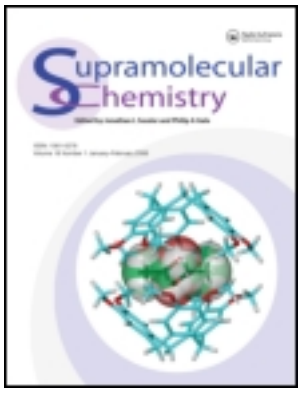

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Selective sensing of Cu (II) by a simple anthracene-based tripodal chemosensor

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Selective sensing of Cu (II) by a simple anthracene-based tripodal chemosensor

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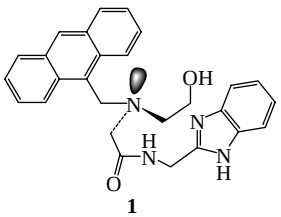
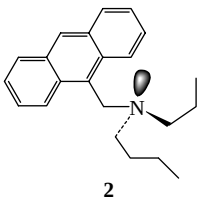
A new and an easy-to-make simple tripodal shaped chemosensor **1** has been designed and synthesised for metal ions. In CH_3CN containing 0.04% DMSO, upon excitation at 370 nm, chemosensor **1** exhibited structured emission centred at 418 nm, which increased to a significant extent upon complexation of Cu (II). The other metal ions except Zn^{2+} and Hg^{2+} examined in this study did not exhibit any marked change in emission of **1** under a similar condition. Although Cu^{2+} ion showed strong interaction with **1**, Zn^{2+} and Hg^{2+} ions exhibited moderate binding.

Keywords: anthracene-based sensor; benzimidazole-based chemosensor; Cu (II), Zn (II) and Hg (II) metal ion recognition; fluorescence enhancement

The development of fluorescent chemosensors capable of selective recognition of metal ions is an active field of research in supramolecular chemistry (*1*). Among the heavy metal ions in the human body, copper ion is the third in abundance after Fe^{2+} and Zn^{2+} ions and, thus, draws significant attention for its recognition (*2*). Copper plays a pivotal role in a variety of fundamental physiological processes in organisms ranging from bacteria to mammals. This metal ion causes environmental pollution and also serves as a catalytic cofactor for a variety of metalloenzymes (*3*). However, exposure to high levels of copper, even for a short period of time, can cause gastrointestinal disturbance, whereas long-term exposure can lead to liver or kidney damage (*4*). Thus, a number of fluorescent sensors for Cu^{2+} have been synthesised and reported (*2*). In major cases, Cu^{2+}-induced fluorescence quenching is observed. But the fluorescent chemosensors that display fluorescence enhancements upon addition of Cu^{2+} ion are very few in numbers (*5*, *2k*). In this context, in continuation of our previous work (*6*), we report, here, the synthesis and the metal binding studies of a simple and easy-to-make receptor **1** that shows selective sensing of Cu^{2+} by exhibiting significant enhancement in emission of CH_3CN containing 0.04% DMSO. Although Cu^{2+} ion showed strong interaction with **1**, other important cations such as Zn^{2+} and Hg^{2+} ions exhibited moderate binding.



1



2

Sensing of Hg^{2+} and Zn^{2+} is also equally important like Cu^{2+}. Hg^{2+} is a well-known pollutant. Its exposure to human body can lead to neurological diseases (*7a*,*b*). On the other hand, zinc ion is an abundant component in the human body and plays an important role in various fundamental biological processes, such as gene transcription, regulation of metalloenzymes, mammalian reproduction and neural signal transmission (*7c*). Therefore, sensing of such multiple metal ions by a single chemosensor is attractive. The present example in this article belongs to this class, although chemosensor **1** is more effective in sensing Cu^{2+}.

Chemosensor **1** was synthesised according to Scheme 1. Our previously reported 4-anthracenyl substituted morpholin-2-one **5** (*6*) was subjected to the reaction with amine **8** which was obtained starting from Boc-protected glycine after performing a series of reactions as mentioned in Scheme 1(b). Compound **2** was obtained according to our previously reported method (*6*). All the compounds were characterised by ^{1}H NMR, ^{13}C NMR, FTIR and mass analysis (supporting data).

The ability of chemosensor **1** towards sensing of different metal ions was investigated in CH_3CN containing 0.04% DMSO using fluorescence and UV–vis spectroscopic tools. Additionally, ^{1}H NMR was studied in $CDCl_3$ containing DMSO to understand the nature of interaction in the binding site.

Figure 1 shows the change in emission of **1** in the presence of 15 equiv. amounts of the different metal ions in CH_3CN containing 0.04% DMSO on excitation at 370 nm. It is evident from Figure 1 that the receptor is more sensitive to Cu^{2+} ion. Other metal ions except Zn^{2+} and Hg^{2+} merely perturbed the emission of **1**. Upon gradual

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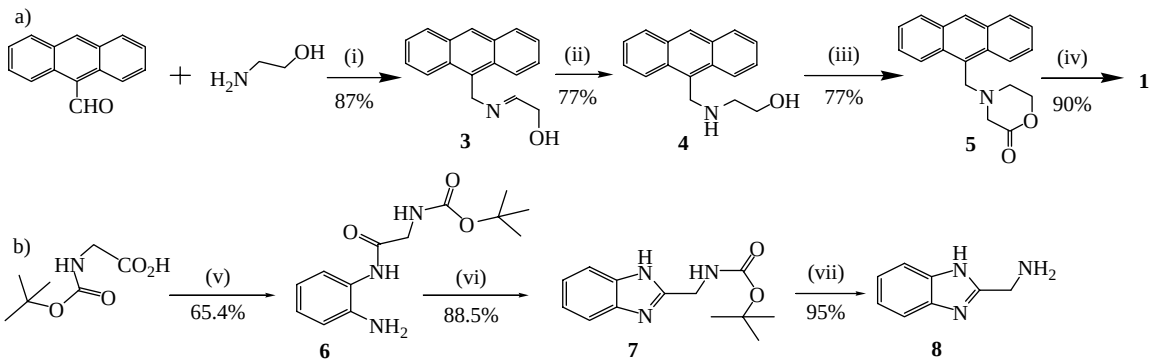

Scheme 1. Reagents and conditions: (a) – (i) Dry MeOH, reflux, 9 h; (ii) $NaBH_4$, dry MeOH, reflux, 3 h; (iii) ethyl 2-chloroethanoate, K_2CO_3, dry Me_2CO, reflux, 7 h; (iv) amine **8**, THF, stirring, 4 h; (b) – (v) *o*-phenylenediamine, DCC, DMAP, stirred in CH_2Cl_2 for 19 h; (vi) AcOH, heat, 2 h and (vii) 50% TFA in CH_2Cl_2, stirred for 3 h.

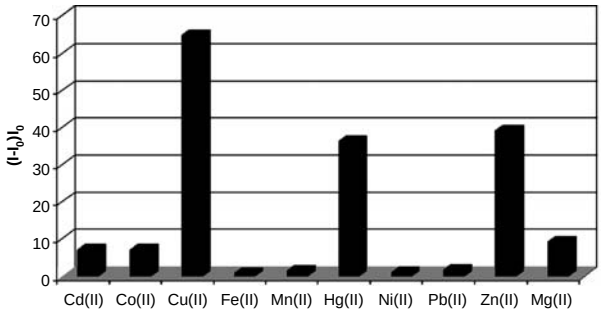

Figure 1. Change in fluorescence ratio of **1** ($c = 4.10 \times 10^{-5}$ M) upon addition of 15 equiv. amounts of cations at 418 nm.

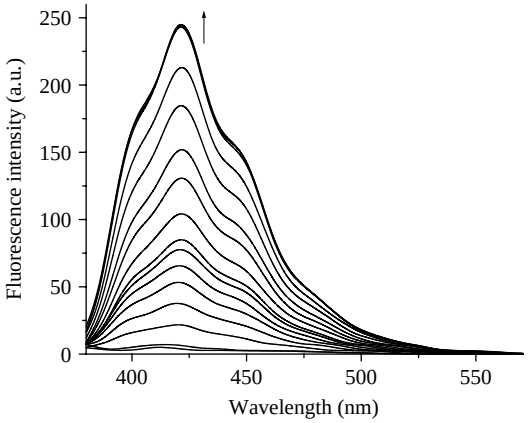

Figure 2. Change in emission of **1** ($c = 4.10 \times 10^{-5}$ M) upon gradual addition of $Cu(ClO_4)_2$.

addition of $Cu(ClO_4)_2$ solution to the solution of **1** ($c = 4.10 \times 10^{-5}$ M) in CH_3CN containing 0.04% DMSO, the structured emission centred at 418 nm increased to the significant extent without showing any other change in the emission spectra. During progression of titration, a red shift of 3 nm of the emission peak at 418 nm was observed. Figure 2, in this regard, shows the change in emission titration spectra with Cu^{2+} ions. Other metal ions except Zn^{2+} and Hg^{2+} revealed relatively insignificant responses in this region, manifesting the pronounced OFF–ON type of Cu^{2+} selectivity of **1**. In this connection, it is well known that Cu^{2+} is a paramagnetic ion with an unfilled d-shell and could strongly quench the emission of the fluorophore near it *via* electron or energy transfer. But in our case, the enhancement of emission of **1** after binding of Cu^{2+} ion is quite interesting and mentionable along with other few related existing systems (*5*, *2k*,*n*). To our opinion, such significant change in emission of **1** in the presence of Cu^{2+} is attributed to the better coordination of Cu^{2+} by aliphatic amine nitrogen, benzimidazole ring nitrogen and amide, alcohol functionalities in the open cavity for which either the change in geometry or the flexibility of the molecule is reduced. The consequence of which the metal–fluorophore interaction is modulated (*5a*,*b*) and the photo-induced electron transfer (PET) from the binding sites to the excited state of anthracene is inhibited. In this context, the role of amide carbonyl as blocking moiety for PET cannot be ruled out (*8a–c*). This is also true for Zn^{2+} and Hg^{2+} ions. The difference is in only lying with the extent of change. We believe that it is due to the difference in coordinating ability of the binding site towards Cu^{2+}, Zn^{2+} and Hg^{2+}.

In the interaction process, the stoichiometry of the Cu-complex, Zn-complex and Hg-complexes was found to be 1:1, as evident from the break of the titration curve (Figure 3) and also job plots (*9*) (Figure 4 for Cu^{2+} and see supporting data for Zn^{2+} and Hg^{2+}). From the titration data, association constants (K_a) for the formation of **1**-Cu^{2+} and **1**-Hg^{2+} complexes were estimated by the nonlinear curve-fitting procedure (*10*) and found to be $(7.16 \pm 0.473) \times 10^3\,M^{-1}$ and $(5.67 \pm 0.88) \times 10^2\,M^{-1}$, respectively. We were unable to fit the titration data for Zn^{2+} by the nonlinear curve-fit method to determine the binding constant value. In addition, we determined the

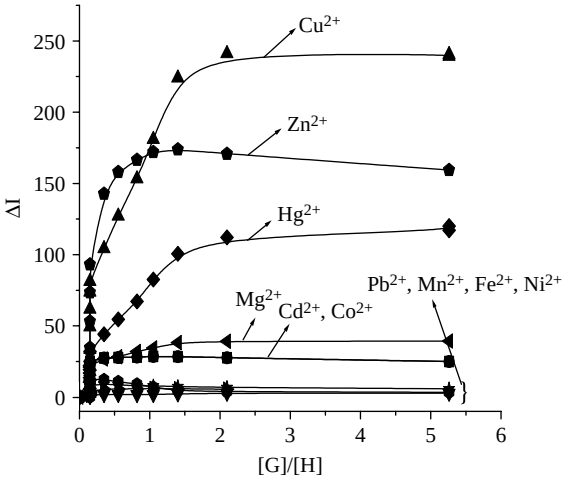

Figure 3. Fluorescence titration curves ([guest]/[host] vs. change in emission) of **1** ($c = 4.10 \times 10^{-5}$ M) measured at 418 nm in CH_3CN containing 0.04% DMSO.

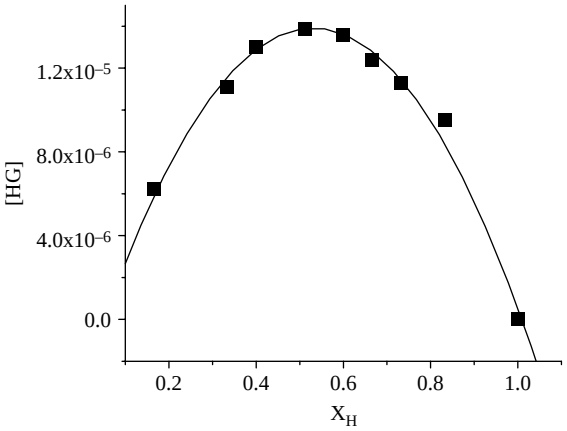

Figure 4. UV–vis job plot for receptor **1** ([H] = [G] = 4.45×10^{-5} M) with Cu^{2+} at 365 nm.

fluorescence enhancement factor[1](relative indicator of binding strength) of **1** at an emission of 418 nm in the presence of 15 equiv. amounts of each metal ion in CH_3CN containing 0.04% DMSO to realise the selectivity in the binding process. Figure 5, in this regard, shows the plot of fluorescence enhancement factor (*Z*) in the presence of different cations. From the plot, it is evident that the response of the simple sensor **1** towards Cu^{2+} is significant and also selective over Zn^{2+} and Hg^{2+} ions. In relation to this, we established earlier that compound **2**(*6*) was incapable of showing sensing selectivity towards the same metal ions and explained the necessity of the presence of proper functionalities around the tripodal nitrogen centre of **2**.

However, to comprehend the selectivity in the sensing of Cu^{2+} by **1**, we recorded emission spectra of **1** upon

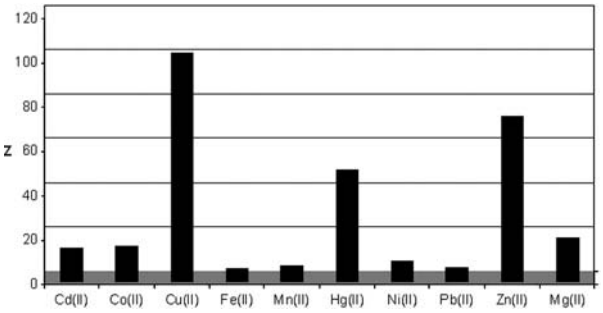

Figure 5. Fluorescence enhancement factor (*Z*) of receptor **1** ($c = 4.10 \times 10^{-5}$ M) upon addition of 15 equiv. amounts of various metal ions.

adding 5 equiv. amounts of Cu^{2+} in the presence of 5 equiv. amounts of other metal ions, examined in this study. Figure 6 displays the relative view on the change in emission of **1** in the presence of Cu^{2+} when the other metal ions are absent and present in the receptor solution. Small increase in emission upon addition of Cu^{2+} to the solution of **1** containing other metal ions (Figure 6) demonstrates the lower selectivity in the binding process. When the same experiment was done in the absence of Zn^{2+} and Hg^{2+} ions, a better increase in emission of **1** was noted (supporting data). This underlined the fact that both Zn^{2+} and Hg^{2+} ions interfere in the binding of Cu^{2+} towards the binding site of **1**.

Furthermore, to investigate the effect of the counter anion of copper salt in the binding process, change in emission of **1** in CH_3CN containing 0.04% DMSO was recorded upon gradual addition of $Cu(NO_3)_2$ solution (supporting data). It was noted that the change in emission of **1** upon addition of $Cu(NO_3)_2$ was identical to that of $Cu(ClO_4)_2$. This experimental finding reveals that in the binding of Cu^{2+} into the tripodal core of **1**, the counter anion has no effect.

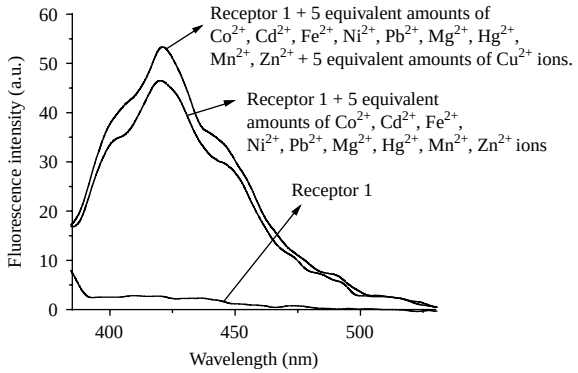

Figure 6. Change in emission of receptor **1** ($c = 4.10 \times 10^{-5}$ M) upon addition of Cu^{2+} in the presence of other metal ions.

To get insight into the enhancement of emission behaviour in the **1**-Cu^{2+} complex, we investigated the fluorescence decay behaviour of **1** itself and in the presence of equivalent amount of Cu^{2+} ion (Figure 7). Table 1 summarises the exponential fit results. Compound **1** ($c = 4.10 \times 10^{-5}$ M) exhibited a triexponential fluorescence decay. Upon addition of equivalent amount of Cu^{2+} ($c = 8.21 \times 10^{-4}$ M), while the fast decay components were less affected, the time constant (τ_2) of the lifetime decay component was greatly affected and contributed to the total emission with a larger pre-exponential factor.

Furthermore, we investigated the interaction of **1** with the metal ions in aqueous CH_3CN, and no characteristic change in emission was observed (supporting data). In relation to this, we also noticed the interaction of **1** in more polar non-aqueous solvent such as DMSO. Interestingly, the light red coloured solution of **1** in DMSO ($c = 2.2 \times 10^{-3}$ M) was discharged in the presence of $Cu(ClO_4)_2$ and resulted in light green colour of the solution. Other metal ions did not bring any detectable colour change in the solution of **1**. The appearance of colour upon complexation of Cu^{2+} in DMSO is presumably attributed to the charge transfer occurring in between the benzimidazole ligand and metal ion. It is noteworthy that this change in colour is pronounced in the high concentration level of **1** ($\sim 10^{-3}$ M) (Figure 8). At a concentration level $\sim 10^{-5}$ M of **1**, no change in colour was noticeable. However, at the concentration range $\sim 10^{-3}$ M of **1**, we carried out the fluorescence titration upon gradual addition of Cu^{2+} ion (supporting data). It is mentionable that the Cu^{2+}-induced change in emission of **1** was less than the change in CH_3CN containing 0.04% DMSO and thereby demonstrated the role of polar solvent in the interaction process. DMSO being more polar than CH_3CN reduces the interaction of Cu^{2+} at the tripodal core of **1**. Similar is the case with Zn^{2+} and Hg^{2+} (supporting data).

The UV–vis study of **1** in the presence of all the metal ions except Cu^{2+}, under similar conditions, showed minor change in absorbance (supporting data). For example, Figure 9 shows the change in absorbance upon gradual addition of Cu^{2+}. During the interaction, a small red shift ($\Delta\lambda = 5$ nm) of the absorption peak for anthracene

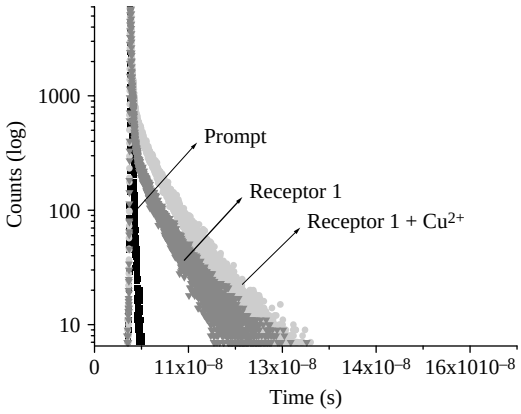

Figure 7. Fluorescence decays (at $\lambda_{max} = 418$ nm) of receptor **1** upon addition of 1 equiv. of $Cu(ClO_4)_2$ ([H] $= 4.10 \times 10^{-5}$ M, [G] $= 8.21 \times 10^{-4}$ M) in CH_3CN containing 0.04% DMSO.

Table 1. Fluorescence decay times (τ) and pre-exponential factors (a) for **1** and **1**-Cu^{2+} in CH_3CN containing 0.04% DMSO.

Compound **1** and its complex with Cu^{2+}	τ_1 ns (a_1)	τ_2 ns (a_2)	τ_3 ns (a_3)	χ^2
1	0.916 (11.40)	4.53 (46.58)	0.035 (42.03)	1.00
1 + Cu^{+2} (1:1)	0.967 (8.30)	6.24 (76.63)	0.043 (15.07)	0.997

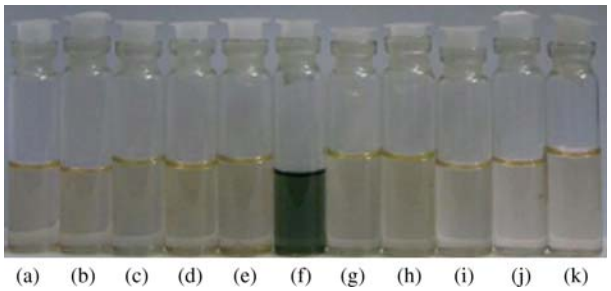

Figure 8. Change in colour of **1** ($c = 2.2 \times 10^{-3}$ M) upon addition of 10 equiv. amounts of different metal ions ($c = 8.9 \times 10^{-4}$ M) in DMSO: (a) receptor **1** with (b) Ni^{2+}, (c) Mn^{2+}, (d) Co^{2+}, (e) Cd^{2+}, (f) Cu^{2+}, (g) Mg^{2+}, (h) Fe^{2+}, (i) Zn^{2+}, (j) Hg^{2+} and (k) Pb^{2+}.

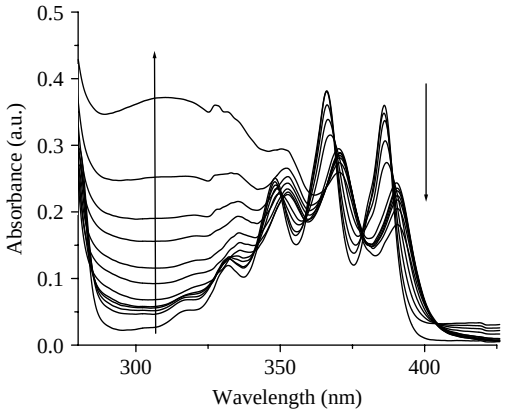

Figure 9. Change in absorbance of **1** ($c = 4.10 \times 10^{-5}$ M) upon gradual addition of Cu^{2+} ion.

occurred. Decrease in absorption with significant red shift of **1** with Cu^{2+} is presumably due to cation–π interaction when the metal ion interacts in the tripodal core of **1** in a 1:1 stoichiometric fashion under the guidance of alcohol, amide and benzimidazole groups. The metal coordination property of benzimidazole as well as 2-substituted benzimidazole is well established (*11*). It is worth mentioning that the 2-benzimidazole derivatives allow coordination towards metal ions through a variety of sites, with groups bearing nitrogen, oxygen and sulphur atoms, and the coordination takes place through imidazolic nitrogen (*11*). This enables us to presume a binding mode (Figure 10), where the metal ion is anchored at the tripodal core involving the benzimidazole ring nitrogen, aliphatic amine, amide and alcoholic groups altogether. This is clearly understood from the disposition of the binding moieties in AM1 optimised geometry of $\mathbf{1}^2$ (Figure 11). The Mulliken charge densities on the different centres are also shown in Figure 11. Closely spaced benzimidazole and anthracene moieties possibly partially shield the space in between them so that the metal ion (Cu^{2+})–fluorophore interaction is minimised, and the PET process from the binding site to the excited state of anthracene is blocked.

We further recorded the ^{1}H NMR of **1** in the presence of equivalent amount of Cu^{2+} ion in $CDCl_3$ containing 0.1% d_6-DMSO to be acquainted with the involvement of the binding site for complexation. But the NMR spectrum upon addition of Cu^{2+} ions resulted in broadening particularly for the resonances of the benzimidazolyl amide and alcoholic moieties of **1**. The anthracenyl ring protons of types 'b' and 'c' moved to the downfield direction by 0.02 ppm and other protons of types 'a' and 'd' were positionally unaffected. The benzimidazole ring protons of types 'e' and 'f' indicated a greater downfield chemical shift ($\Delta\delta = 0.20$ ppm). In addition, the signals for the methylene protons adjacent to the aliphatic amine

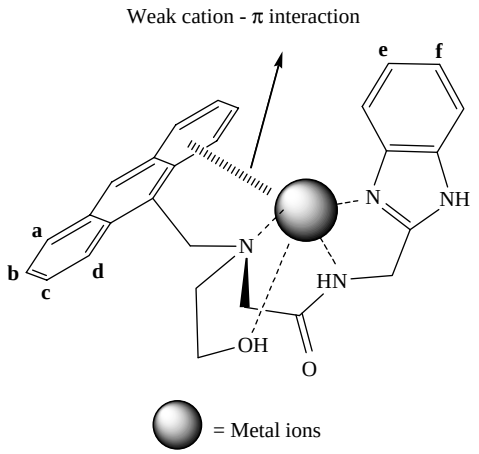

Figure 10. Suggested mode of binding of **1** for the metal ions.

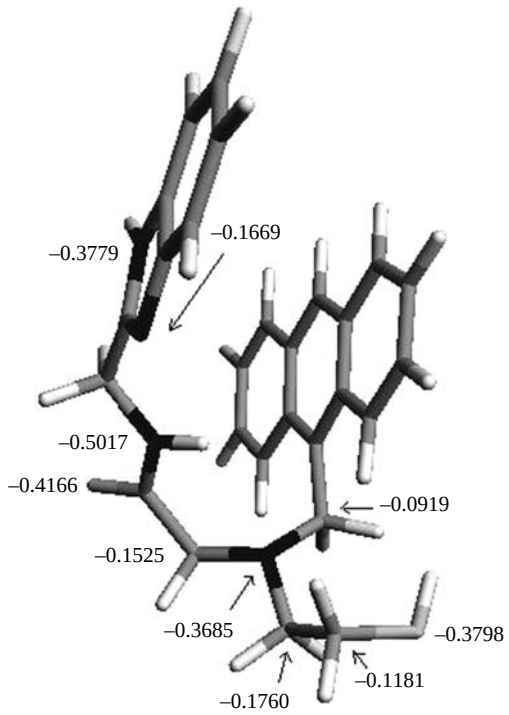

Figure 11. AM1 optimised geometry of **1** in gas phase ($E = -194.067$ au; the closest distance between anthracene and benzimidazole is 4.89 Å).

nitrogen underwent downfield movement by 0.04–0.06 ppm. This intimated the information that Cu^{2+} ion shows the preferential coordination at the aliphatic amine nitrogen centre involving the aid of benzimidazolyl amide and the alcoholic groups.

In conclusion, tripodal shaped compound **1**, comprising anthracene as fluorophore, benzimidazolyl amide, aliphatic amine and alcohol functionalities as binders/chelators, functions as a new chemosensor for Cu^{2+} in preference to a variety of other metal ions studied except Hg^{2+} and Zn^{2+} ions. Although the tripodal cavity of **1** preferentially binds Cu^{2+} ion, it shows moderate sensing behaviour towards Zn^{2+} and Hg^{2+} ions. Cu^{2+} ion binding induced significant enhancement of emission of **1** in CH_3CN containing 0.04% DMSO, and also the change in colour in pure DMSO upon complexation of Cu^{2+} is the insight into this study for selective sensing of Cu^{2+} by the new candidate **1**. Further study is underway in our laboratory.

Supporting data

Characterisation data of **1**, figures showing the change in absorption and fluorescence spectra and the job plots of receptor **1** in the presence of Zn^{2+} and Hg^{2+}, selectivity study in the absence of Zn^{2+} and Hg^{2+}, binding constant curve for **1** with Cu^{2+}, change in emission and absorption of **1** upon addition of $Cu(NO_3)_2$, change in fluorescence

ratio of **1**, change in emission in DMSO and details of the experiments are available online.

Acknowledgements

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Notes

(1) Fluorescence enhancement factor (Z) was calculated based on the equation $Z = (F/F_0)\ [(V_0 + V)/V_0]$ where $F =$ observed fluorescence, $F_0 =$ fluorescence of sample before guest addition, $V_0 =$ volume before addition of guest, $V =$ volume after addition of guest.

(2) AM1 calculation was performed using minimal valence basis as STO 3G in Argus Lab 4.0.1, copyright (c) 1972-2004 Mark Thompson and Planaria Software LLC, http://www.Arguslab.com.

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