

# Calix Receptor Edifice; Scrupulous Turn Off Fluorescent Sensor for Fe(III), Co(II) and Cu(II)

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**Abstract** Novel Supramolecular fluorescence receptor derived from calix-system i.e. calix[4]resorcinarene bearing dansylchloride as fluorophore was designed and synthesized. The compound was purified by column chromatography and characterized by elemental analysis, NMR and Mass spectroscopy. Tetradansylated calix[4]resorcinarene (**TDCR**) shows a boat conformation with  $C_{2v}$  symmetry. The complexation behaviour of metal cations [Ag(I), Cd(II), Co(II), Fe(III), Hg(II), Cu(II), Pb(II), Zn(II), U(VI) ( $1 \times 10^{-4}$  M)] with tetra dansylated calix[4]resorcinarene ( $1 \times 10^{-6}$  M) was studied by spectrophotometry and spectrofluorometry. Red shift in the absorption spectra led us to conclude that there is strong complexation Fe(III), Co(II) and Cu(II) with **TDCR**. These metal cations also produce quenching with red shifts in the emission spectra. The maximum quenching in emission intensity was observed in the case of Fe(III) and its binding constant was also found to be significantly higher than that of Co(II) and Cu(II). Quantum yield of metal complexes of Fe(III) was found to be lower in comparison with Co(II) and Cu(II) complexes. Stern Volmer analysis indicates that the mechanism of

fluorescence quenching is either purely dynamic, or purely static.

**Keywords** Fluorescent Quenching · Calix[4]resorcinarene · Ion-binding · Dansyl chloride

## Introduction

The development of selective artificial fluorescence receptors for the detection of biologically and environmentally important metal ions has been an important goal in the field of supramolecular chemistry [1] and chemical sensors [2]. Fluorescent chemosensors typically consist of an ion recognition unit (ionophore) and a fluorogenic unit (fluorophore) linked through the proper spacer [3], are also called as fluoroionophore [4]. The ionophore is required for selective binding of the substrate, while the fluorophore provides the means of signaling this binding, either by fluorescence enhancement or quenching [5, 6]. The ideal fluorophore in chemosensors has high quantum yields of fluorescence, high extinction coefficients, long excitation and emission wavelengths, a long lifetime and photostability. Therefore, the choice of fluorophore is the most important factor in the design of new fluorescent chemosensors [7]. Different chemosensors have been used for investigation of their selective fluorescent responses upon complexation with various cations [8, 9]. Recently, there has been strong interest in dansyl derivatives as potential fluorophores [10–13]. Dansyl chloride is an attractive fluorophore due to the strong fluorescence, relatively long emission wavelength ( $E_m=400\text{--}600$  nm), Stokes shift ( $E_x=330\text{--}350$  nm) and is also easy to introduce in a molecular skeleton to obtain fluorescent sensors [14]. Calixarenes [15, 16] which are cyclic oligomers of phenolic and methylene moieties, their preorganized binding

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sites, easy derivatization and flexible three dimensional structures make them perfect construction platforms for molecular design to generate fluorescent receptors [17, 18]. Calix[4]resorcinarenes which are analogous of calixarenes (resorcinol derived calixarenes) have a variable number of reactive positions for attaching the ligating functions. Calix[4]resorcinarenes with appropriate appended groups have been found to be good candidates for recognition of cations and anions. Calix[4]resorcinarenes have received increased interest in synthesis of variety of chemosensors [19–21] bearing different fluorescent groups.

Among all metal ions Fe(III) and Co(II) are very important for most organisms and play significant role in many biochemical processes. Fe(III) is the most essential transition element responsible for carrying the oxygen in heme and acts as a cofactor in enzymatic reactions of mitochondrial respiratory chain. The deficiency of Fe(III) causes anaemia, hemochromatosis, liver damage, diabetes, Parkinson's disease and cancer. Accumulation of copper, iron, and subsequent over production of  $H_2O_2$  in tissues causes oxidative stress and neurodegenerative diseases [22]. On the other hand Co (II) plays an important role in the metabolism of iron and synthesis of haemoglobin and Vitamin  $B_{12}$  [23–26]. As a consequence, intense research, efforts have been directed to develop sensitive and selective sensors for such metal ions. Fluorescent sensor for Cu(II) is actively investigated, as it is a significant metal pollutant due to its widespread use, but it is also an essential trace element in biological systems [27]. Although Cu(II) toxicity for humans is rather low compared with other heavy-metal ions, certain microorganisms are affected by sub-micromolar concentrations of metallic materials.

With a view to develop calix[4]resorcinarene based fluorionophores, herein we report the synthesis and characterization of tetradansylated calix[4]resorcinarene (**TDCR**) and its complexation behaviour with a large number of cations [Ag(I), Co(II), Fe(III), Zn(II), Cd(II), Hg(II), Pb (II), Cu(II) and U(VI)]. Cation binding constants have also been determined from fluorescence titration data. Although there are multiple factors which affect the emission intensity and hence no single guideline can be used for their quantitative interpretation, we have tried to explain the red shift in absorbance and emission spectra and quenching of emission intensity of **TDCR** in presence of Fe(III), Co(II) and Cu(II).

## Experimental Section

**Reagents** Dansyl chloride, triethyl amine, metal nitrate salts and other chemicals were obtained from Sigma-Aldrich. Silica gel and fluorescence active TLC plates (F-2009) were

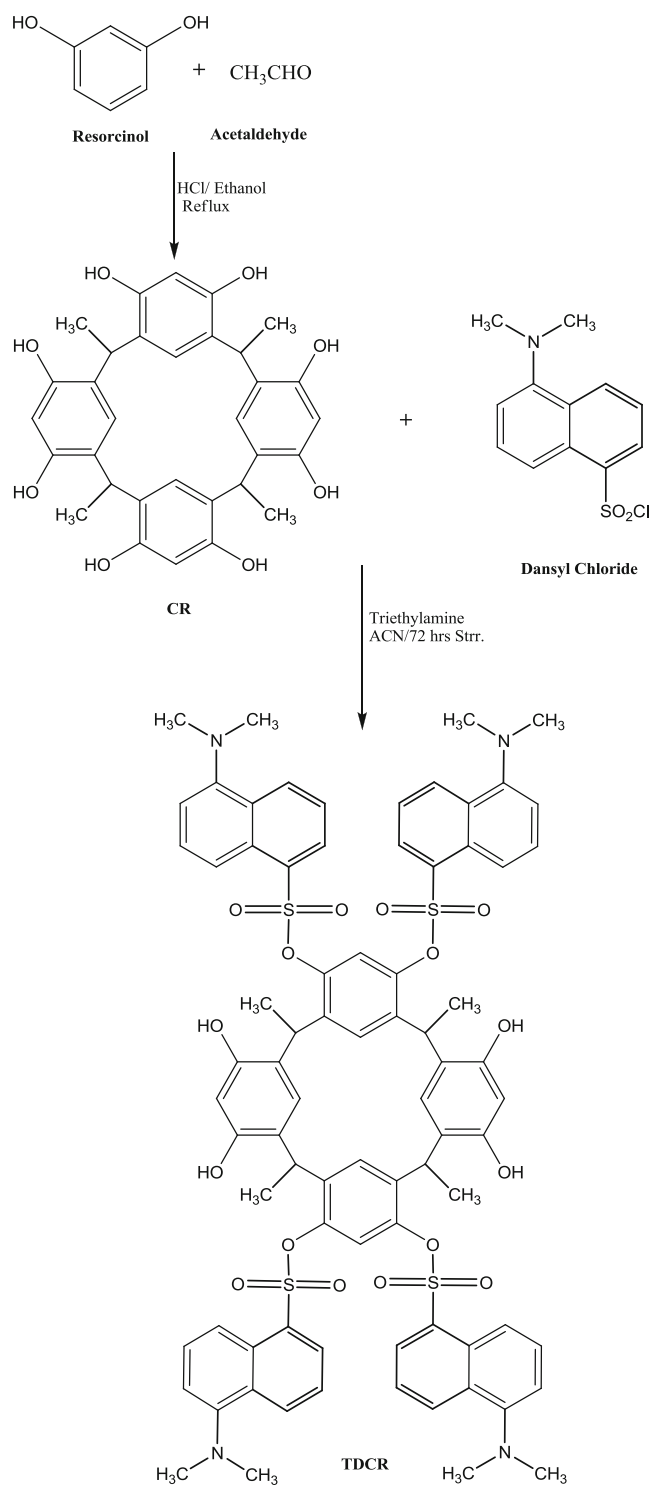
purchased from the Merck. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. All the solvents employed for synthesis were commercially available and used as received without further purification.

**Methods** The melting points (uncorrected) were obtained from a VEEGO (Model; VMP-DS, (Mumbai, India). Samples for infrared spectra were prepared as KBr pellets, spectra were recorded on tensor Bruker 27 (Ettlingen, Germany) and expressed in  $cm^{-1}$ . Elemental analysis (C, H and N) was performed on varioMICRO-Variant elemental analyzer (Mt. Laurel, USA). Electrospray ionization (ESI) mass spectra (MS) were determined using MicromassQuarter2 (Utah, USA). NMR spectra were recorded on a model DPX 200 MHz and Avance II 500 MHz Bruker FT-NMR instruments (Ettlingen, Germany). UV-Vis spectra were recorded on a JASCO spectrophotometer (Easton, US). Fluorescence spectra were obtained on an EDINBURGH Uf-920 H (Xenon lamp head Xe900) spectrometer (Livingston, US).

## Synthesis of Ligands

### Synthesis of **TDCR** (Scheme 1)

Calix[4]resorcinarenes (CR) can easily be obtained by the acid-catalyzed condensation of resorcinol with acetaldehydes [28–30]. To the solution of CR (0.15 g, 0.27 mmol) and  $Et_3N$  (0.26 mL, 1.08 mmol) was dissolved in MeCN (10 mL) with vigorous stirring. A pink coloured precipitate was formed and the reaction mixture was stirred for 2 h. A solution of dansyl chloride (0.25 g, 1.08 mmol) in MeCN (20 mL) was added to the suspension and the reaction mixture was vigorously stirred to facilitate dissolution of the precipitates. The reaction mixture was further stirred at room temperature for 72 h to get the desired precipitate of tetradansylated calix[4]resorcinarene (**TDCR**). The precipitate formed was filtered off, washed with MeCN (30 mL) and water (50 mL). Excess of solvent was removed under reduced pressure and product was separated by column chromatography using silica gel ( $< 74 \mu m$ ) with *n*-hexane: ethyl acetate (8.0:2.0) as an eluent. The fraction was recrystallised from chloroform to give yellowish crystal of **TDCR** (0.20 g, 60 %) with melting point of 103 °C.  $^1H$  NMR (500 MHz,  $d_6$ - $CHCl_3$ ): 1.34(1d, 12 H), 2.85 (1 s, 24 H(Dansyl  $NCH_3$ )); 4.22(1q, 4 H); 6.07–6.86 (4 s, 8 H (ArCH)); 7.21–7.60 (3d, 12 H (Dansyl ArCH)); 8.17–8.61 (3d, 12 H(DAN ArCH));. Anal. Calcd. For  $C_{80}H_{76}N_4O_{16}S_4$ : Found: C 65.02, H 5.18, N 3.79, S 8.68.  $m/z$  (ESI-MS) 1478.5  $[M+H]^+$ .



Scheme 1 Synthesis of TDCR

## Results and Discussion

### Absorption and Emission Studies

Tetradansylated calix[4]resorcinarene shows a boat conformation with  $C_{2v}$  symmetry. The four hydroxyl groups form

hydrogen bonds to the sulfoxide oxygens of the dansyl moieties and stabilize the  $C_{2v}$  conformation in solution [31] which is also indicated by four singlets of aromatic protons ( $\delta$  6.07–6.86) of resorcinarene in  $^1\text{H}$ NMR. Usually, the dansyl group is attached through the S-atom to an amine, obtaining amino-naphthalensulfonate derivatives. The band is affected by the polarity of the solvent and shows a considerable charge-transfer character arising from the promotion of a lone-pair electron on the amino group into an antibonding orbital of the naphthalene ring [32].

The absorption spectra of ligand **TDCR** ( $1 \times 10^{-6}$  M) upon addition of several metal ions (Ag(I), Co(II), Fe(III), Zn(II), Cd(II), Hg(II), Pb(II), Cu(II) and U(VI)) ( $1 \times 10^{-4}$  M), in excess (100 equivalent) were recorded in methanol. Only metal ions, Fe(III), Co(II) and Cu(II) exhibited significant changes in the spectra compared to other metal ions, Fig. 1. The absorption band of **TDCR** was found at 332 nm. Changes in absorption spectra were noted in presence of metal ion like Fe(III) with a colour change from colourless to yellow and the band at 332 nm was shifted to 362 nm. In case of Co(II) it was seen that absorption bands shifted to 341 nm, while in case of Cu(II) it was shifted to 342 nm. This new band due to red-shift, Fig. 1, indicates that these cations are interacting strongly with the ligand **TDCR**, because when a cation is coordinated with the oxygen, the excited state is more stabilized by the cation than the ground state, and this leads to a red shift of the absorption and emission spectra [33].

For emission titration studies, the same stock solutions of the TDCR and metal ions were used which were used for absorption studies. The fluorescence spectra of the compounds (**TDCR**) were recorded in methanol in presence of 0.1–100-fold excess of various metal ions (Fe(III), Co(II) and Cu(II)) and the spectra thus obtained were compared with TDCR to ascertain the complexing ability of the fluoroionophore (TDCR). TDCR exhibits significant quenching in emission intensity in presence of Fe(III), Co(II) and Cu(II). When excited at 328 nm, ligand TDCR gives emission

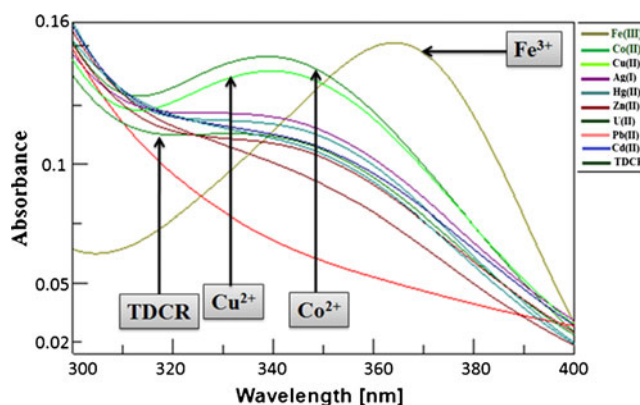
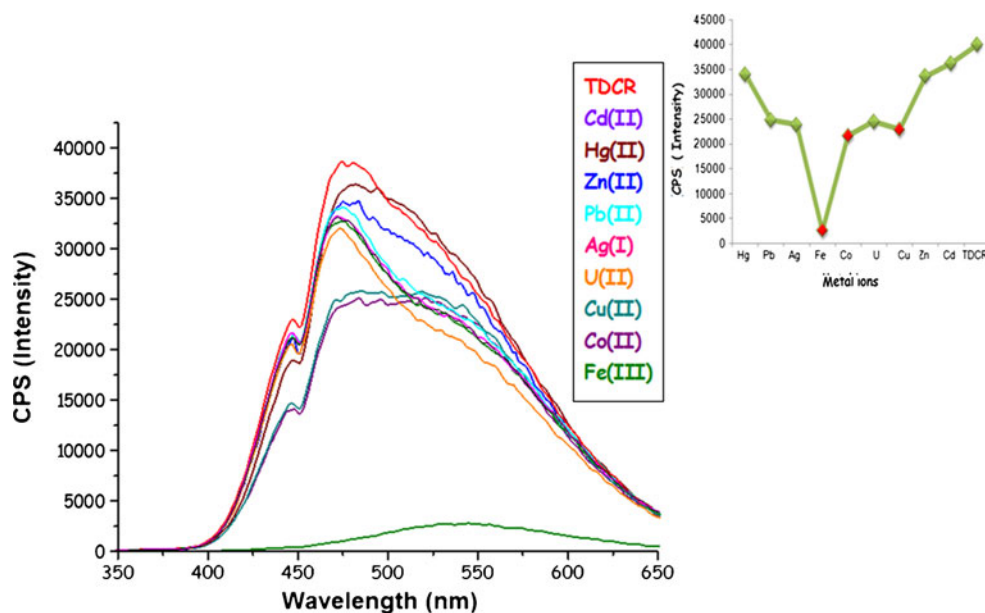


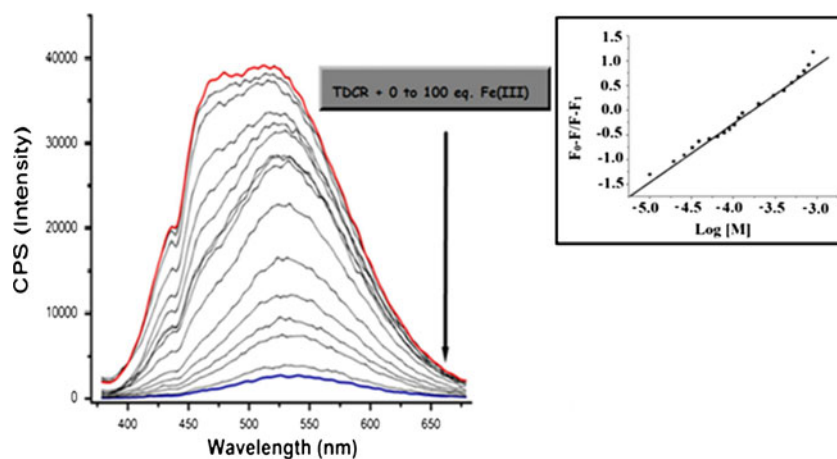
Fig. 1 UV-Visible spectra of TDCR (Methanol,  $1.0 \times 10^{-6}$  mol  $\text{L}^{-1}$ ) upon addition of various metal ions in methanol, ( $1.0 \times 10^{-4}$  mol  $\text{L}^{-1}$ ) 100 eq

**Fig. 2** Fluorescence spectra of TDCR (Methanol,  $1.0 \times 10^{-6}$  mol L $^{-1}$ ) upon addition of various metal ions in methanol. Equivalents of metal ions: 100, Ex=328 nm



bands with maxima at 472 nm. Figure 2 shows the effects of metal cations on the fluorescence spectra of TDCR. Red shifts and strong quenching of the emission intensity were observed in the presence of Fe(III), Co(II) and Cu(II) because introduction of a harder O-dansyl electron donor instead of HN-dansyl fluoroionophores which shifts coordination preferences for these transition metal ions [34]. This results in strong complex formation with Fe(III), Co(II) and Cu(II), however other metal ions (Ag(I), Zn(II), Cd(II), Hg(II), Pb(II), and U(II)) did not induce any significant change in the emission spectra. Stronger complex formation will not only induce red shift in absorption and emission spectra rather it will also remove the hydrogen bonding of four hydroxyl groups which form hydrogen bonds to the sulfoxide oxygens of the dansyl moieties. This will facilitate the deprotonation of phenolic protons and simultaneous protonation of nitrogen of dimethylamino group which will reduce the available charge density on nitrogen and prevent charge transfer, thereby decreasing the emission intensity.

**Fig. 3** The fluorescence spectral change of TDCR ( $1.0 \times 10^{-6}$  mol L $^{-1}$ ) upon addition of various amount of Fe(III) ions in methanol. Equivalents of metal ions: 0–100, Ex=362 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of concentration of metal ion



### Binding Constant

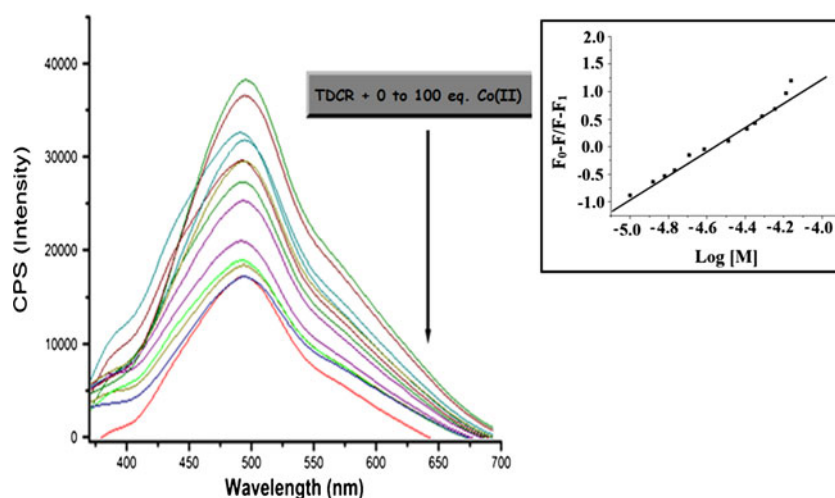
Cations, which exhibited substantial changes in emission intensity, were considered for emission titration to evaluate binding constant for TDCR following the literature procedure [35, 36]. A few representative spectra showing the changes observed in emission intensities upon addition of increasing concentration of ions are shown in (Figs. 3, 4 and 5) According to this procedure, the fluorescence intensity (F) scales with the metal ion concentration ([M])

$$(F_0 - F)/(F - F_1) = ([M]/K_{\text{diss}})^n \quad (1)$$

The binding constant (Ks) is obtained by plotting  $\log [(F_0 - F)/(F - F_1)]$  versus  $\log [M]$ , where  $F_0$  and  $F_1$  are the relative fluorescence intensities of the complex without addition of guest metal ion and with maximum concentration of metal ion, respectively. The value of  $\log [M]$  at  $\log [(F_0 - F)/(F - F_1)] = 0$  gives the value of  $\log (K_{\text{diss}})$ , the reciprocal of which is the binding constant (Ks). The plots



**Fig. 4** The fluorescence spectral change of TDCR (Methanol,  $1.0 \times 10^{-6}$  mol L<sup>-1</sup>) upon addition of various amount of Co(II) ions in methanol. Equivalents of metal ions: 0–100, Ex=341 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of concentration of metal ion



log  $[(F_0 - F)/(F - F_1)]$  versus log [M] for selected metal ions are shown as insets in (Figs. 3, 4 and 5). The titration data showed very good linear fit ( $R=0.99$ ) with the above equation. The binding constants of all complexes are summarized in Table 1. Analysis of the data (Table 1) shows that, the binding constant of Fe(III) is significantly higher than that of Co(II) and Cu(II) with TDCR in methanol. These metal ions are hard acids, when compared to other metal ions used in the present study and will prefer to bind oxygen donor (hard base) atoms to form stronger complex.

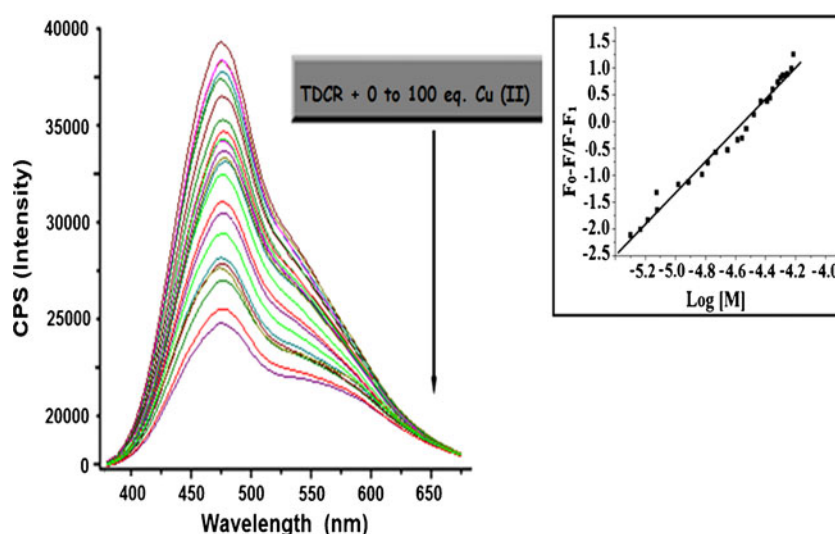
**Quantum Yield**

Fluorescence quantum yields (FF) were determined by the comparative method (Eq. (2) [37, 38])

$$\Phi = \Phi_{std} \frac{F \cdot A_{std} \cdot n^2}{F_{std} \cdot A \cdot n_{std}^2} \tag{2}$$

Where  $F$  and  $F_{std}$  are the areas under the fluorescence emission curves of the metal {Fe(III), Co(II) and Cu (II)} complexes with TDCR and the standard (TDCR), respectively.  $A$  and  $A_{std}$  are the relative absorbance of the sample and standard at the excitation wavelength, respectively.  $n$  and  $n_{std}$  are the refractive indices of solvent (Methanol) used for the sample and standard, respectively. Both the sample and the standard were excited at the same relevant wavelength. Quantum yield [39, 40] of fluoroionophores (TDCR) was obtained using emission spectra of Standard (dansyl chloride). Reported quantum yield of dansyl chloride is approximately 0.7 and that of fluoroionophore (TDCR) was found to be 0.78. It was observed that number of emitted photons decreases with the addition of increasing concentration of metal ions i.e. quenching takes place. Quantum yield of metal complexes of Fe(III) was found to be lower in comparison with Co(II) and Cu(II) complexes which are summarized in Table 1.

**Fig. 5** The fluorescence spectra change of TDCR (Methanol,  $1.0 \times 10^{-6}$  mol L<sup>-1</sup>) upon addition of various amount of Cu(II) ions in methanol. Equivalents of metal ions: 0–100, Ex=342 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of concentration of metal ion



**Table 1** Binding constant ( $K_s$ ) and Quantum yield for ligand TDCR in presence of metal ions

Ligand	Selective metal ion	Solvent	Binding Constant ( $K_s$ ) $M^{-1}$	$\phi$ (Quantum Yield)	$R^2$
TDCR	Fe(III)	Methanol	$8.25 \times 10^4$	0.036	0.9928
	Co(II)		$5.64 \times 10^4$	0.058	0.9915
	Cu(II)		$5.27 \times 10^4$	0.062	0.9838

### Stern-Volmer Analysis

Stern-Volmer plots are useful for understanding the mechanism of emission quenching [41, 42] and hence were utilized to probe the nature of the quenching process in the complexation of Fe(III), Co(II) and Cu(II) with ligand TDCR. From the data, dynamic or static quenching processes can be determined by plotting relative emission intensities ( $I_0/I$ ) against quencher concentration [Q]. Expressed by the following equation, the slope of the plotted line yields  $K_{sv}$  (the static quenching constant).

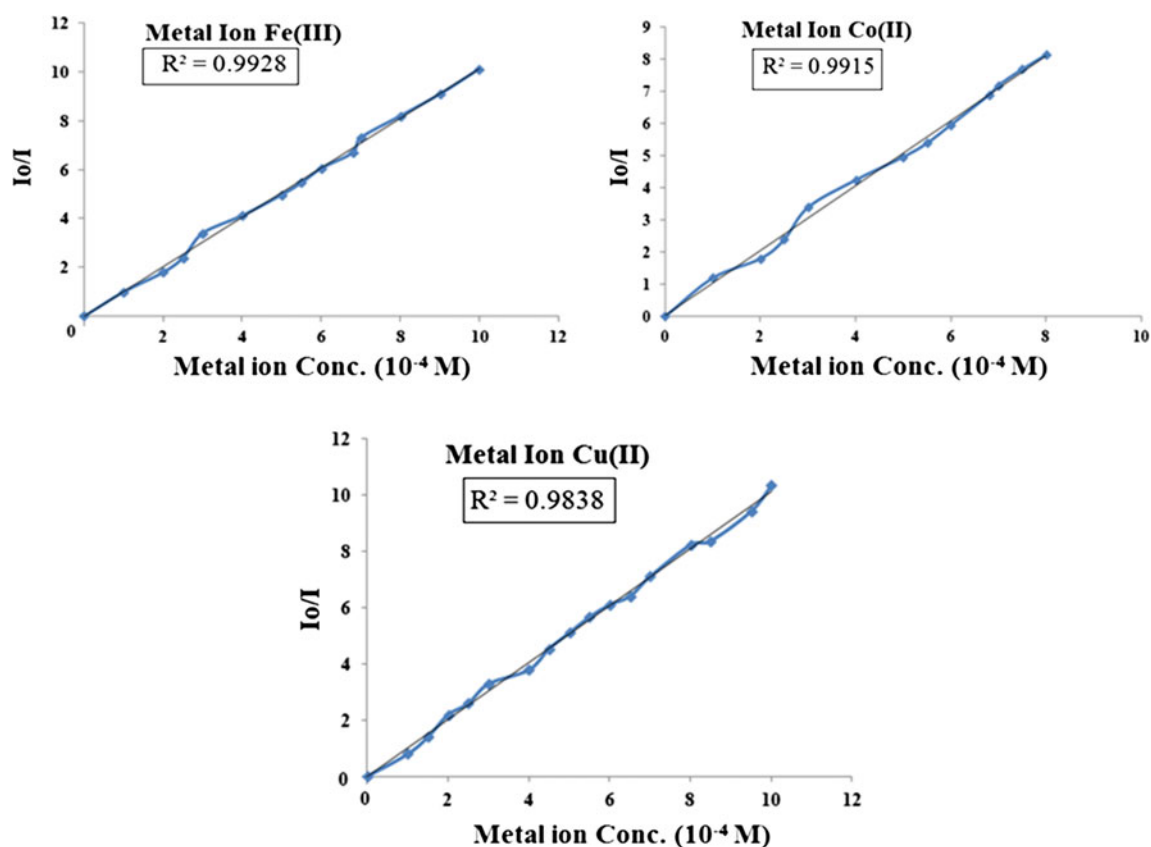
$$I_0/I = 1 + K_{sv}[Q] \quad (3)$$

If the evolution of  $I_0/I$  plots, according to the concentration of quencher, is linear for the whole range of quencher concentrations, fluorescence quenching can be attributed

either to being purely dynamic, or purely static, the latter mechanism being due to the formation of a ground-state non-fluorescent complex. In contrast, if the ratio  $I_0/I$  are not linear and show an upward curve at higher quencher concentrations, the fluorescence quenching mechanism can be attributed to the presence of simultaneous dynamic and static quenching [43]. In all our cases, Fig. 6, typical linear plots for Fe(III), Co(II) and Cu(II) metal ions with TDCR were observed which indicate that fluorescence quenching is either purely dynamic, or purely static.

### Conclusion

To summarize, we have successfully synthesised and characterized tetradansylated calix[4]resorcinarene (TDCR). Its



**Fig. 6** Stern-Volmer plots for quenching of the ligand (TDCR) ( $1.0 \times 10^{-6}$  M) in Methanol by (A) Fe(III), (B) Co(III) and (C) Cu(II) ( $1.0 \times 10^{-4}$ )

complexation behavior with large number of metal ions was studied by spectrophotometry and spectrofluorimetry which has revealed its strong complexing ability and selectivity for Fe (III), Co(II) and Cu(II) leading to a red shift in the absorption and emission spectra. The maximum quenching in emission intensity was observed in the case of Fe(III) and its binding constant was also found to be significantly higher. Stern Volmer analysis indicates that the mechanism of fluorescence quenching is either purely dynamic, or purely static. Quenching is due to the formation of metal complex which helps removal of hydrogen bonding and thereby deprotonation of phenolic hydrogen and protonation of dimethylamino group which prevents charge transfer thereby decreasing the emission intensity.

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## References

- Atwood JL, Davies JED, MacNicol DD, Vogtle F (1996) *Comprehensive Supramolecular Chemistry*, ed.; Elsevier: Exeter
- De Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE (1997) Signaling recognition events with fluorescent sensors and switches. *Chem Rev* 97:1515–1566
- Lee SH, Kim SH, Kim SK, Jung JH, Kim JS (2005) Bifunctional fluorescent Calix[4]arene chemosensor for both a cation and an anion. *J Org Chem* 70:1463–1466
- Hamdi A, Kim SH, Abidi R, Thuery P, Kim JS, Vicens J (2009) A dipyrrenyl calixazacrown chemosensor for  $Mg^{2+}$ . *Tetrahedron* 65:2818–2823
- Anger P, Bharadwaj P, Novotny L (2006) Enhancement and quenching of single-molecule fluorescence. *PRL* 96:113002-1-4
- Lakowicz JR, Weber G (1973) Quenching of fluorescence by oxygen. Probe for structural fluctuations in macromolecules. *Biochemistry* 12(21):4161–4170
- Guo X, Qian X, Jia L (2004) A highly selective and sensitive fluorescent chemosensor for  $Hg^{2+}$  in neutral buffer aqueous solution. *J Am Chem Soc* 126(8):2272–2273
- Aragoni MC, Arca M, Bencini A, Blake AJ, Caltagirone C, Danesi A, Devillanova FA, Garau A, Gelbrich T, Isaia F, Lippolis V, Hursthouse MB, Valtancoli B, Wilson C (2007) New fluorescent chemosensors for heavy metal ions based on functionalized pendant arm derivatives of 7-anthracenylmethyl-1,4,10-trioxo-7,13-diazacyclopentadecane. *Inorg Chem* 46:8088–8097
- Misra A, Shahid M, Srivastava P, Dwivedi P (2010) Fluorescent chemosensor: recognition of metal ions in aqueous medium by fluorescence quenching. *J Inclusion Phenom Macrocyclic Chem* 69:119–129
- Chen QY, Chen CF (2005) A new  $Hg^{2+}$  selective fluorescent sensor based on a dansyl amide-armed calix[4]-aza-crown. *Tetrahedron Lett* 46:165–168
- Talanova GG, Elkarim NSA, Talanov VS, Bartsch RA (1999) A calixarene-based fluorogenic reagent for selective mercury(II) recognition. *Anal Chem* 71:3106–31109
- Talanova GG, Roper ED, Buie NM, Gorbunova MG, Bartsch RA, Talanov VS (2005) Novel fluorogenic calix[4]arene-bis(crown-6-ether) for selective recognition of thallium(I). *Chem. Commun.* 5673–5675
- Schonefeld K, Ludwig R, Feller KH (2006) Fluorescence studies of host–guest interaction of a dansyl amide labelled Calix[6]arene. *J Fluoresc* 16:449–454
- Fusi V, Giorgi L, Micheloni M (2012) New fluorescent chemosensors for metal ions in solution Mauro Formica. *Coord Chem Rev* 256:170–192
- David Gutsche C (2008) Calixarenes: an introduction, 261-276, Ed. RSC publication
- Kim JS, Lee SY, Yoon J, Vicens J (2009) Hyperbranched calixarenes: synthesis and applications as fluorescent probes. *Chem Commun* 4791–4802
- Kim JS, Quang DT (2007) Calixarene-derived fluorescent probes. *Chem Rev* 107(9):3780–3799
- Sahin O, Yilmaz M (2011) Synthesis and fluorescence sensing properties of novel pyrene-armed calix[4]arene derivatives. *Tetrahedron* 67:3501–3508
- Roberts BA, Cave GWV, Raston CL, Scott JL (2001) Solvent-free synthesis of calix[4]resorcinarenes. *Green Chemistry* 3:280–284
- McIlldowie MJ, Mocerino M, Ogden MI (2010) A brief review of C-symmetric calixarenes and resorcinarenes. *Supramol Chem* 22(1):13–39
- Pandey S, Ali M, Bishnoi A, Azam A, Pandey S, Chawla HM (2008) Quenching of pyrene fluorescence by Calix[4]arene and Calix[4]resorcinarenes. *J Fluoresc* 18:533–539
- Fix OK, Kowdley KV (2008) Hereditary hemochromatosis. *Minerva Med* 99:605–617
- Li CY, Zhang XB, Jin Z, Han R, Shen GL, Yu RQ (2006) A fluorescent chemosensor for cobalt ions based on a multi-substituted phenol-ruthenium(II) tris(bipyridine) complex. *Anal Chim Acta* 580:143–148
- Santander PJ, Kajiwarra Y, Williams HJ, Scott AI (2006) Structural characterization of novel cobalt corrinoids synthesized by enzymes of the vitamin B12 anaerobic pathway. *Bioorg Med Chem* 14:724–731
- Frank A, McPartlin J, Danielsson R (2004) Nova Scotia moose mystery—a moose sickness related to cobalt- and vitamin B12 deficiency. *Sci Total Environ* 318:89–100
- Al-Habsi K, Johnson EH, Kadim IT, Srikandakumar A, Annamalai K, Al-Busaidy R, Mahgoub O (2007) Effects of low concentrations of dietary cobalt on liveweight gains, haematology, serum vitamin B (12) and biochemistry of Omani goats. *Vet J* 173:131–137
- Da Silva JJRF, Williams RJP (1991) *The biological chemistry of the elements*. Clarendon, Oxford
- Hogberg AGS (1980) Stereoselective synthesis and DNMR study of two 1,8,15,22-Tetraphenyl [14]metacyclophan-3,5,10,12,17,19,24,26-octols. *J Am Chem Soc* 102:6046–6050
- Hogberg AGS (1980) Two stereoisomeric macrocyclic resorcinol-acetaldehyde condensation products. *J Org Chem* 45:4498–4500
- Timmerman P, Verboom W, Reinhoudt DN (1996) Resorcinarenes. *Tetrahedron* 52:2663–2704
- Beyeh NK, Aumanen J, Ahman A, Luostarinen M, Mansikkamaki H, Nissinen M, Tommola JK, Rissanen K (2007) Dansylated resorcinarenes. *New J Chem* 31:370–376
- Li YH, Chan LM, Tyer L, Moody RT, Himel CM, Hercules DM (1975) Solvent effects on the fluorescence of 1-(dimethylamino)-5-naphthalenesulfonic acid and related compounds. *J Am Chem Soc* 97:3118–3126
- Prodi L, Bolletta F, Montalti M, Zaccheroni N (2000) Luminescent chemosensors for transition metal ions. *Coord Chem Rev* 205:59–83
- Talanova GG, Talanov VS (2010) Dansyl-containing fluorogenic calixarenes as optical chemosensors of hazardous metal ions: a mini-review. *Supramol Chem* 22:838–852

35. Patra S, Paul P (2009) Synthesis, characterization, electrochemistry and ion-binding studies of ruthenium(II) bipyridine receptor molecules containing calix[4]arene-azacrown as ionophore. *Dalton Trans* 40:8683–8695
36. Boricha VP, Patra S, Chouhan YS, Sanavada P, Suresh E, Paul P (2009) Synthesis, characterization, electrochemistry and ion-binding studies of ruthenium(II) and rhenium(I) bipyridyl crown ether receptor molecules. *Eur J Inorg Chem* 1256–1267
37. Maree D, Nyokong T, Suhling K, Phillips D (2002) Effects of axial ligands on the photophysical properties of silicon octaphenoxypthalocyanine. *J Porphyr Phthalocyanine* 6:373–376
38. Fery-Forgues S, Lavabre D (1999) Are fluorescence quantum yields so tricky to measure? A demonstration using familiar stationery products. *J Chem Educ* 76:1260–1264
39. El-Sedik M, Almonasy N, Nepras M, Bures F, Dvorak M, Michl M, Cermak J, Hrdina R (2012) Synthesis, absorption and fluorescence properties of N-triazinyl derivatives of 2-aminoanthracene. *Dyes Pigments* 92:1126–1131
40. Wurth C, Gonzalez MG, Niessner R, Panne U, Haisch C, Genger UR (2012) Determination of the absolute fluorescence quantum yield of rhodamine 6 G with optical and photoacoustic methods – Providing the basis for fluorescence quantum yield standards. *Talanta* 90:30–37
41. Murphy CB, Zhang Y, Troxler T, Ferry V, Martin JJ, Jones WE (2004) Probing Forster and Dexter energy-transfer mechanisms in fluorescent conjugated polymer chemosensors. *J Phys Chem B* 108:1537–1543
42. Larsen RW, Helms MK, Everett WR, Jameson DM (1999) Ground- and excited-state characterization of an electrostatic complex between tetrakis(4-sulfonato-phenyl)porphyrin and 16-pyrimidinium crown-4. *Photochem Photobiol* 69:429–434
43. Michon J, Frelon S, Garnier C, Coppin F (2010) Determinations of Uranium(VI) Binding Properties with some Metalloproteins (Transferrin, Albumin, Metallothionein and Ferritin) by Fluorescence Quenching. *J Fluoresc* 20(2):581–590