

Fluorescent chemosensor for Cu²⁺ ion based on iminoanthryl appended calix[4]arene

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Abstract Calix[4]arene based podands **1a** of *cone* conformation and **1b** of 1,3-*alternate* conformation possessing imine units and bearing anthracene moieties have been synthesized by a 1 + 2 Schiff base condensation in good yields and examined for their cation recognition abilities towards cations such as lithium, sodium, potassium, nickel, cadmium, copper, zinc, lead, silver and mercury ions by UV–vis and fluorescence spectroscopy. The calix[4]arene derivative **1b** shows a selective fluorescence enhancement in presence of Cu²⁺ ions among the various metal ions tested (Li⁺, Na⁺, K⁺, Ni²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺ and Hg²⁺ ions). The colour of the solution changes from colourless to light yellow in the presence of Cu²⁺ ions. The stoichiometry of the complex formed between **1b** and Cu²⁺ was found to be 1:1 as established by Job's plot.

Keywords Sensor · Copper · Fluorescence · Calixarene · Imine

Introduction

Recently, there has been a lot of interest in the design and synthesis of functional molecules having optical sensing ability for different types of analytes [1–4]. Thus, a large number of optical sensors have been developed for the alkali and alkaline earth metal ions [5–7]. However, there are, relatively few examples of designed optical sensors for the copper, which is the third most abundant element (after Fe²⁺ and Zn²⁺) amongst essential heavy metal ions present

in human body. The selective signaling of copper ion is a very important topic for the detection and treatment of this ion in various chemical systems including living systems [8–11]. It plays an important role in fundamental physiological processes in organisms ranging from bacteria to mammals [8, 9]. However, copper can be toxic if the level exceeds cellular needs. It is also capable of displacing other metals which act as co-factors in enzyme-catalysed reactions [10, 11]. Thus, designing sensors for copper has recently drawn worldwide attention. In most of the fluorescent sensors reported for copper so far, the binding of the copper with the ionophore results in nonspecific fluorescence quenching via photo-induced electron transfer [12–20], however, fluoroionophores which undergo fluorescence enhancement as a result of metal-ion binding are preferred over those which show fluorescence quenching. Recently, some examples of fluoroionophores which undergo fluorescence enhancement upon binding with copper have been reported [21–23].

Calix[4]arenes with appropriately appended groups have been good candidates for cation and anion sensing [24–31]. There are some examples of calixarene based fluoroionophores [32] selective for alkali metal ions [33–42], TI⁺ [43], Hg²⁺ [44–46], Pb²⁺ [32, 47, 48], Co²⁺ [49], Ni²⁺ [49], Cd²⁺ [50], and Zn²⁺ [51, 52], respectively. Apart from this Liu et al. [53] reported a calix[4]arene based receptor with iminoanthracene appendage on the upper rim which undergoes fluorescence enhancement in the presence of Ca²⁺ ions. Gao et al. [54] reported an upper rim calix[4]arene salicylidene derivative as an effective fluorogenic sensor for Cu²⁺ ions. From our laboratory, we have also reported a number of calix[4]arene [55–57] and thiocalix[4]arene [58–60] based receptors possessing imine units at the lower rim which selectively interact with silver ions. Recently, Rao et al. reported calixpodands with imine units by condensation of

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O,O'-bis(2-aminoethyl)-*p-tert*-butylcalix[4]arene with 2-hydroxy-1-naphthaldehyde [51] and with 9-anthraldehyde [61]. It was found that these receptors bound Zn^{2+} ions by imino nitrogens and by the hydroxyl groups of the naphthalene moiety, while Cu^{2+} ions bind through imino nitrogens and through alkoxyphenyl oxygens, however, Fe^{2+} ion binds through the phenolic oxygens apart from the imino nitrogens and the alkoxyphenyl oxygens. Based on these reports, we planned to change the coordination environment by employing *O,O'*-bis(2-aminoethoxy)-*O',O''*-dipropoxy-*p-tert*-butylcalix[4]arene **2** of *cone* and **4** of 1,3-*alternate* conformation as a molecular scaffold for the preparation of calix[4]podands **1a** and **1b**, respectively. Preliminary studies on the complexation abilities of these calixpodands have shown that the modification actually changes the coordination sites and that calixpodand **1b** of 1,3-*alternate* conformation has selective fluorescent enhancement in the presence of Cu^{2+} ions, while calixpodand **1a** of *cone* conformation shows indiscriminate fluorescent enhancement in presence of all metal ions tested. While this work was in progress, Li et al. [62] reported a fluorescent sensor for Cu^{2+} ion based on calix[4]arene bearing imine units on the upper rim.

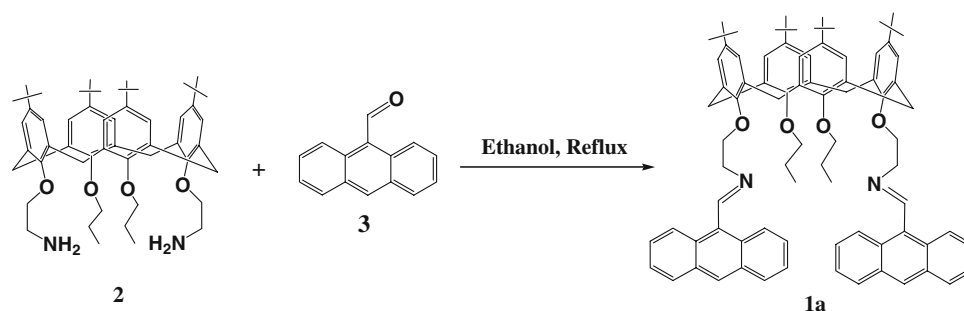
Result and discussions

Calix[4]arene based imino receptors **1a** (Scheme 1) and **1b** (Scheme 2) were synthesized from known precursors

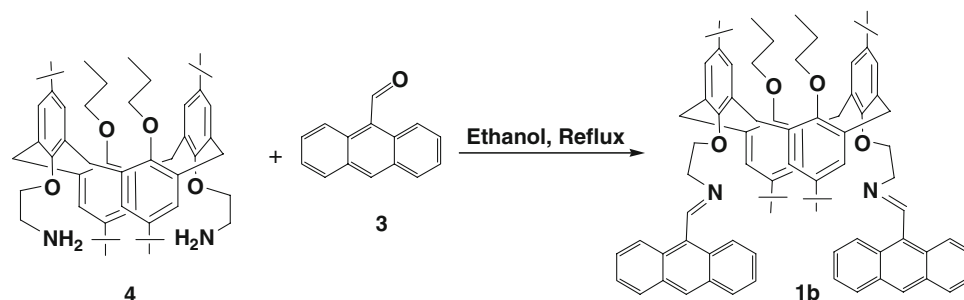
2 [63] and **4** [64], respectively. Condensation of calix-1,3-diamine **2** [63] of *cone* conformation, with 2.2 mol equiv of 9-anthraldehyde, **3**, in refluxing ethanol gave calixpodand **1a** in 52% yield (Scheme 1).

Similarly, condensation of calix-1,3-diamine **4** [64] of 1,3-*alternate* conformation with 2.0 mol equiv of 9-anthraldehyde, **3**, in refluxing $CH_2Cl_2/MeOH$ (1:2) gave calixpodand **1b** in 82% yield (Scheme 2). Both the products **1a–b** separated out as pure solids, and gave satisfactory elemental analysis after single crystallization.

The structures of compounds **1a–b** were confirmed from their spectroscopic and analytical data. The IR spectra of compounds **1a** and **1b** showed characteristic C=N stretching bands at 1,632 and 1,624 cm^{-1} , respectively. The FAB mass spectra of these compounds showed parent ion peaks corresponding to 1:2 condensation products. The 1H NMR spectra of compounds **1a–b** showed two singlets (18H each) corresponding to *tert*-butyl protons, triplets (4H each) corresponding to OCH_2 protons, two singlets (4H each) corresponding to aromatic protons and one singlet (2H) for the imino protons. The bridging methylene protons of compound **1a** appear as a AB quartet separated by $\Delta\delta > 0.9$ ppm. The 1H NMR data suggests a C_{2v} -symmetric structure that is *cone* conformation for compound **1a**. In the ^{13}C NMR spectrum of compound **1b**, all the bridging methylene carbons are equivalent, giving a singlet at 39.2 ppm suggesting a C_{2v} -symmetric structure that is 1,3-*alternate* conformation for compound **1b** [65].



Scheme 1 Synthesis of receptor **1a**



Scheme 2 Synthesis of receptor **1b**

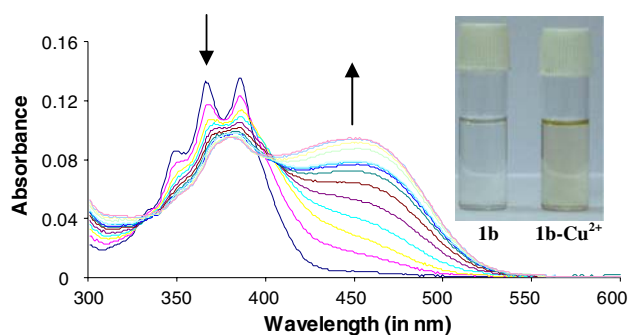


Fig. 1 UV-Vis changes of receptor **1b** (1×10^{-5} M) upon addition of Cu^{2+} ions (0–100 equiv) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1, v/v), *Inset* showing the color change of receptor **1b** upon addition of 100 equiv Cu^{2+} ions

The cation binding properties of compounds **1a** and **1b** were investigated by UV-Vis and fluorescence spectroscopy. The titration experiments were carried out in $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ (1:1 v/v) by adding aliquots of different metal ions. The UV-Vis absorption spectrum of the compound **1b** (1×10^{-5} M) exhibits typical anthracenyl absorption bands at λ_{max} 350, 369 and 387 nm, respectively (Fig. 1).

Upon addition of increasing amounts of Cu^{2+} ions (0–100 equiv) to a solution of **1b**, the absorption peak due to the anthracenyl moiety decreases while a new peak gradually moving to longer wavelength finally reaching a maximum value at 451 nm is appeared with an isosbestic point at 405 nm indicating a well defined **1b**- Cu^{2+} complex (Fig. 1). The colour of the solution of **1b** changes from colourless to pale yellow in presence of Cu^{2+} ions (inset of Fig. 1).

In the fluorescence spectra, compounds **1a** and **1b** exhibited a very weak emission from locally excited lowest ($\pi \rightarrow \pi^*$) state in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) as compared to the simple anthracene. This weak emission from these compounds is due to photoinduced electron transfer (PET) from the lone pair of imine nitrogen to the photo-excited anthracene which leads to fluorescence quenching. Upon addition of Cu^{2+} ions to solution of receptor **1b**, a

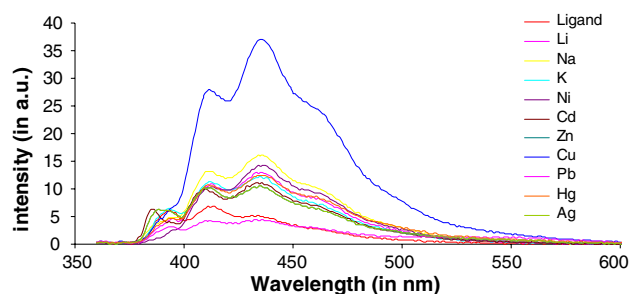


Fig. 2 Fluorescence emission spectra of receptor **1b** (1×10^{-5} M) upon addition of 100 equiv of different metal (Li^+ , Na^+ , K^+ , Ni^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} and Ag^+) perchlorates

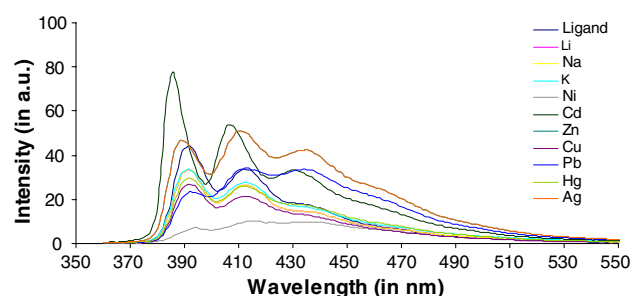


Fig. 3 Fluorescence emission spectra of receptor **1a** (1×10^{-5} M) upon addition of 100 equiv of different metal (Li^+ , Na^+ , K^+ , Ni^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} and Ag^+) perchlorates

significant fluorescence enhancement was observed (Fig. 2). Under the same conditions as above no significant fluorescence changes (Fig. 2) were observed for other tested metal ions (Li^+ , Na^+ , K^+ , Ni^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Ag^+). These observations indicate that the compound **1b** has selectivity for Cu^{2+} ions.

However, upon addition of different metal ions (Li^+ , Na^+ , K^+ , Ni^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , Ag^+) to the solution of receptor **1a**, no selective fluorescence enhancement was observed for any metal ion (Fig. 3).

The fluorescence titrations of compound **1b** were then performed with Cu^{2+} ions (Fig. 4). The addition of increasing amounts of Cu^{2+} ions to the solution of receptor **1b** showed a 10-fold fluorescence enhancement in the anthracenyl triplet of receptor **1b**, centered at 437 nm (Fig. 4). This is due to the fact that when Cu^{2+} ions are added to the receptor **1b**, the lone pair of electrons on nitrogen gets involved in the coordination with the Cu^{2+} ion. This leads to the decrease in the electron density on nitrogen atom as a result of which the electron transfer from the nitrogen to the photoexcited anthracene moiety is suppressed and hence allows the fluorescence emission. Similar reports exist for imine based fluorogenic receptors, where the signaling mechanism is through photoinduced electron transfer (PET) in particular, for Cu^{2+} ions [22, 53, 61, 62]. Fitting the changes in fluorescence spectra of compound **1b** with Cu^{2+} ions, using the nonlinear regression analysis program SPECFIT [66] gave good fit and demonstrated that 1:1 stoichiometry (Host: Guest) is the most stable species in the solution with binding constant $\log \beta_{11} = 4.83$ (M^{-1}). Similarly, fitting the changes in fluorescence spectra of compounds **1a–b** with various other metal ions, using the nonlinear regression analysis program SPECFIT [66] gave good fit with 1:1 (Host: Guest) stoichiometry. The stability constants determined for both receptors **1a–b** with various metal ions are summarized in Table 1. These values indicate that Cu^{2+} preferentially binds to compound **1b** though other metal ions also bind with **1b** but with lower binding constants. For compound **1a**, there is no preferential binding for any metal ion.

Fig. 4 Change in fluorescence of receptor **1b** (1×10^{-5} M) upon addition of 0–500 equiv of Cu^{2+} ions. *Inset* showing the binding isotherm for receptor **1b** at 437 nm

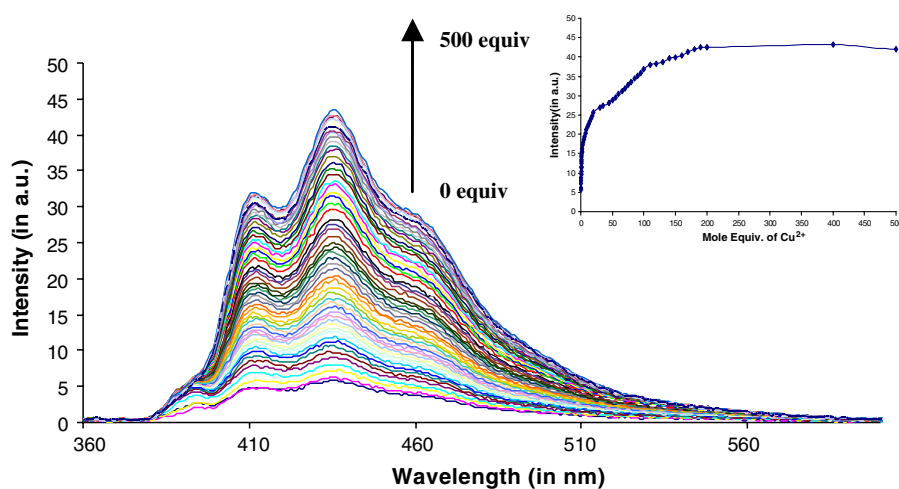


Table 1 Stability constants [$\log \beta$ (in M^{-1})] of 1:1 complex of receptor **1a–b** and various metal ions as calculated using SPECFIT32 v3.0

Receptor	Li^+	Na^+	K^+	Cd^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Ag^+
1a	–	–	3.49 (± 0.14)	3.98 (± 0.70)	5.47 (± 0.15)	1.95 (± 0.26)	3.94 (± 0.06)	3.36 (± 0.12)	2.62 (± 0.26)	4.33 (± 0.12)
1b	1.41 (± 0.10)	1.94 (± 0.11)	1.47 (± 0.05)	1.47 (± 0.10)	1.31 (± 0.08)	4.83 (± 0.20)	1.36 (± 0.11)	1.47 (± 0.11)	2.30 (± 0.06)	1.19 (± 0.10)

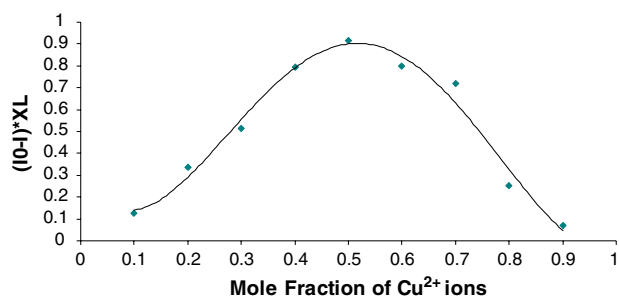


Fig. 5 Job's plot for **1b** and Cu^{2+} , [**1b**] + [Cu^{2+}] = 2.5×10^{-5} M in CH_2Cl_2 : CH_3CN (1:1)

In order to determine the stoichiometry of the **1b**– Cu^{2+} complex, the method of continuous variation (Job's plot) was also used. The total concentration of the receptor **1b** and Cu^{2+} was kept constant (2.5×10^{-5} M), with a continuous variable molar fraction of guest ($[\text{Cu}^{2+}]/[\text{1b}] + [\text{Cu}^{2+}]$). Figure 5 shows the Job's plot of compound **1b** with Cu^{2+} at 437 nm. The **1b**– Cu^{2+} complex concentration approaches a maximum when the molar fraction of Cu^{2+} is 0.5, which means **1b** and Cu^{2+} formed a 1:1 (Host: Guest) complex.

Further, to test the practical applicability of compound **1b** as a Cu^{2+} -selective fluorescence sensor, competitive experiments were carried out in the presence of Cu^{2+} ions at 1×10^{-3} M mixed with Li^+ , Na^+ , K^+ , Cd^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Hg^{2+} , and Ag^+ at 1×10^{-3} M, and as shown in Fig. 6, no significant variation in the fluorescence was

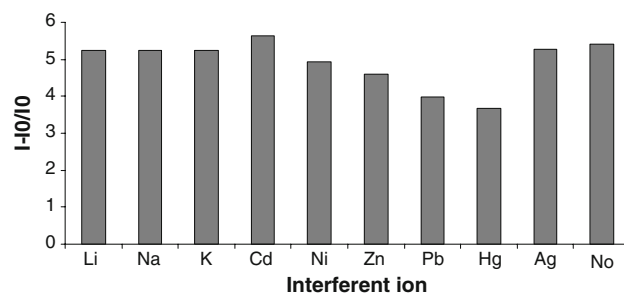


Fig. 6 Fluorescent response of receptor **1b** (1×10^{-5} M) to Cu^{2+} (100 equiv) over selected metal ions (100 equiv)

found by comparison with that without the other metal ions besides Cu^{2+} ion except Ni^{2+} , Zn^{2+} , Hg^{2+} , and Pb^{2+} which slightly interfere leading to a quenching of fluorescence due to the **1b**– Cu^{2+} complex.

Conclusions

Thus, we have synthesized new calix[4]arene based receptors **1a** and **1b** by simple condensation of 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dipropoxy-calix [4]arene of *cone* and 1,3-*alternate* conformation with 9-anthraldehyde, respectively. Receptor **1b** selectively recognizes copper among the different metal ions tested. A colour change from colourless to light yellow was observed by naked eye when receptor **1b** was treated with copper ions.

Experimental

General methods and instrumentation

All reagents were purchased from Aldrich and used without further purification. CH₃CN was dried over P₂O₅ and with K₂CO₃ and kept over molecular sieves overnight before use. Fluorescence spectra were recorded on SHIMADZU RF-5301 spectrofluorimeter. UV–vis Spectra were recorded on SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length: 1.0 cm). The cell holder was thermostatted at 25 °C. ¹H and ¹³C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using CDCl₃ as solvent and TMS as internal standards. Solutions of compound **1a–b** and various metal perchlorates (Li⁺, Na⁺, K⁺, Ni²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Ag⁺) for UV–vis and fluorescence studies were prepared in CH₂Cl₂ and CH₃CN AR grade. All spectrophotometric titration curves were fitted with SPECFIT\32 software.

Synthesis of receptor **1a**

To a stirred solution of diamine **2** (409 mg, 0.50 mmol) in ethanol (25 mL) was added a solution of 9-anthraldehyde (227 mg, 1.10 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 6 h to separate a solid, which was filtered, washed with ethanol and recrystallised from dichloromethane/methanol. Yield (412 mg, 52%), mp 178 °C; IR ν_{\max} (KBr, cm⁻¹) 1,632 (C=N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.92 (s, 18H, C(CH₃)₃), 1.09 (t, J = 7.5 Hz, 6H, CH₃), 1.32 (s, 18H, C(CH₃)₃), 2.15–2.20 (m, 4H, CH₂), 3.25 (d, J = 12.6 Hz, 4H, ArCH₂Ar), 3.82 (t, J = 7.5 Hz, 4H, OCH₂), 4.58–4.67 (m, 8H, OCH₂, ArCH₂Ar), 4.82 (t, J = 8.1 Hz, 4H, NCH₂), 6.60 (s, 4H, ArH), 7.08–7.12 (m, 6H, ArH), 7.21–7.25 (m, 6H, ArH), 7.78 (d, J = 8.7 Hz, 4H, ArH), 8.21 (s, 2H, CH=N), 8.35 (d, J = 8.7 Hz, 4H, ArH), 9.56 (s, 2H, ArH); ¹³C NMR (75 MHz, CDCl₃) : 10.9 (CH₃), 23.9 (CH₂), 31.3 (C(CH₃)₃), 31.4 (ArCH₂Ar), 31.7 (C(CH₃)₃), 33.7 (C(CH₃)₃), 34.1 (C(CH₃)₃), 62.5 (OCH₂), 74.0 (OCH₂), 77.6 (NCH₂), 122.2 (ArC), 124.5 (ArC), 124.7 (ArC), 125.5 (ArC), 126.2 (ArC), 127.0 (ArC), 128.1 (ArC), 130.8 (ArC), 132.5 (ArC), 135.2 (ArC), 140.0 (ArC), 145.0 (ArC), 154.3 (ArCO), 157.2 (ArCO), 160.9 (CH=N); FAB-MS (*m/z*) 1196 (M + 1)⁺; EA Calcd for C₈₄H₉₄N₂O₄: C, 84.38; H, 7.92; N, 2.34%. Found: C, 84.29; H, 7.62; N, 2.45%.

Synthesis of receptor **1b**

To a stirred solution of diamine **4** (204, 0.25 mmol) in CH₂Cl₂ (5 mL)/MeOH (5 mL) was added a solution of 9-anthraldehyde (114 mg, 0.55 mmol) in methanol (5 mL).

The reaction mixture was refluxed for 6 h to separate a solid, which was filtered and washed with ethanol. The yellow solid obtained was further recrystallized from dichloromethane/methanol. Yield (245 mg, 82%), mp 263 °C; IR ν_{\max} (KBr, cm⁻¹) 1624 (C=N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 0.68 (t, J = 7.5 Hz, 6H, CH₃), 1.05–1.13 (m, 4H, CH₂), 1.31 (s, 18H, C(CH₃)₃), 1.37 (s, 18H, C(CH₃)₃), 3.41 (t, J = 7.5 Hz, 4H, OCH₂), 3.67 (t, J = 7.5 Hz, 4H, OCH₂), 3.90–4.05 (m, 12H, NCH₂, ArCH₂Ar), 7.05 (s, 4H, ArH), 7.26 (s, 4H, ArH), 7.34–7.45 (m, 8H, ArH), 7.99 (d, J = 7.8 Hz, 4H, ArH), 8.41 (d, J = 7.8 Hz, 4H, ArH), 8.48 (s, 2H, CH=N), 9.44 (s, 2H, ArH); ¹³C NMR (75 MHz, CDCl₃) : 10.1 (CH₃), 22.4 (CH₂), 31.6 (C(CH₃)₃), 32.0 (C(CH₃)₃), 34.0 (C(CH₃)₃), 34.2 (C(CH₃)₃), 39.2 (ArCH₂Ar), 61.6 (OCH₂), 69.0 (OCH₂), 71.7 (NCH₂), 124.7 (ArC), 125.2 (ArC), 125.8 (ArC), 125.9 (ArC), 126.7 (ArC), 128.2 (ArC), 128.8 (ArC), 129.9 (ArC), 131.3 (ArC), 133.4 (ArC), 144.0 (ArC), 144.1 (ArC), 154.3 (ArCO), 154.9 (ArCO), 161.1 (CH=N); FAB-MS (*m/z*) 1196 (M + 1)⁺; EA Calcd for C₈₄H₉₄N₂O₄: C, 84.38; H, 7.92; N, 2.34%. Found: C, 83.78; H, 7.59; N, 2.42%.

UV–Vis and fluorescence studies

The stock solution of ligands **1a–b** and metal perchlorates were prepared in CH₂Cl₂/CH₃CN (1:1, v/v). The concentrations of the solutions were maintained at 1 × 10⁻⁵ M. The fluorescence experiments were carried out on a SHIMADZU RF-5301 PC. The samples were excited at 350 nm in a 1.0 cm quartz cell. The slit width was set at 3 nm (Excitation and Emission). Absorption spectra of the solutions were measured on Shimadzu UV-2450PC in the range of 250–600 nm with a slit width of 1.0 nm. Job's plot experiment was carried out using fluorescence, by keeping the total concentration [**1b**] + [Cu²⁺] = 2.5 × 10⁻⁵ M.

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