 8.0 Hz), 7.34 (t, 1H, H_{py}, J = 5.6 Hz), 7.20 (d, 1H, H_{np}, J = 7.6 Hz), 7.12 (d, 2H, H_{ph}, J = 8.4 Hz), 2.80 (d, 6H, H_{CH3}). MS: m/z 474.0 $(M+H)^+$, m/z 496.1 $(M+Na)^+$.

Compound DN2. The crude product was purified by column chromatogram (ethyl acetate) and dried under vacuum. Yield 44.7% (Calc. methyl 4-aminobenzoate). Anal. Calc. for $C_{29}H_{25}N_5O_4S$: H, 4.67; C, 64.55; N, 12.98. Found: H, 4.72; C, 64.21; N, 12.77. ^{1}H NMR (d_6-DMSO, ppm): 12.00 (s, 1H, H_{CONH}), 11.18 (s, 1H, H_{SO2NH}), 9.81 (s, 1H, H_{OH}), 8.54 (s, 1H, $H_{CH=N}$), 8.47 (d, 1H, H_{ql}, J = 8.8 Hz), 8.38 (d, 1H, Hnp, J = 8.8 Hz), 8.32 (m, 2H, H_{np}), 8.05 (d, 1H, H_{ql}, J = 8.0 Hz), 7.75 (d, 2H, H_{ph}, J = 8.4 Hz), 7.64 (t, 2H, H_{np}, J = 8.4 Hz), 7.45 (t, 1H, H_{ql}, J = 7.6 Hz), 7.39 (d, 2H, H_{ql}, J = 7.2 Hz), 7.26 (d, 1H, H_{np}, J = 7.6 Hz), 7.18 (d, 2H, H_{ph}, J = 8.4 Hz), 7.12(d, 1H, H_{ql}, J = 7.2 Hz), 2.80 (d, 6H, H_{CH3}). MS: m/z 540.3 $(M+H)^+$; m/z 562.2 $(M+Na)^+$.

Compound DN3. The solid was recrystallized from dichloromethane/methanol (10:1) dried under vacuum. Yield: 45.1% (Calc. from methyl 4-aminobenzoate). Anal. Calc. for $C_{26}H_{24}N_4O_4S$: H, 4.95; C, 63.92; N, 11.47%. Found: H, 5.09; C, 63.00; N, 11.71%. ^{1}H NMR (d_6-DMSO, ppm): 11.90 (s, 1H, H_{CONH}), 11.26 (s, 1H, H_{OH}), 11.17 (S, 1H, H_{SO2NH}), 8.54 (S, 1H, $H_{CH=N}$), 8.46 (d, 1H, H_{np}, J = 8.4 Hz), 8.37 (d, 1H, H_{np}, J = 8.4 Hz), 8.32 (d, 1H, H_{np}, J = 7.2 Hz), 7.74 (d, 2H, H_{ph}, J = 8.0 Hz), 7.64 (t, 2H, H_{np}, J = 8.0 Hz), 7.49 (d, 1H_{ph}, J = 7.6 Hz), 7.26 (m, 2H, $H_{ph}+H_{np}$), 7.17 (d, 2H, H_{ph}, J = 8.4 Hz), 6.89 (t, 2H, $H_{ph}+H_{ql}$). MS: m/z 489.2 $(M+H)^+$, 511.1 $(M+Na)^+$.

Crystallography. Intensity data of compound **DN3**·MeOH were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the SMART and SAINT programs.[14] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1.[15] Crystal data for **DN3**·MeOH: $C_{27}H_{28}N_4O_5S$, M_r = 520.59, triclinic, $P\bar{1}$, a = 10.143 (2) Å, b = 10.185 (2) Å, c = 14.427(3) Å, α = 94.337(9)°, β = 108.283 (8)°,

γ = 111.195(8), V = 1289.1(4) Å^3; Z = 2; D_{calcd} = 1.341 g cm^{-3}; T = 293(2) K. The final refinement gave R_1 = 0.0501, wR_2 = 0.1578 and Gof = 1.026 for 3566 observed reflections with $I > 2\sigma(I)$. Non-hydrogen atoms were refined anisotropically. Except for the solvent molecule, hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms with the isotropic displacement being fixed at 1.2 and 1.5 times of the aromatic and methyl carbon atoms, respectively.

Results and discussion

Spectroscopic properties of DN1

Compound **DN1** was easily synthesized from the reaction of *N*-dansyl 4-aminobenzene carbohydrazide with 2-pyridinecarbaldehyde. Its molecular structure was characterized by ^{1}H NMR spectroscopy and MS. UV-vis titration of the **DN1** compound with Cr^{3+} was carried out in DMF/H_2O (9 : 1) solution (Fig. 1). **DN1** exhibited an absorption band centered at *ca.* 350 nm (log ε = 4.56). The addition of Cr^{3+} caused an obvious absorbance decrease at 350 nm. At the same time, a new peak at 315 nm appeared and developed significantly. The presence of a sharp isosbestic point at 325 nm indicated that only two species coexisted in the equilibrium. The individual profile of the absorbance at 315 nm demonstrated a 2 : 1 stoichiometric host–guest complex for **DN1** and Cr^{3+}, with the overall association constant being calculated as $K_{ass} = 6.07 \pm 0.10 \times 10^7$ M^{-2} ($K_{ass1} = 5.55 \pm 0.10 \times 10^3$ M^{-1}, $K_{ass2} = 1.09 \pm 0.10 \times 10^4$ M^{-1}, respectively‡).

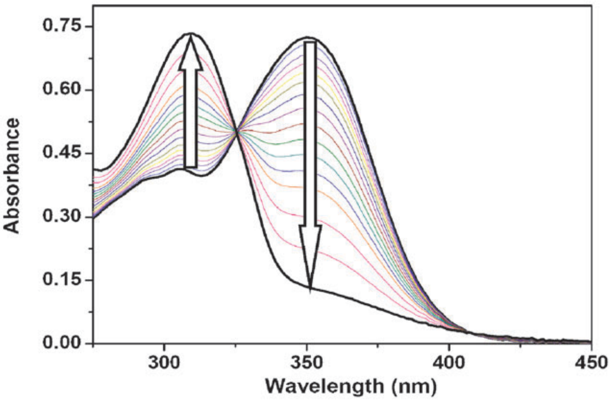

Fig. 1 Absorption spectra of **DN1** (20 μM) upon addition of increasing amounts of Cr^{3+} (0 to 0.2 mM) in DMF/H_2O (9:1) solution.

Free **DN1** exhibited a emission band centred at about 545 nm in DMF/H_2O (9:1, v/v, pH = 8.0) solution (20 μM) when excited at 350 nm. Addition of of Cr^{3+} (40 μM, 2 ppm) caused *ca.* 5-fold enhancement of the typical dansyl-based fluorescence (λ_{max} = 545 nm, Fig. 2).[13] In fact, due to the dramatic decrease in the absorbance of **DN1** at 350 nm upon the addition of Cr^3, the enhancement of the quantum yield for Cr^{3+}-bound **DN1** was more impressive. In this case, the quantum yield of the Cr^{3+}-bound complex (Φ = 0.86) was about 28-fold larger than that of the free **DN1**. This quantum yield is the highest reported to date for a Cr^{3+} fluorescent sensor, making **DN1** a promising fluorescent sensor to detect Cr^{3+} at low concentrations in aqueous systems.

For practical applications, the best conditions for successful operation of **DN1** were evaluated. Upon addition of HCl (up to 1 mM) aqueous solution, the fluorescence intensity of the **DN1** (20 μM)–Cr^{3+} (100 μM) mixture varied less than 15% (Fig. S2†). At the same time, the addition of NaOH aqueous solution (up to 0.05 mM) did not cause any significant fluorescence variation of the **DN1**(20 μM)–Cr^{3+} (100 μM) mixture (Fig. S3†). In this regard, **DN1** could be used to detect Cr^{3+} in environments with pH values in the approximate range of 5.0 to 9.0.

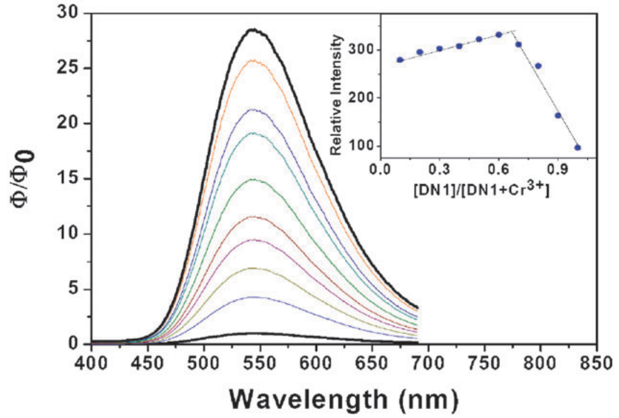

Fig. 2 Fluorescent response of **DN1** (20 μM) upon addition of Cr^{3+} (0–40 μM) in a DMF/H_2O (9:1) solution. The emission intensities were integrated at 545 nm (excitation at 350 nm) The inset shows the Job plot evaluated from the fluorescence at 545 nm with a total concentration of 20 μM and excitation at 350 nm.

To determine whether **DN1** functions as a highly selective chemosensor for Cr^{3+}, some other metal ions including alkali, alkaline earth and transition metal ions as well as heavy metal ions were added respectively into a solution of **DN1** under the same conditions (DMF/H_2O (9:1), excitation at 350 nm), As shown in Fig. 3, no significant spectral changes of **DN1** were observed in the presence of alkali metal cations such as Li^+, Na^+ and K^+. The alkaline-earth cations Mg^{2+} and Ca^{2+}, and the transition metal ion Mn^{2+}, induced a slight increase in fluorescence. The presence of 0.2 mM Zn^{2+}, Cd^{2+}, Fe^{3+}, Hg^{2+} and Pb^{2+} just caused slight fluorescence quenching.

The Job plot evaluated from the fluorescence spectra of the titration solution exhibited an inflection point at about 0.66, confirming the formation of a 2:1 **DN1**–Cr^{3+} complex in the aqueous solution, which was further supported by the ESI-MS spectra of **DN1** in the presence of Cr^{3+} in a DMF/H_2O (9:1) solution. As shown in Fig. 4, the peak at m/z 996.40 could be attributed to the [(**DN1** − H)$_2$ + Cr]$^+$ species, based on the measured and the simulated isotopic patterns. In this

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‡ An approximate linear fit formula is used to calculate the single association constant K_{ass1} and K_{ass2}:

$$\frac{1}{n}\frac{F-F_0}{F_l-F}=\frac{2k_1K_{ass2}C_0}{F_l-F_0}(F_l-F)+K_{ass1}C_0$$

where n is the number of equivalents of the added metal ions, F_0 is the fluorescence intensity of the free sensor, and F_l is the fluorescence intensity in the presence of excess cation. K_{ass1} and K_{ass2} can be obtained by a linear analysis of $(F_l - F)$ (x) *versus* $\frac{1}{n}\frac{F-F_0}{F_l-F}$ (y).

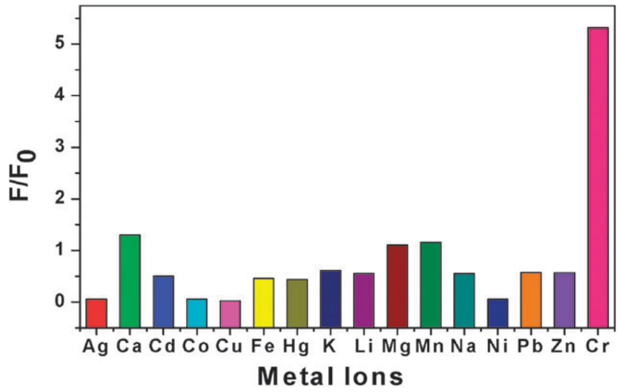


Fig. 3 Fluorescence responses of **DN1** (20 μM) to various cations in a DMF/H_2O (9:1) solution. The bars represent the emission intensities of **DN1** in the presence of 0.2 mM of relevant metal ions (excitation at 350 nm).

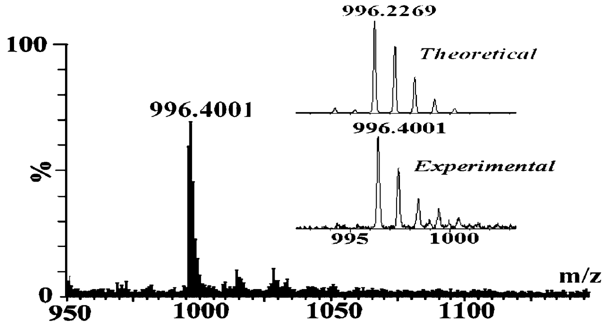


Fig. 4 ESI-MS of **DN1** in the presence of Cr^{3+} in a DMF/H_2O (9:1) solution. The inset shows the measured and the simulated isotopic patterns at 996.40 Dalton.

occurrence, **DN1** could be acting as a tridentate chelator, and the carbonyl O, imine N and pyridine N atoms from the two different ligands are the most likely binding sites for Cr^{3+}.

Spectroscopic properties of DN2

To further investigate the coordination effect of such dansyl-based chemosensors, the receptor **DN2** was synthesised by the same procedure as for **DN1** by replacing 2-pyridine carbaldehyde with 8-hydroxyquinoline-2-carboxaldehyde. With the additional binding site of the hydroxy O atom, **DN2** was anticipated to act as a tetradentate ligand. **DN2** exhibited two absorption bands centered at *ca.* 300 and 360 nm ($\log \varepsilon = 4.53$ and 4.49, respectively). The addition of Cr^{3+} caused an obvious decrease in absorbance at 360 nm, and an increase at 300 nm (Fig. S5†). The individual profile of the absorbance of the band at 300 nm (increasing) demonstrated the 1:1 stoichiometry for **DN2** and Cr^{3+}, with the association constant being calculated as $K_{ass} = 9.59 \pm 0.03 \times 10^3$ M^{-1}.

Free **DN2** exhibited similar fluorescence behavior to that of **DN1**, with an emission at about 540 nm in DMF/H_2O (9 : 1) aqueous solution (20 μM) when excited at 360 nm (Fig. 5). The addition of Cr^{3+} (40 μM) caused a 4-fold fluorescence enhancement and 11-fold quantum yield enhancement ($\Phi = 0.059$ for the Cr^{3+}-bound complex). **DN2** also showed good selectivity for Cr^{3+} over other metal ions, and the working conditions for response of **DN2** to Cr^{3+} were similar to that for **DN1**.

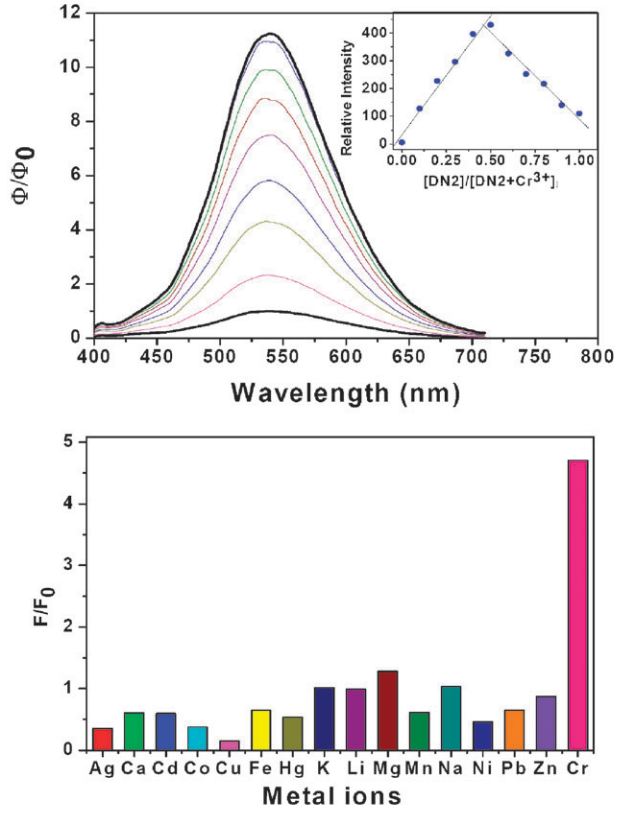


Fig. 5 (*Top*) Fluorescent response of **DN2** (20 μM) upon addition of Cr^{3+} in a DMF/H_2O (9:1) solution. The inset shows the Job plot evaluated from the fluorescence with a total concentration of 20 μM. (*Bottom*) Fluorescence responses of **DN2** (20 μM) in a DMF/H_2O (9:1) solution to various relevant metal ions (100 μM). The emission intensities were integrated at 540 nm (excitation at 360 nm).

The 1 : 1 binding mode was further supported by a Job plot of the **DN2**–Cr^{3+} fluorescence spectra, with the inflection point at about 0.5, and the presence of a peak at *m*/*z* 589.9 (calc 590.1, Fig. 6) corresponding to $[(\mathbf{DN2} - 2H) + Cr]^+$ in the ESI-MS spectrum of a mixture of **DN2** and Cr^{3+}.

The possible binding mode of **DN1** and **DN2** to Cr^{3+} is shown in Scheme 3. **DN1** provides three coordination sites and thus tends to form a complex with $Cr^{3+}$with 2:1 stoichiometry. In accordance with the coordination number of 6 for Cr^{3+}, the most likely binding sites for Cr^{3+} are the conjugated moiety including carbonyl O, imino N, and quinoline N and O atoms of **DN2**. The other two coordination sites of Cr^{3+} may be taken by solvents and/or the counter-anions, resulting in a 1:1 stoichiometry with Cr^{3+}.

Structure and spectroscopic properties of DN3

Compared to **DN1**, the much lower quantum yield of the Cr^{3+}–**DN2** complex might be attributed to the presence of the OH group. In the Cr^{3+} fluorescent sensor **FD7**, containing an 8-hydroxyquinoline carboxhydrazone ionophore, the Cr^{3+}-binding quantum yield reached 0.18 when the proton of the OH group was displaced.[7c]

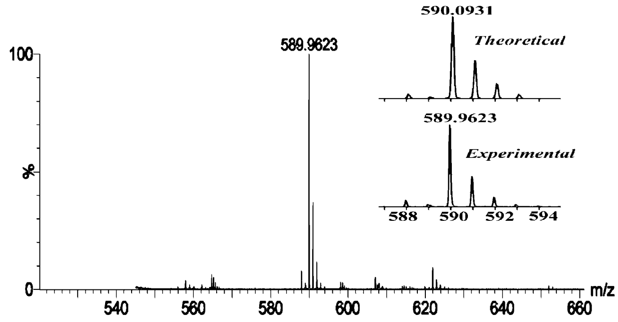
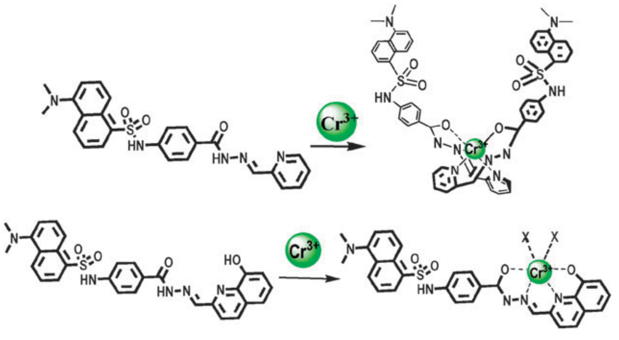


Fig. 6 ESI-MS of **DN2** in the presence of Cr^{3+} in a DMF/H_2O (9:1) solution. The inset shows the measured and the simulated isotopic patterns at 589.96.



Scheme 3 Possible binding mode of **DN1** and **DN2** with Cr^{3+} (**X** is the coordinating anion or solvent).

To further investigate the selectivity of the different ionophores and effect of the OH group on the sensitivity of the chemosensors toward Cr^{3+}, **DN3** was designed and obtained from the reaction of *N*-dansyl 4-aminobenzene carbohydrazide with salicaldehyde. Evaporating a dichloromethane/methanol (10:1) solution of **DN3** in air provided crystals suitable for X-ray structural analysis. As shown in Fig. 7, the salicaldehyde atom O(4), the imine nitrogen N(4) and the carboxyl oxygen atom O(3) point in the same direction. The C=O, C–N(H) and C=N bond distances within the tridentate chelator moiety are intermediate between the typical single bond and double bond distances, demonstrating extensive electron delocalization within the whole skeleton.

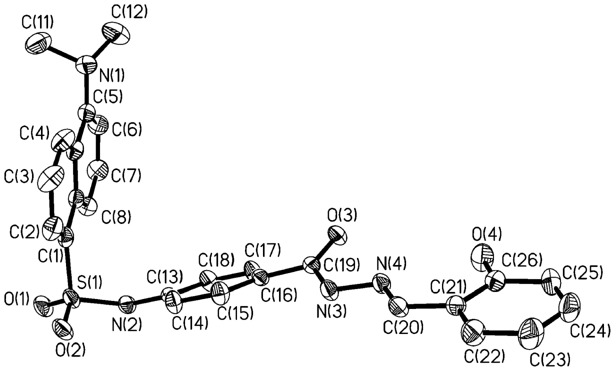


Fig. 7 ORTEP plot of molecular structure of **DN3** in 30% ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and bond angles (°): N(2)–S(1) 1.617(2), C(19)–O(3) 1.225(3), C(19)–N(3) 1.350(3), C(20)–N(4) 1.274(3); C(1)–S(1)–N(2) 106.5(1), S(1)–N(2)–C(13) 125.5(2), C(19)–N(3)–N(4) 118.7(2), N(3)–N(4)–C(20) 116.6(2).

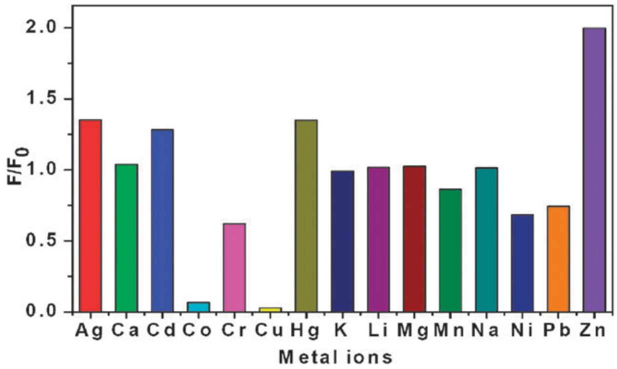


Fig. 8 Fluorescence responses of **DN3** to various cations in a DMF/H_2O (9:1) aqueous solution ([**DN3**] = 1 μM; λ_{ex} = 390 nm). The bars represent the emission intensities of **DN3** in the presence of 10 μM of relevant metal ions or 2 μM Zn^{2+}.

DN3 exhibited three absorption bands centered at *ca.* 290, 300 and 340 nm ($\log \varepsilon = 4.33, 4.34$ and 4.49, respectively). The addition of Cr^{3+} caused an obvious absorbance decrease and blue-shift of the peak at 340 nm, and an increasing at 290 and 300 nm (Fig. S6†). Free **DN3** (1 μM) exhibited luminescence at about 540 nm in DMF/H_2O (9:1) solution upon excitation at 390 nm. However, the addition of Cr^{3+} did not cause any obvious fluorescence enhancement, even when 10 equivalents of Cr^{3+} was added. In contrast, there was a *ca.* 2-fold fluorescence enhancement upon the addition of Zn^{2+} (2 μM) to the solution of **DN3** (Fig. 8). It is suggested that the presence of an OH group in the ionophore moiety of the sensors is a disadvantage for its sensitivity toward Cr^{3+}, and thus the selectivity of the Cr^{3+}-specific ionophore can be subtly controlled.

Conclusion

In summary, by combining a dansyl unit as the fluorophore and carboxhydrazone derivatives as the ionophores into one conjugated molecule, three fluorescent chemosensors have been prepared. By introducing suitable additional coordination units into the molecules, **DN1** and **DN2** showed selective fluorescence response to Cr^{3+} in aqueous media with 1:1 and 2:1 binding modes, respectively. **DN1** is among the brightest fluorescent sensor of Cr^{3+}, with the quantum yield being 0.86. A systematic investigation into chelating ionophores will help in the design of fluorescent chemosensors for the Cr^{3+} ion, which currently lacks a suitably selective ligand system.

Acknowledgements

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