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# A quinoline-based turn-off fluorescent cation sensort

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A quinoline-based cation sensor shows turn-off fluorescent behavior in the presence of  $Hg^{2+}$ ,  $Fe^{3+}$  and  $Cu^{2+}$  over other cations and offers discrimination of these cations from each other on the basis of the extent of quenching. The observed electronic absorption perturbations are in good agreement with theoretical (DFT, TD-DFT) calculations.

Development of functional chemosensors for the detection and quantification of important physiological and environmental analytes such as Hg2+, Cu2+ and related cations has received increased interest in recent years.1 Effective operational usage of these chemosensors requires their high sensitivity and selectivity towards the analytes. Although a large variety of highly selective<sup>2</sup> single as well as multianalyte chemosensors<sup>3</sup> have been reported, the development of sensors for multianalyte detection in real time is still a challenge. With this aim, the emphasis in recent years has been placed on the development of optically responsive sensors for the detection of analytes. The use of fluorescence as the signal transducing method in optical sensors offers distinct advantages in terms of sensitivity, selectivity and response time.<sup>4</sup> Consequently, fluorescent molecular sensors have attracted considerable recent interest.5 Moreover, the development of fluorescent sensors for transition metals is of increasing importance for biological and environmental applications. In continuation of our interest in the development of chemosensors and chemodosimeters,6 herein we report a quinoline-based turnoff fluorescent cation sensor 5 (Scheme 1) which additionally discriminates between the detected cations by differential fluorescence emission quenching. The quinoline-based sensing reported so far is mainly based on dynamic and/or static

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quenching processes in the presence of analytes. Receptor 5 was synthesized<sup>7</sup> by following the steps described in Scheme 1 and was fully characterized using different spectroscopic techniques (S1, ESI<sup>†</sup>) before use.

Our preliminary investigation revealed that the emission (Fig. 1) as well as absorption spectra (Fig. S1, ESI<sup>†</sup>) of 5 were perturbed only in the presence of Fe<sup>3+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup> and not by the other cations, which led us to quantify the results for these three ions only. The fluorescence emission spectrum ( $\lambda_{ex} = 330$  nm) of 5 (30 µM in CH<sub>3</sub>OH) exhibits an emission band at 376 nm. The calculated quantum yield is 0.024 (ESI<sup>†</sup>) which is relatively low compared to the usual values.

The incremental addition of  $Hg^{2+}$ ,  $Fe^{3+}$  and  $Cu^{2+}$  solutions (0– 1.0 equiv. in distilled  $H_2O$ ) caused 69–94% quenching of the emission which was stabilized when the addition of 1 equiv. of the cation was achieved (Fig. 2a, Table 1). No significant change in the position of the emission maximum was observed up to the addition of 1 equiv. of  $Hg^{2+}$  as depicted in Fig. 2(a). (For the fluorescence spectra upon addition of 0–1.5 equiv. see Fig. S2†). Furthermore, a Job plot suggested 1 : 1 stoichiometry where the maximum emission change was observed when the mole fraction of 5 *versus* the cation was 0.5 in each case (Fig. 2b, Fig. S2†). The



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Fig. 1 Fluorescence intensities of 5 (30  $\mu$ M) in CH<sub>3</sub>OH upon addition of different metal ions (60  $\mu$ M) in distilled H<sub>2</sub>O ( $\lambda_{ex}$  = 330 nm) at pH 7.4.

detection limits (DL) for Fe<sup>3+</sup>, Hg<sup>2+</sup> and Cu<sup>2+</sup> ions using 5 were determined from the calibration curves of absorbance *versus* composition and were found to be  $9.24 \times 10^{-5}$  M,  $2.94 \times 10^{-4}$  M and  $4.17 \times 10^{-4}$  M, respectively.<sup>8</sup> During competition experiments under similar experimental conditions, no interference from other metal ions was observed (Fig. 3, Fig. S3<sup>†</sup>). Further, the sensing event was reversed upon addition of CN<sup>-</sup>, which snatches away the metal ions from 5, forming the metal cyanide complexes (Fig. 4).<sup>9</sup>

Stern–Volmer plots were created for the titration of these cations (Fig. 5). Typically, Stern–Volmer plots are linear for dynamic (collisional) quenching which occurs when the excited fluorophore experiences interaction with an atom or molecule which can facilitate non-radiative transitions to the ground state, and for static quenching due to the formation of a non-fluorescent stable complex with a quencher. They deviate from linearity when



**Fig. 2** (a) Fluorescence spectra of **5** (30  $\mu$ M) in CH<sub>3</sub>OH upon addition of Hg<sup>2+</sup> (0–1.0 equiv.) in distilled H<sub>2</sub>O ( $\lambda_{ex}$  = 330 nm) at pH 7.4 (for 0–1.5 equiv. see Fig. S2t); (b) Job plot of Hg<sup>2+</sup> complex formation,  $x = [5]/[5] + [Hg^{2+}]$  is the mole fraction of **5**,  $F_0$  is the fluorescence intensity when x = 1 and F is the fluorescence intensity at respective values of x (for Fe<sup>3+</sup> and Cu<sup>2+</sup> titration profiles for 0–1.5 equiv., see Fig. S2t).

CompoundFluorescence qua	antum yield <sup><i>a</i></sup> $\Phi\%$	Fluorescence c	uenching <sup><i>b</i>, <i>c</i></sup>
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5	0.024	_
5:Fe <sup>3+</sup>	0.002	94 (94)
5:Hg <sup>2+</sup>	0.003	87 (92)
5:Cu <sup>2+</sup>	0.004	69 (80)

<sup>*a*</sup> Quinine sulfate was used as standard with a quantum yield of 0.55 in 0.1 N  $H_2SO_4$  at  $\lambda_{ex}$  = 320 nm. <sup>*b*</sup> Calculated at 1 equiv. of metal ions. <sup>*c*</sup> Values in parentheses correspond to 1.5 equiv. of metal ions.

both of these quenching mechanisms operate in combination. The non-linear nature of the Stern–Volmer plot with an upward curvature (Fig. 5) indicates the possible involvement of combined dynamic and static quenching.<sup>10</sup> However, it is interesting to note that the degree of quenching is large for  $Fe^{3+}$  followed by  $Hg^{2+}$  and lower for  $Cu^{2+}$ , which is important for discriminating these cations from each other (Fig. 5). A similar type of Stern–Volmer plot behaviour has been reported by Giri *et al.*<sup>11</sup> for fluorescein, rhodamine 6G and quinine sulfate in the presence of single walled carbon nanotubes.

The UV-vis absorption spectrum of 5 exhibited bands at 330 nm ( $\varepsilon_{max}$  15 733 L mol<sup>-1</sup> cm<sup>-1</sup>) and 255 nm ( $\varepsilon_{max}$  46 433 L mol<sup>-1</sup> cm<sup>-1</sup>) (Fig. 6, Fig. S4†). Addition of aqueous solutions of Hg<sup>2+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> ions (0–1.5 equiv., as ClO<sub>4</sub><sup>-</sup> salts) to a solution of 5 (30  $\mu$ M in CH<sub>3</sub>OH) resulted in the appearance of twin absorption bands at 330 and 343 nm with increased variable intensities [330 nm:  $\varepsilon_{max}$  21 633 L mol<sup>-1</sup> cm<sup>-1</sup> (Hg<sup>2+</sup>), 24 566 L mol<sup>-1</sup> cm<sup>-1</sup> (Fe<sup>3+</sup>), 22 433 L mol<sup>-1</sup> cm<sup>-1</sup> (Cu<sup>2+</sup>); 343 nm:  $\varepsilon_{max}$  20 126 L mol<sup>-1</sup> cm<sup>-1</sup> (Hg<sup>2+</sup>), 24 194 L mol<sup>-1</sup> cm<sup>-1</sup> (Fe<sup>3+</sup>), 19 393 L mol<sup>-1</sup> cm<sup>-1</sup> (Cu<sup>2+</sup>)]. The high energy band at 255 nm was not perturbed significantly other than some broadening. Fitting the titration data using HypSpec, a non-linear least squares fitting programme,<sup>12</sup> established the1 : 1 stoichiometry of the most stable species present in the solution with binding constant values, log  $\beta_{1,1} = 5.20$  (Fe<sup>3+</sup>), 4.69 (Hg<sup>2+</sup>) and 4.45 (Cu<sup>2+</sup>), respectively.

In order to understand the nature of these transitions in terms of the participation of different frontier orbitals in the observed electronic changes, we carried out TD-DFT calculations for 5 and  $5:M^{n+}$  using the Gaussian 09 suite of programs.<sup>13</sup> The best



**Fig. 3** Changes in the fluorescence intensity of **5** (30  $\mu$ M) in CH<sub>3</sub>OH at 376 nm upon titration with increasing concentration of Hg<sup>2+</sup> (5, 15 and 30  $\mu$ M) in distilled H<sub>2</sub>O, in the presence of other metal ions (30  $\mu$ M) in distilled H<sub>2</sub>O at pH 7.4.





Fig. 6 Changes in the UV-vis absorption spectra of 5 (30  $\mu$ M) in CH<sub>3</sub>OH and its complexes with Fe<sup>3+</sup> (32  $\mu$ M), Hg<sup>2+</sup> (35  $\mu$ M) and Cu<sup>2+</sup> (40  $\mu$ M) in distilled H<sub>2</sub>O at pH 7.4.

Fig. 4 Changes in the fluorescence spectra of metal complexes (5:Fe<sup>3+</sup>, 5:Hg<sup>2+</sup> and 5:Cu<sup>2+</sup>) in the presence of CN<sup>-</sup> (60  $\mu$ M) in distilled H<sub>2</sub>O.

optimized structures are shown in Fig. S5<sup>†</sup>. The TD-DFT calculations (Table S1<sup>†</sup>) predict that the low energy band of 5 has a main contribution from the  $H \longrightarrow L + 1$  transition and these orbitals are located on the quinoline part of 5 with some contribution from the  $H \rightarrow L$  transition (Fig. 7). The high energy band at 255 nm has contributions from the H  $\rightarrow$  L + 3, H - 2  $\rightarrow$  L + 2, H - 4  $\rightarrow$  L + 2, H - 4  $\rightarrow$  L, H - 7  $\rightarrow$  L + 3 transitions (Table S1<sup>†</sup>). In the case of 5:Hg<sup>2+</sup>, the twin absorption band has contributions from the  $H \rightarrow L + 1$  and  $H \rightarrow L + 2$  transitions (Table S2<sup>†</sup>). As shown in Fig. 7, we noticed that on interaction with  $Hg^{2+}$ , the HOMO (located on quinoline) was stabilized ( $\Delta E 0.14 \text{ eV}$ ) in comparison to 5 and the L + 1 was raised in energy to a very small extent ( $\Delta E$  0.03 eV). This suggests that the interaction of Hg<sup>2+</sup> with the quinoline part of the molecule is responsible for the quenching of the fluorescence emission. On the other hand, in the case of Cu<sup>2+</sup>, of the twin absorptions at 330 and 343 nm, the high energy dominating absorption band is suggested to have a main



Fig. 5 Stern–Volmer plots for  $M^{n+}$ , where  $M^{n+} = Fe^{3+}$ ,  $Hq^{2+}$ , and  $Cu^{2+}$ .

contribution from the H  $\rightarrow$  L + 3 transition (Fig. 7, Table S3†). Although the HOMO in this case is more stabilized ( $\Delta E 0.76 \text{ eV}$ ) as compared to 5:Hg<sup>2+</sup> (Fig. 7), the close values of the appropriate HOMO-LUMO gap ( $\Delta E_2$ ,  $\Delta E_3$  and  $\Delta E_4$ ) corroborate the calculated binding constant values of the complexes of Hg<sup>2+</sup> and Cu<sup>2+</sup> with 5. DFT calculations on the 5:Fe<sup>3+</sup> system did not yield reproducible results.

#### Conclusions

In conclusion, the present study demonstrates that the quinolinebased chemosensor detects  $Hg^{2+}$ ,  $Fe^{3+}$  and  $Cu^{2+}$  through fluorescence quenching to different extents which is helpful in discriminating these cations from each other. Dynamic and static quenching mechanisms have been proposed to operate in combination. The perturbation in the electronic behaviour of **5** 



Fig. 7 Energy level diagrams of HOMO (H) and LUMO (L) orbitals (isovalue 0.02) of 5,  $5:Hg^{2+}$  and  $5:Cu^{2+}$  calculated at the DFT level (for optimized structures of 5,  $5:Hg^{2+}$  and  $5:Cu^{2+}$  see Fig. S5†).

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