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Spectroscopic studies on a 'turn-on' fluorescent sensor for transition metals with selective 'turn-off' for mercury(II) ions

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Spectroscopic studies on a dansyl-based fluorescent sensor *N*-(4-aminophenyl)-5-(dimethylamino)naphthalene-1-sulphonamide (**1**) and its interactions with transition metals are reported. The sensor's absorption and emission spectra exhibited different profiles at different polarities and pH values. Enhanced fluorescence was observed in the presence of chromium(III) ions in methanol, while the emission was quenched significantly in the presence of mercury(II) ions both in methanol and aqueous solution. The binding constants of **1** to chromium(III) in methanol and to mercury(II) ions in methanol and aqueous solution were calculated.

Keywords: fluorescent sensors; dansyl fluorophores; transition metals detection; Cr(III) detection; Hg(II) detection

Introduction

Transition metal ions are crucial for the proper functioning of several biological systems and have a significant effect on the environment even at very low concentrations (*1*). Among these metals, chromium and iron are essential for several biochemical and physiological processes and insufficient or excess intake of these metals induces variety of diseases (*1–5*). Besides, pollution by chromium and mercury is of considerable concern especially with its utilisation in many industries. Therefore, there has been a demand for the design and synthesis of chemosensors of these metals for environmental and medical applications (*1*, *6*). Fluorescent sensors are especially attractive due to their sensitivity and simple detection procedures.

Several fluorescent sensors for transition metal ions have been reported recently (*2–23*). For example, Chen and Chen (*2*) have reported a dansyl-based molecule with calix[4]-aza-crown as a ligand for mercury(II) ions which quenched its florescence emission. Another fluorescent sensor selective for zinc(II) was reported by Ngwendson and Banerjee (*9*). The sensor consisted of anisole moiety flourished with acetate ligands and it exhibited emission enhancement upon binding to zinc(II) ions.

In this paper, we report the synthesis, spectroscopic properties and binding studies of a novel chemical sensor *N*-(4-aminophenyl)-5-(dimethylamino)naphthalene-1-sulphonamide (**1**), which is composed of a dansyl fluorophore coupled to 4-aminoaniline moiety. The sensor was designed such that the coordination of the amino group to the metal ions perturbs the electronics of the system and leads to a concomitant change in the fluorescence profile of dansyl moiety. This sensor (**1**) showed enhanced fluorescence in the presence of chromium(III) ions in methanol, while its emission was significantly quenched in the presence of mercury(II) ions both in methanol and in aqueous solution.

Results and discussion

The sensor was prepared (*24*) first by the coupling of 4-nitroaniline to dansyl chloride in pyridine/dichloromethane solvent at room temperature (Scheme 1). The obtained product was then reduced in ethanol with hydrazine in the presence of Pd/C. The overall yield of the reaction was 68%.

The absorption spectrum of **1** in polar and non-polar solvents showed two characteristic bands at ~300 and ~345 nm (Figure 1(A)). The position of the higher energy peak (~300 nm) was not significantly affected by the polarity of the solvent. However, the position of the lower energy absorption peak (~345 nm) depended on the dielectric constant and the hydrogen-bonding ability of the solvent. The peak experienced a red shift in polar aprotic solvent with a high dielectric constant but a blue shift in hydrogen-bonding solvents, relative to the ability of the solvent.

The emission spectrum of **1** in the non-polar solvent mixture hexane/dichloromethane (4:1) exhibited a maximum peak at ~475 nm upon excitation at 335 nm. The same excitation, however, showed higher emission at higher wavelength (~500 nm) in the more polar aprotic solvents. As the polarity of the solvent and its ability of hydrogen bonding further increased, the emission band shifted to higher wavelength which suggests the

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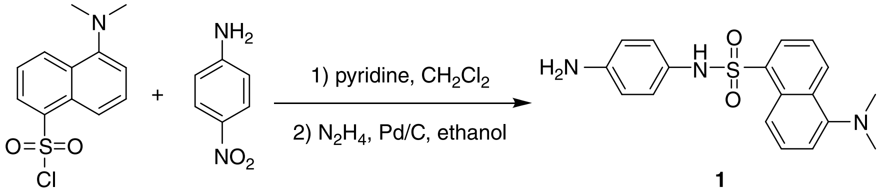


Scheme 1. The reaction scheme for the preparation of **1**.

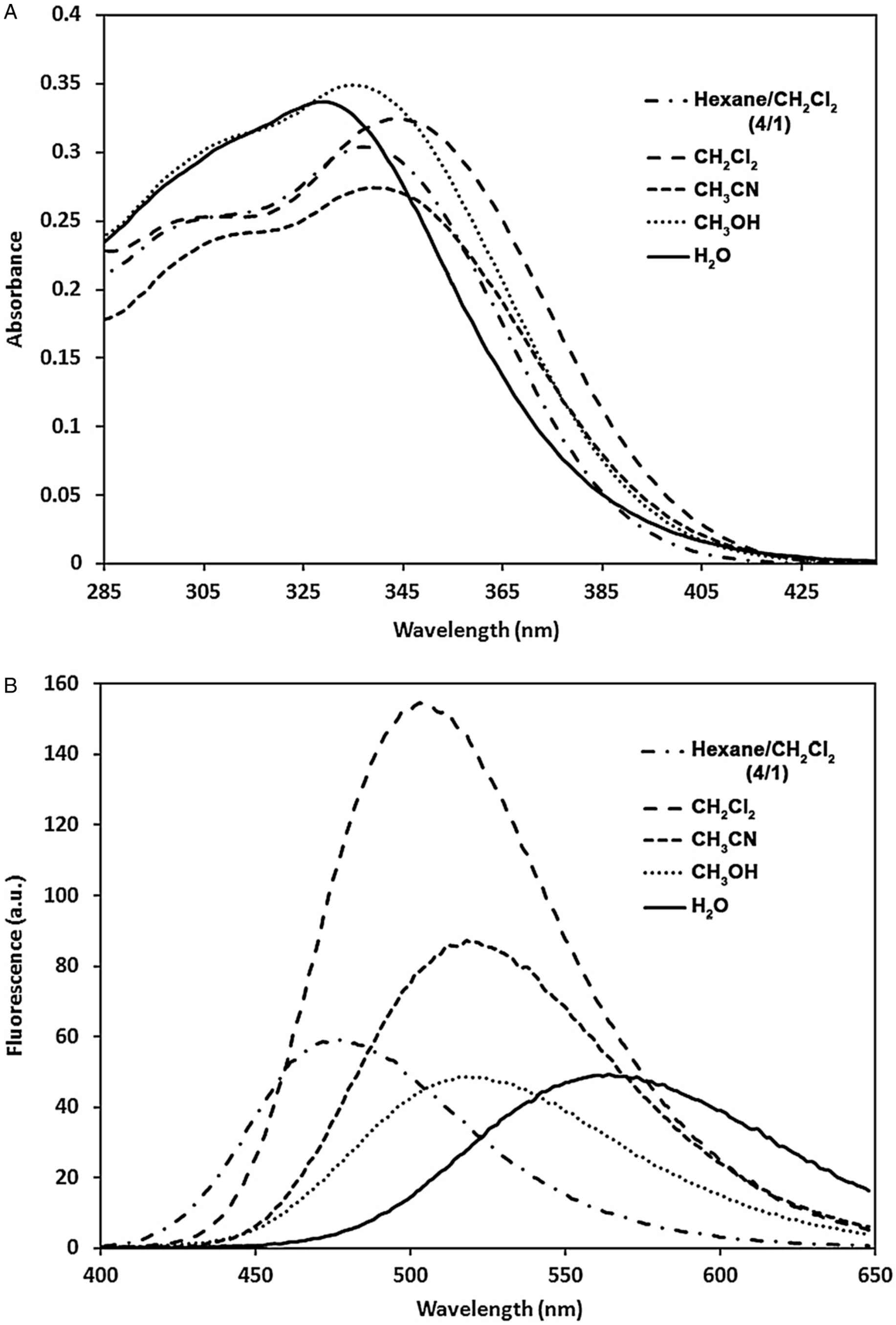


Figure 1. (A) Absorption and (B) emission spectra of **1** (50 μM) in different solvents.

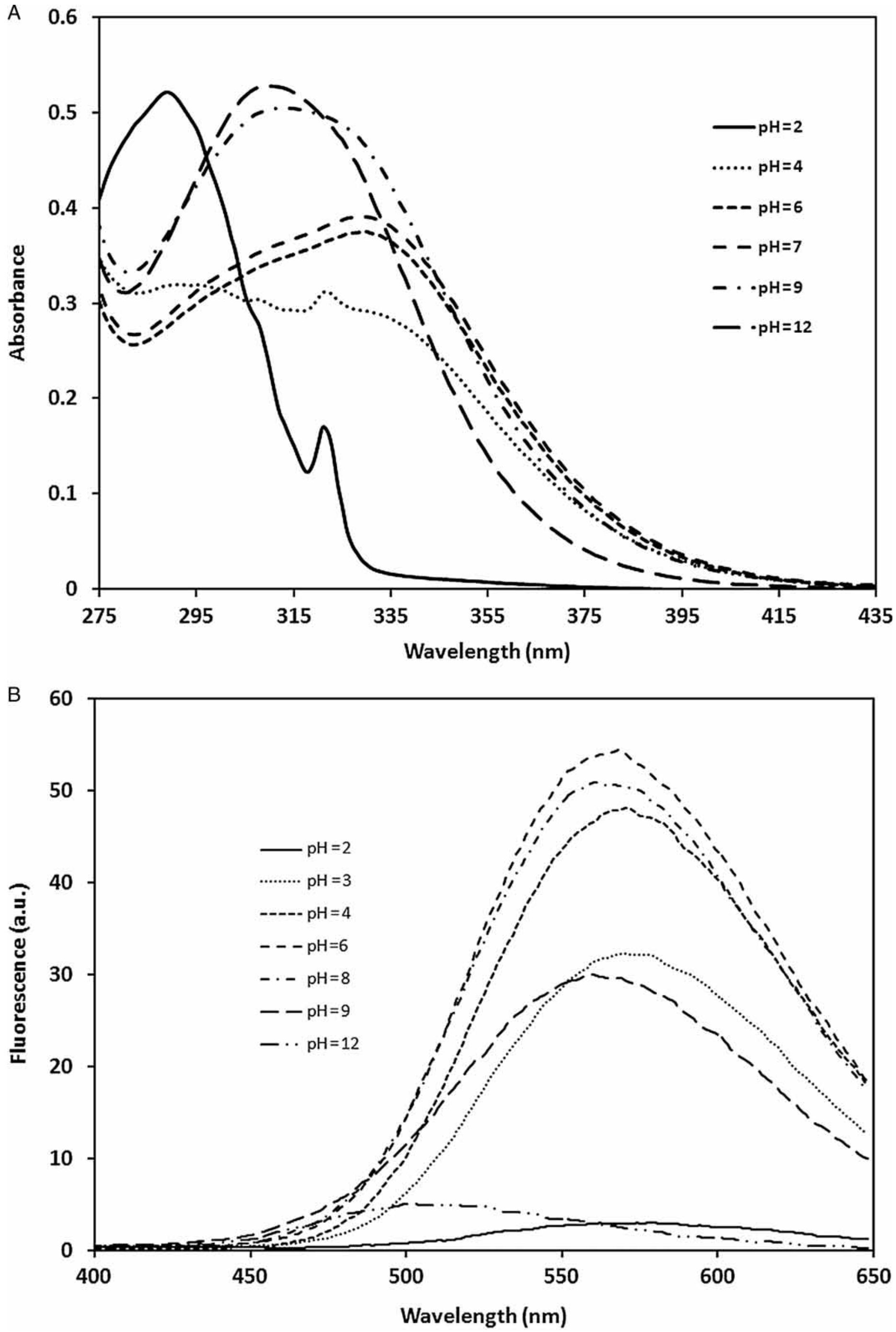
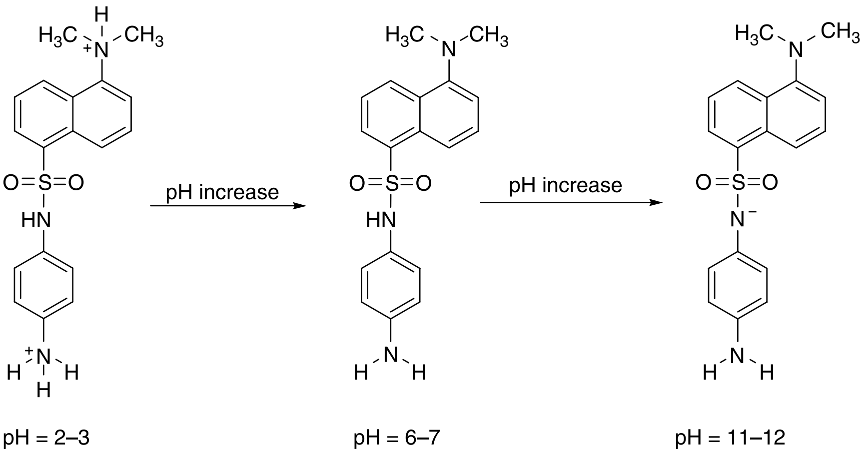


Figure 2. (A) Absorption and (B) emission spectra of **1** (50 μM) in HEPES buffer (10 mM) at different pH values.

generation of intramolecular charge-transfer (ICT) emitting state (*24–26*).

The studies of the absorption and emission spectra of **1** at different pH values further support the CT emitting state (*24*). These spectra exhibited significant changes as the pH increased from 2 to 12. The absorption spectrum (Figure 2(A)) of **1** showed a strong band at ~290 nm in pH 2; however, as the pH increased, the peak shifted to lower energy levels (~310 nm at pH 4 and ~330 nm at pH 7). These shifts of the band are due to the fully protonated sensor at low pH (Scheme 2) and the neutral compound at neutral pH, respectively (*24*). Further increase in the pH to strongly basic solution caused the absorption band to reverse the shift into the blue region at ~310 nm for pH 12. This shift was likely due to deprotonation of the sulphonamide group of the sensor (Scheme 2) (*26*).



Scheme 2. Changes in the structure of **1** as pH increases.

On the other hand, the fluorescence spectra (Figure 2(B)) of **1** showed, at pH 2, a very low intensity emission peak at ~570 nm. As the pH increased, the emission intensity at ~570 nm increased until it reached its maximum at pH 6. These changes supported the ICT emitting state of **1** which is most stable at the neutral conditions. When the medium became basic, the emission of **1** diminished and the emission band shifted to lower wavelengths. At pH 12, the emission maximum was at ~500 nm, which corresponds to the deprotonated sensor at the sulphonamide group (Scheme 2) (*26*).

The titration of transition metal solutions into aqueous solution of **1** at pH 7 (HEPES, 10 mM) has led to different changes in the emission spectra. The addition of cadmium(II), cobalt(II), chromium(III) and zinc(II) ions to **1** had induced little enhancement in the emission intensity of the sensor at 560 nm even after more than 10 equivalents of the metal have been added (Figure 3). However, the addition of the copper(II) and lead(II) ions had caused noticeable quenching of the sensor's fluorescence but less than that of mercury(II) ions. The latter decreased the emission of **1** by half just after five equivalents of the metal have been added. However, the sensor regained its emission intensity upon further addition of EDTA solution to sensor–mercury mixture. This means that the quenching was due to the coordination

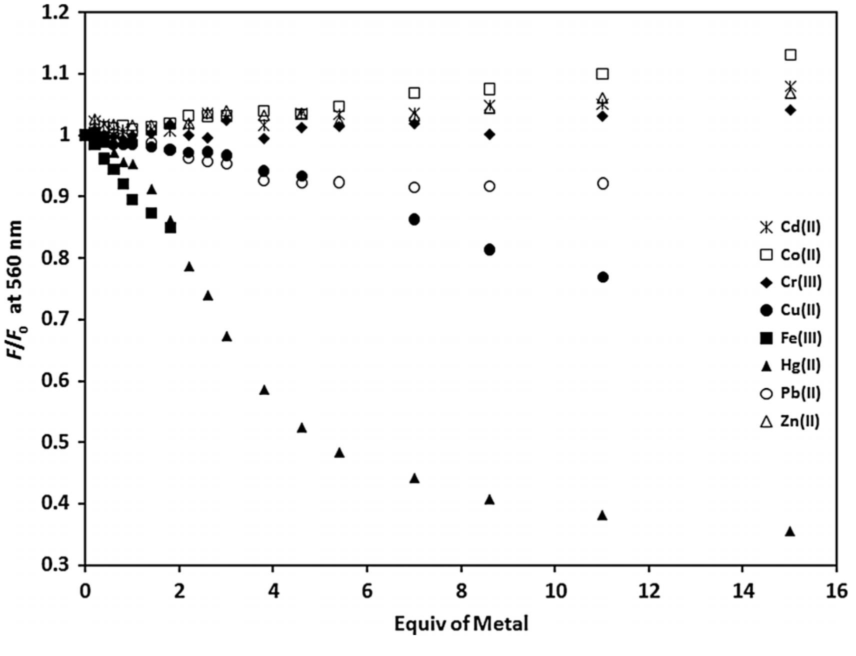


Figure 3. Relative change in the emission of **1** (50 mM) at 560 nm in HEPES solution (10 mM) upon the addition of different transition metals.

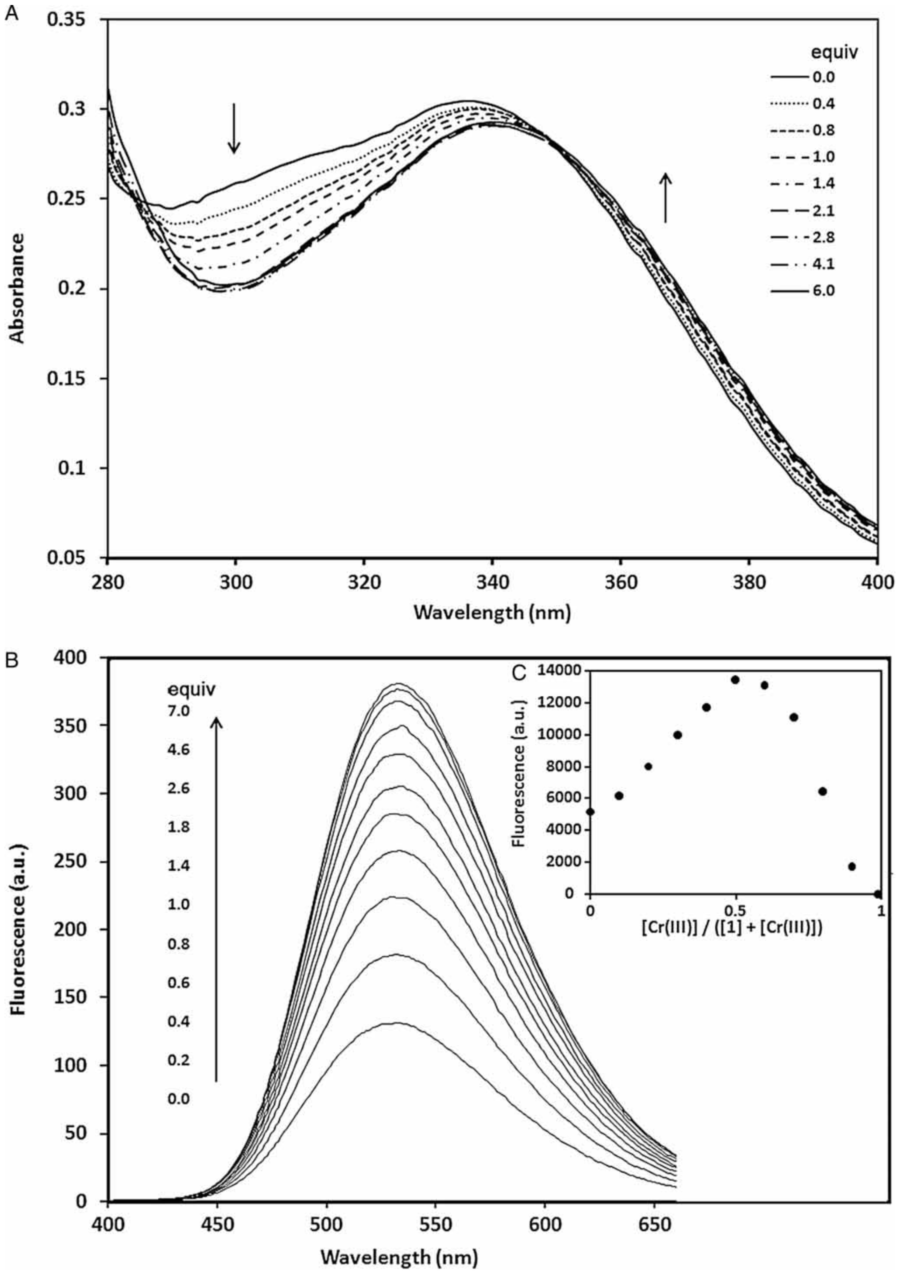


Figure 4. (A) Absorption and (B) emission spectra of **1** (50 μM) upon the addition of $Cr(NO_3)_3$ solution in methanol. (C) Job's plot for the titration of **1** with $Cr(NO_3)_3$ solution in methanol.

of the metal to the sensor through a reversible process. Such coordination perturbed the electronics of the sensor such that the electron-donor ability of amino group was diminished (*27*, *28*).

The interaction of **1** with the metals in methanol was significantly different from that of the aqueous solution. The absorption spectra (Figure 4(A)) of **1** in methanol exhibited an increase in absorbance at 270 nm concurrent and a decrease in absorbance at 400 nm with isosbestic points at 285 and 350 nm upon the addition of the chromium(III) ions. Besides, the sensor had a characteristic maximum emission peak of dansyl fluorophore at 515 nm upon excitation at 335 nm (Figure 4(B)). The titration of a solution of **1** in methanol with chromium(III) ions resulted in a significant enhancement in its emission accompanied with a red shift of the maximum peak from 515 to 530 nm. The enhancement of the sensor's emission could be attributed to the coordination of chromium(III) and iron(III) ions with the sulphonamide oxygen atoms. Such previously reported coordination (*29*, *30*) forces the

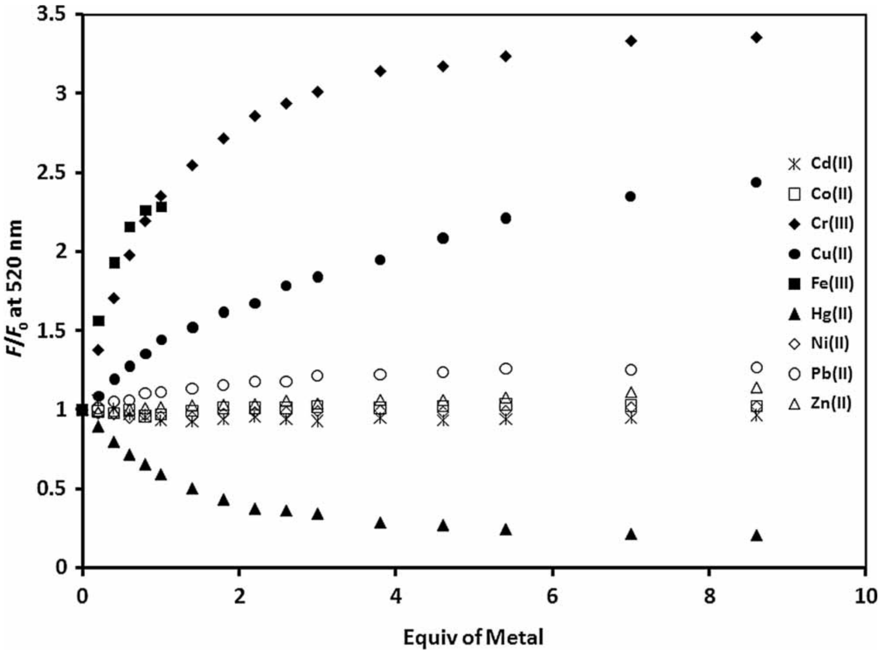


Figure 5. Relative change in the emission of **1** (50 μM) at 520 nm in methanol upon the addition of different transition metals.

molecule into a twisted conformation in the ground state and, thus, increases the effective concentration of the twisted ICT emitting state of the molecule. As a result, the emission intensity of the molecule is enhanced.

The addition of iron(III) ions to sensor **1** resulted in a similar effect on the fluorescence of **1** as chromium(III). However, it was not possible to obtain a full profile for the effect of iron(III) ions due to the strong absorbance of the iron–methanol complex at the excitation wavelength of 335 nm. The titration of **1** with copper(II) ions enhanced the fluorescence of **1** similar to chromium(III) but to lower extent. The other transition metals cobalt(II), zinc(II), lead(II) and cadmium(II) caused insignificant increase in the fluorescence of **1** even when around 10 equivalents of the metal have been added (Figure 5). However, the addition of mercury(II) to **1** resulted in opposite effect to that of the other transition metals. As mercury(II) ions were titrated into a solution of **1** in methanol, the fluorescence of **1** was quenched significantly reaching about 20% of its initial emission after the addition of 10 equivalents of the metal.

The apparent binding constants of **1** to the metals in methanol were calculated from the change in the fluorescence of the sensor as a function of the concentration of the metal added (*21–23*). The estimated binding constants for chromium(III) and copper(II) ions were $1.91 \pm 0.06 \times 10^4$ and $3.8 \pm 0.3 \times 10^3\,\mathrm{M}^{-1}$, respectively (Figure 6(A)). The binding constants of the other metals that exhibited little emission enhancement were too low to be fitted to the binding model. On the other hand, the reverse Stern–Volmer plots (Figure 6(B)) for the fluorescence quenching of **1** by mercury(II) ions were generated from the relative change of fluorescence of **1** as a function of mercury(II) ions. The data points of the binding of **1** to mercury(II) in methanol and HEPES buffer (10 mM) solution were fitted to a 1:1 binding model with $K_{\mathrm{SV}} = 1.38 \pm 0.04 \times 10^4$ and $4.9 \pm 0.3 \times 10^3\,\mathrm{M}^{-1}$, respectively.

Conclusion

In summary, we have reported the synthesis, spectroscopic properties and the binding studies of *N*-(4-aminophenyl)-5-(dimethylamino)naphthalene-1-sulphonamide with transition metals. The sensor showed strong binding to chromium(III) and mercury(II) ions with different outputs in methanol and aqueous solution. An enhancement of the fluorescence of the sensor was observed in the presence of chromium(III) ions in methanol while quenching was observed upon the addition mercury(II) ions. Further studies are underway to determine the exact nature of the emitting state and the sensor–metal interactions.

Experimental

Organic chemicals were determined from Sigma-Aldrich (Darmstadt, Germany), while metal salts and solvents were obtained from BDH and/or Panreac (Barcelona, Spain). Materials were used as received from the commercial suppliers and without any further purification except where noted. Thin layer chromatography was carried out using Merck 60 F_{254} plates and flash

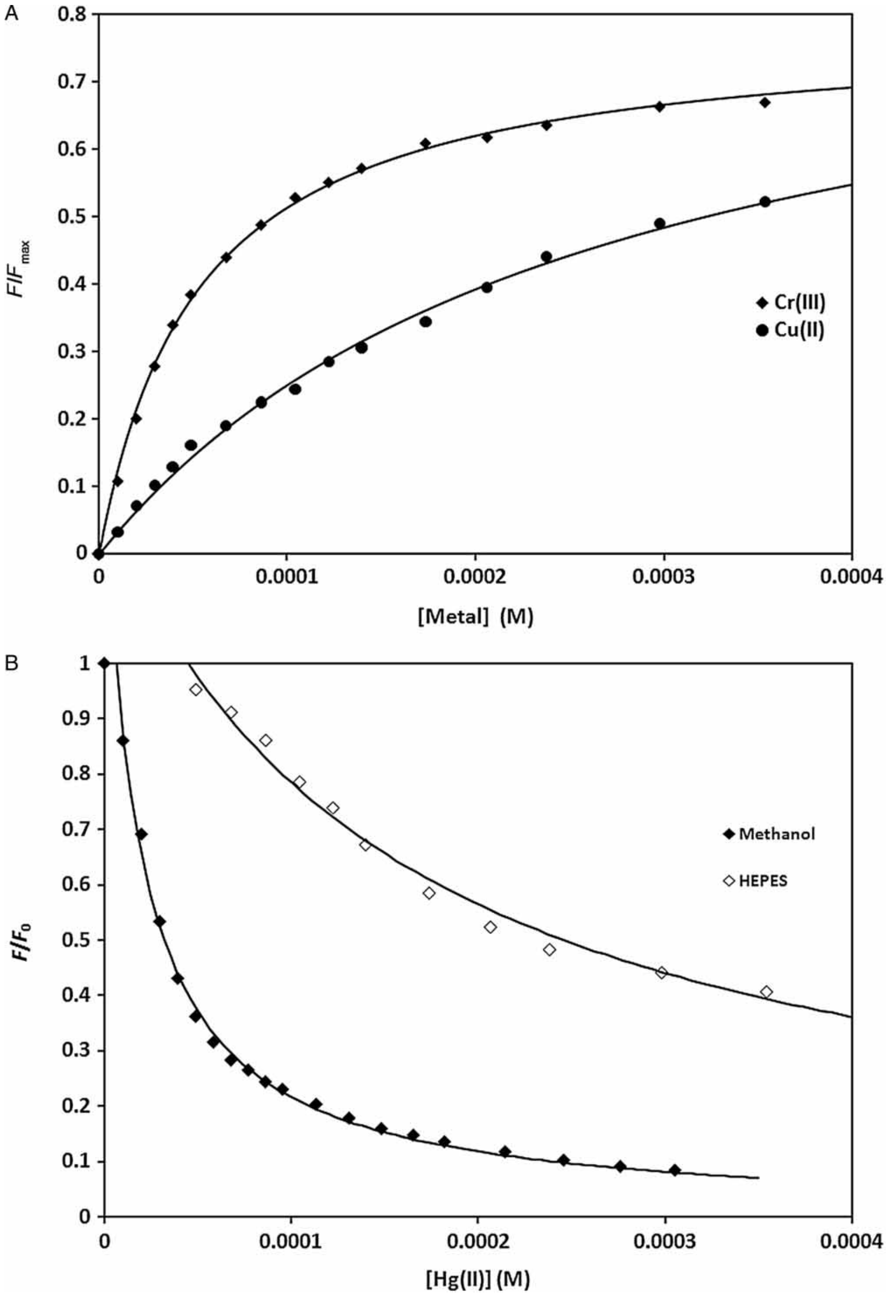


Figure 6. (A) Binding isotherms of **1** with Cr(III) (◆) and Cu(II) (●) and the theoretical binding model fit (—) for each. (B) Reverse Stern–Volmer plot for the binding of **1** with Hg(II) in methanol (◆) and HEPES (10 mM) solution (◇). The solid line is the fit of the binding model.

chromatography carried out on silica gel 60 (230–400 mesh; Merck, Darmstadt, Germany).

Uncorrected melting points were measured using a Buchi 530 melting point apparatus, and ^{1}H NMR spectra were recorded using a Varian 300 spectrometer while ^{13}C NMR spectra were recorded using a Bruker 500 spectrometer. Chemical shifts were expressed in parts per million, using solvent residuals as internal standard. Mass spectra were obtained using Agilent ESI-TOF Mass Spectrometer. Fluorescence studies were conducted using Varian Eclipse (Varian, Inc., Mulgrave, Australia) and the absorption studies were conducted on Varian Cary 50 (Varian, Inc.).

N-*(4-aminophenyl)-5-(dimethylamino)naphthalene-1-sulphonamide (1)*

To a solution of 4-nitroaniline (70 mg, 0.5 mmol) in pyridine/CH_2Cl_2 (1 ml/20 ml) solvent mixture, dansyl chloride (135 mg, 0.5 mmol) was added and the mixture was stirred at room temperature for 12 h. The mixture was then washed with $NaHCO_3$ (2×10 ml), water (1×10 ml) and brine (1×10 ml). After drying over Na_2SO_4, the solvent was evaporated under vacuum to leave a yellow residue. The solid residue was taken in ethanol (20 ml) and Pd/C (50 mg, 5%) was added followed by aqueous hydrazine solution (1 ml, 35%). The mixture was heated under reflux for 2 h. The hot solvent was then filtered through celite and the celite was further washed with hot ethanol (2×10 ml). The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography (silica, EtOAc/hexane 1:1) to afford **1** a yellowish solid (116 mg, 68%). Mp = 126–127°C. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.432 (d, $J = 8.1$ Hz, 1H), 8.279 (d, $J = 8.1$ Hz, 1H), 7.969 (d, $J = 6.9$ Hz, 1H), 7.519 (t, $J = 7.8$ Hz, 1H), 7.334 (t, $J = 7.8$ Hz, 1H), 7.141 (d, $J = 7.5$ Hz, 1H), 6.783 (s, 1H), 6.570 (d, $J = 8.4$ Hz, 2H), 6.339 (d, $J = 8.4$ Hz, 2H), 3.542 (bs, 2H), 2.826 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.3, 145.4, 134.3, 129.9, 126.7, 123.4, 118.7, 115.5, 115.3, 45.6; HR-MS ESI-TOF *m/z* 342.1282 $[M + H]^+$, calculated for $C_{18}H_{20}N_3O_2S$ 342.1271; 364.1079, $[M + Na]^+$, calculated for $C_{18}H_{19}N_3O_2SNa$ 364.1091.

Fluorescence titration procedure

A stock solution of **1** (2 mM, 1 ml) in methanol was added into a 1 × 1 cm cuvette containing either methanol or HEPES solution (10 mM) to make 50 μM solution of the sensor. This solution was then titrated with a solution of the metal (2 mM, methanol). Aliquot amounts of the metal solutions of nitrate salts of Cr(III), Fe(III), Co(II), Zn(II), Cu(II), Ni(II) and Pb(II), the chloride salt of Cd(II) and the acetate salt of Hg(II) were added to the cuvette via a syringe until a total of 10 equivalents of the metal had been added. (Control experiments with sodium chloride and sodium acetate solutions showed that there was no counterion effect). The number of additions was around 20 with an increase in the amount of metal solution added and the experiments were repeated in triplicates. The emission spectrum ($\lambda_{ex} = 335$ nm) was scanned after each addition using Varian Eclipse (Varian, Inc.) spectrometer. The collected data were fitted to the binding models (*21–23*) using Kaleidagraph®.

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