

Attachment of 4-methoxy benzyl units to a tripodal fluoroionophore shows reversal of output functionality with Cu(II) input

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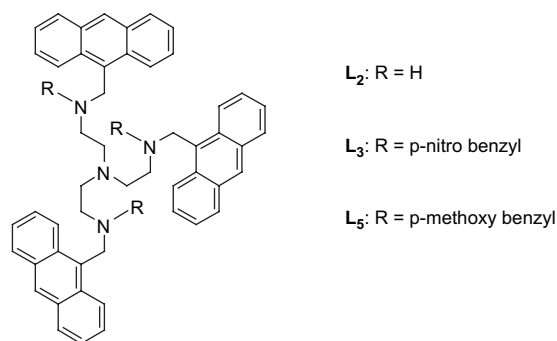
Abstract—Syntheses of three tris-(2-aminoethyl)amine, tren based tripodal fluoroionophores (**L**₂, **L**₃, and **L**₅), are reported. These fluoroionophores are designed based on the fluorophore–spacer–receptor format (choice of fluorophore in all three cases is anthryl unit). In **L**₂, three anthracene moieties are attached to the three arms of tren via –CH₂–spacer whereas **L**₃ and **L**₅ have *p*-nitro benzyl and *p*-methoxy benzyl substitutions, respectively, on **L**₂, which are in close proximity to the photoinduced electron transfer (PET) center. All three fluoroionophores show appreciably lower fluorescence compared to anthracene due to effective PET process in these systems but the quantum yield varies depending upon the nature of substitution at the PET center. In the cases of **L**₂ and **L**₅ different amounts of fluorescence recovery are observed in the presence of different cation inputs whereas **L**₃ is almost inactive toward cation sensing. Detailed fluorescence emission studies on **L**₂ and **L**₅ in the presence of different cation inputs showed that **L**₅ having N4 donor sets bearing three *p*-methoxy benzyl units attached to the three nitrogen centers involving photoinduced electron transfer process is a viable candidate for enhancement of fluorescence with Cu(II) input. In the absence of *p*-methoxy benzyl units at the nitrogen centers' resulting system, **L**₂ shows quenching of fluorescence with the Cu(II) under same experimental conditions.

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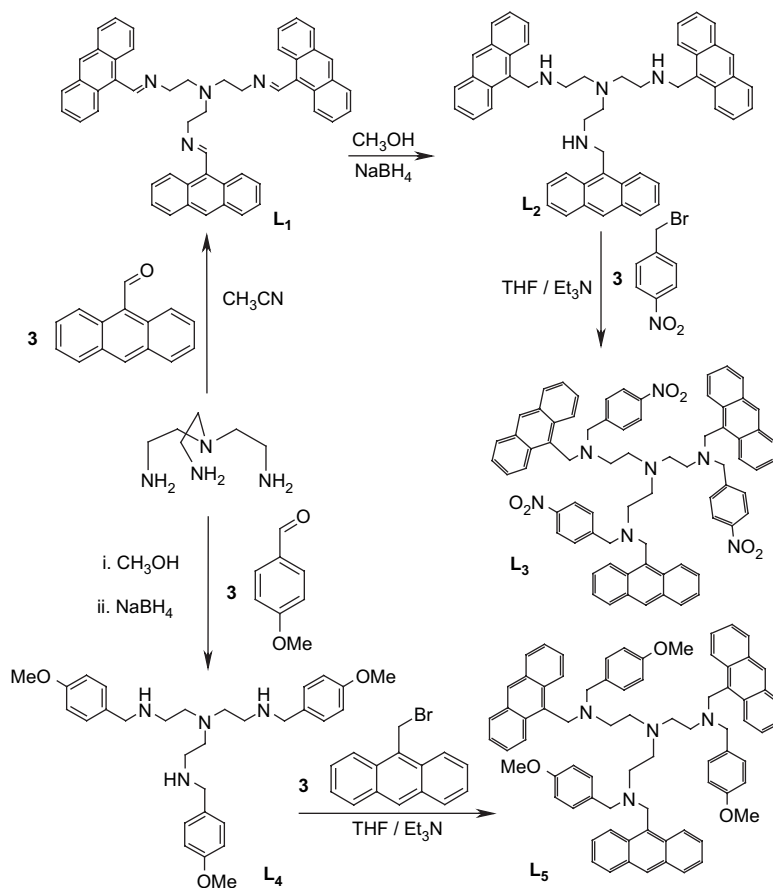
1. Introduction

The development of molecular fluorescent sensors for metal ions is an area of immense research interest in recent years.^{1,3p} Cu(II) is the third most important trace metal ion in various biological systems and one of the most important environmental pollutant.² Detection of Cu(II), especially via methods that allow high detection sensitivity, is of high demand therefore, fluoroionophores showing fluorescence enhancement as a result of guest binding are favored over those exhibiting fluorescence quenching. However, paramagnetic Cu(II) ions are effective fluorescent quenchers either via energy or electron transfer.^{3,4} A few fluoroionophores have been reported for enhancement of fluorescence signal upon Cu(II) binding.^{5–11} These include cryptand,⁵ cyclam,⁶ aryl alkylamines,⁷ substituted boron dipyrromethene dyes,⁸ thioether and amine based acyclic ligand,⁹ acylhydrazone,¹⁰ and aza-1,3-butadiene system.¹⁰ Of course there are number of reports on photoinduced electron transfer (PET) based other metal ion sensors.¹¹ Though the tren moiety has been extensively used in ligand designing for Cu(II) complexation,¹² surprisingly tren based tripodal fluoroionophores reported so far show quenching of fluorescence signal in the presence

of Cu(II).⁴ Herein, we report a tren based tripodal fluoroionophore (**L**₅) having fluorophore–spacer–receptor format and bearing *p*-methoxy phenyl moieties in close proximity (Chart 1) to the photoinduced electron transfer (PET) unit for the enhancement of emission intensity in the presence of paramagnetic Cu(II) ions. We also report that Cu(II) shows quenching of fluorescence in the case of **L**₂ and no effect in the output functionality when electron withdrawing *p*-nitro phenyl unit is attached to **L**₂, i.e., in **L**₃ (Chart 1). To the best of our knowledge **L**₅ is the first example of a PET based acyclic tripodal fluoroionophoric system, which


 Chart 1. Chemical structures of fluoroionophores **L**₂, **L**₃, and **L**₅.

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Scheme 1. Synthetic route to compounds **L**₂, **L**₃, and **L**₅.

exhibits fluorescence enhancement in the presence of Cu(II) ions. We have synthesized **L**₂, **L**₃, **L**₅ and studied their fluorescence properties with the first row transition, alkali and alkaline earth metal ions in dry tetrahydrofuran (THF).

All three ligands are composed of an ionophore having N4 donor sets from the tren moiety for metal-ion binding, and a fluorophore unit (anthracene) attached to three nitrogen centers separated by one methylene spacer whereas they are different in terms of attached pendent moiety, which alters the lone pair availability on the nitrogen centers. Preparation of these ligands was achieved following Scheme 1.

2. Results and discussion

2.1. Synthesis

In brief, **L**₂ was prepared using a two-step reaction. Reaction between tren and 9-anthraldehyde in MeCN yielded Schiff base **L**₁ as a solid product, which was isolated upon filtration, in 95% yield. **L**₁, upon reduction in methanol, produced **L**₂ in 80% yield as brown oil. **L**₃ was synthesized from **L**₂ in a one-step reaction of *p*-nitro benzyl bromide in the presence of triethylamine in THF. The crude product was purified using column chromatography (EtOAc/DCM 4:1) in 60% yield as a yellow solid. **L**₅ was synthesized following a different route. Firstly, **L**₄ was obtained upon reaction between tren and *p*-methoxy benzaldehyde in methanolic solution followed by in situ reduction using NaBH₄, the crude yellow

oily material obtained after usual work up was purified by column chromatography (alumina, CH₃COOC₂H₅/CHCl₃ 2:8) in 65% yield as a bright yellow oil. **L**₄ upon reaction with 9-bromomethyl anthracene¹³ in THF yielded a crude material which was purified by column chromatography (silica gel, CH₃COOC₂H₅/CHCl₃ 1:1) to yield the trianthryl derivative **L**₅ in 80% yield as a yellow solid. Details of the synthesis and characterization of all new compounds (**L**₁–**L**₅) are given in Section 4.

2.2. Fluorescence emission spectra of **L**₂, **L**₃, and **L**₅ in the presence of different cation inputs

Compound **L**₂ containing a fluorophore–spacer–receptor configuration shows a low intense well-resolved anthracene monomer emission (band positions are at 393, 415, 441 nm). The quantum yield (Φ_F) of the system is 0.021 in THF at 298 K versus Φ_F of 0.297 for free anthracene in ethanol under the same experimental conditions, i.e., a reduction by a factor of about 14, which is assumed to be due to PET from the nitrogen lone pairs to the excited state of anthracene. The ionophore **L**₂ contains three secondary and one tertiary nitrogen atoms, which would be expected to promote coordination with transition metal ions. **L**₂ shows fluorescence enhancement ($\Phi_F=0.056$ – 0.117) with a negligible spectral shift in the presence of Co(II)/Mn(II)/Cr(III)/Zn(II) input whereas in the case of Cu(II)/Ni(II), a quenching of fluorescence is observed (Table 1). The fluorescence enhancement factor (FEF), in terms of quantum yield, compared to that of **L**₂ ranges from 3 to about 6 in the cases of

Table 1. Fluorescence output of **L**₂, **L**₃, and **L**₅ with different cation inputs^a

Ionic input	(0,0) Band position (nm)			Fluorescence output (Φ_F)			FEF		
	L ₂	L ₃	L ₅	L ₂	L ₃	L ₅	L ₂	L ₃	L ₅
Nil	392.9	391.0	392.6	0.021	0.072	0.007	1	1	1
Cr(III)	394.7	392.4	398.4	0.089	0.077	0.077	4.2	0.9	11
Mn(II)	394.1	391.0	394.0	0.056	0.068	0.025	2.7	0.9	3.6
Fe(II)	395.1	390.0	399.0	0.034	0.063	0.023	1.6	0.9	2.3
Co(II)	394.2	392.5	396.8	0.060	0.054	0.037	2.9	0.7	5.3
Ni(II)	392.9	390.5	393.2	0.014	0.036	0.006	0.7	0.5	0.9
Cu(II)	393.2	391.2	400.0	0.010	0.050	0.077	0.5	0.7	11
Zn(II)	393.5	392.7	398.3	0.117	0.082	0.042	5.6	1.1	6
HCl	395.2	392.1	400.1	0.508	0.088	0.144	24.2	1.2	20.6

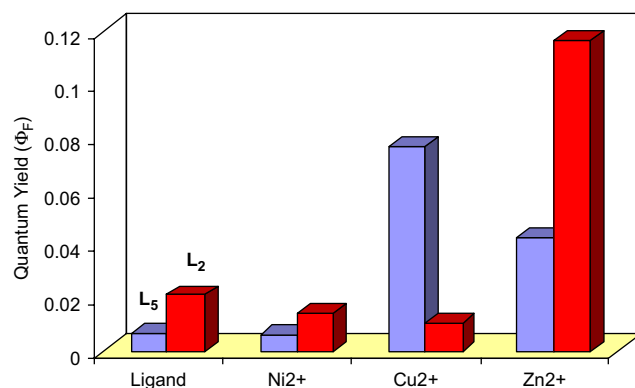
^a Experimental conditions: medium, dry THF; concentration of **L**₂, **L**₃, and **L**₅, 1×10^{-6} M; concentration of ionic input, 1×10^{-4} M. Excitation at 368 nm with band-pass of 3.0 nm; emission band-pass, 3.0 nm; temperature, 298 K; Φ_F calculated by comparison of emission spectrum with that of anthracene ($\Phi_F=0.297$) taking area under the total emission. The error in Φ_F is within 10% in each case, except for free ligands, where the error in Φ_F is within 15%.

transition metal ions Co(II)/Mn(II)/Cr(III)/Zn(II) whereas in the case of H⁺ input FEF is about 24. Though Cr(III) to Co(II) enhances the fluorescence output in **L**₂, Ni(II)/Cu(II) still behaves as a quencher in this system. In our previous study we have shown that when thiophene units are attached in the nitrogen centers of the PET unit in **L**₂ become a viable candidate for sensing of Ce(III) and shows negligible effect of fluorescence with the transition metal ions,¹⁴ which indicates that the substitution in the nitrogen centers might change the input/output functionality in tripodal fluoroionophoric systems. System **L**₅ bearing three *p*-methoxy benzyl units in close proximity to the fluoroionophores shows lower intense ($\Phi_F=0.007$) well-resolved anthracene monomer emission than that of **L**₂ under same experimental conditions, i.e., a reduction of a factor of 42 compared to the free anthracene fluorescence. This indicates that effective PET is operative in the case of **L**₅ compared to **L**₂, which may be due to the close proximity of electron donating moieties to the fluorophore that increases the lone pair availability on all four amino nitrogen centers of the PET units. **L**₅ shows appreciable fluorescence enhancement with a red shift (4–7 nm) in the presence of Co(II)/Fe(II)/Mn(II)/Cr(III)/Zn(II) or H⁺ as an input (Table 1). Interestingly, Cu(II), which quenches the fluorescence of **L**₂, shows appreciable fluorescence enhancement by a factor of 11 in the case of **L**₅ whereas Ni(II) still shows quenching (Table 1). In the case of Cu(II) there is ~7 nm red shift of the anthracene monomer emission whereas there is no shift in the case of Ni(II). The observed differences between Cu(II) and Ni(II) inputs are more difficult to rationalize. Although Cu(II) itself is also a quencher, the quenching efficiency of Cu(II) might be lower than the amino nitrogen atoms, depending upon the nature of the substituents in the amino groups, as evidenced by the different behavior of **L**₂, **L**₃, and **L**₅ (Table 1). Among them, the amino groups (electron donating in nature) in **L**₅ are the strongest quenchers, so the fluorescence quantum yield is lower compared to **L**₂ and **L**₃. However, the amino groups in **L**₅ are also the best electron donors for chelation with the metal ions, so **L**₅ becomes the most sensitive compound in response to metal-ion binding. Probably in the case of **L**₅, Cu(II) is coordinated well by all four nitrogen atoms, but the other metal ion can only interact with some of the four amino groups thus the fluorescence enhancement is larger for Cu(II) than the other metal ions. The observed FEF with Cu(II) input in the case of **L**₅ is even higher than that of Zn(II), which is a non-quencher ion for fluorescence

output, indicating that Cu(II) is strongly bound to the lone pairs of the nitrogen centers and effectively reduces the PET process in **L**₅ which shows appreciable recovery of the fluorescence output of the anthracene units (Fig. 1).

We have also verified the influence of other metal ions on the fluorescence behavior of **L**₅ to determine whether there is any preference of this ionophore toward Cu(II). In the cases of Ni(II), Cu(II), and Zn(II) as an individual input, the **L**₅ shows maximum fluorescence with Cu(II) and minimum output with Ni(II). When premixed inputs of 100 equiv of each of the metal ion, (Cu(II) and Ni(II)), (Cu(II) and Zn(II)), (Cu(II), Ni(II), and Zn(II)), are studied under same experimental conditions, in all cases outputs are close to the Cu(II) input (Fig. 2). These results indicate that Cu(II) has a stronger affinity toward **L**₅ in comparison to Zn(II) and Ni(II), although some influence of Ni(II) quencher on the output is evident in mixed metal ions' system. In another experiment, 100 equiv of Cu(II) is separately added to the solution of **L**₅ containing Ni(II)/Zn(II), in both the cases fluorescence output increases to the value as in the case of premixed metal ions,¹⁵ which indeed explain that **L**₅ has a preference toward Cu(II).

To address the sensitivity of **L**₅ toward Cu(II) sensing we have carried out fluorescence titration of **L**₅ (1 μ M) in dry THF with Cu(II) as an input ion (Fig. 3). There is no such detectable change in the output up to the 2 μ M analyte concentration. An appreciable enhancement of quantum

**Figure 1.** Comparative fluorescence quantum yield data for fluoroionophores **L**₂ and **L**₅ along with metal ion inputs.

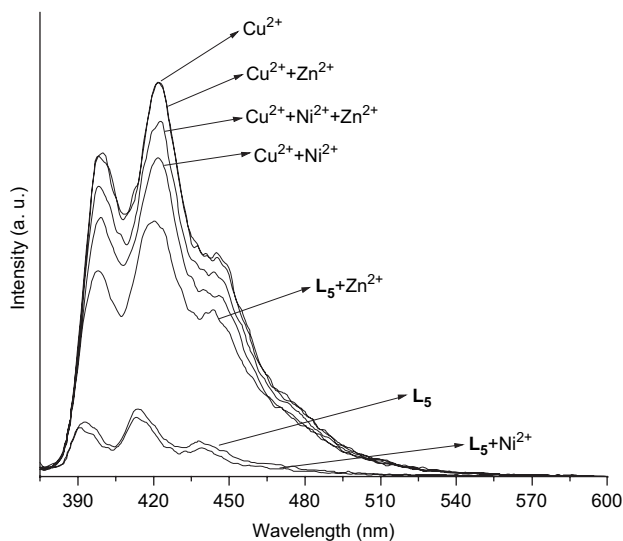


Figure 2. Fluorescence spectra of L_5 ($c=1 \times 10^{-6}$ M) in THF, L_5 in the presence of Cu^{2+} and other metal ions ($\lambda_{exc}=368$ nm).

yield by a factor of 3 is observed in the presence of 3 μ M Cu(II) whereas maximum fluorescence enhancement was observed in the presence 100 μ M Cu(II). In the presence of 500 μ M Cu(II) there is a slight drop in output functionality. This experiment shows that the low detectable limit of Cu(II) in THF medium with L_5 is 3 μ M in our experimental conditions. The binding constant value of Cu^{2+} with L_5 has been determined from the emission intensity data following the modified Benesi–Hildebrand equation,¹⁶ $1/\Delta I = 1/\Delta I_{max} + (1/K[C])(1/\Delta I_{max})$. Here $\Delta I = I - I_{min}$ and $\Delta I_{max} = I_{max} - I_{min}$, where I_{min} , I , and I_{max} are the emission intensities of L_5 considered in the absence of Cu^{2+} , at an intermediate Cu^{2+} concentration, and at a concentration of complete interaction, respectively, and where K is the binding constant and $[C]$ the Cu^{2+} concentration. From the plot of $(I_{max} - I_{min})/(I - I_{min})$ against $[C]^{-1}$ for L_5 (Fig. 4), the value of K ($\pm 15\%$) extracted from the slope is 4.5×10^4 M^{-1} .

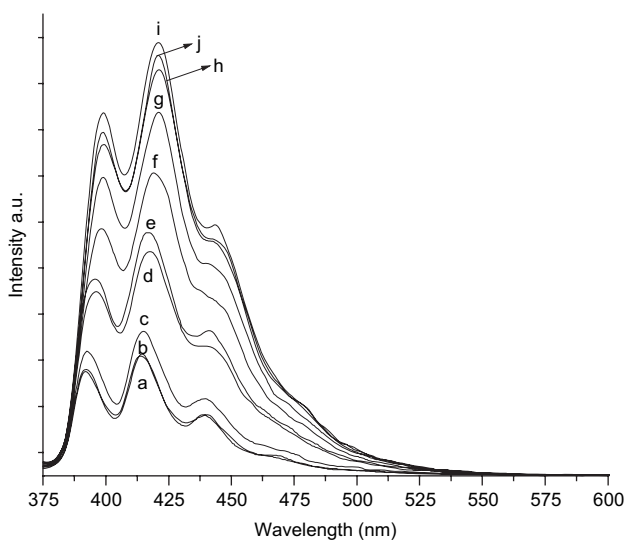


Figure 3. Fluorescence spectra of L_5 ($c=1 \times 10^{-6}$ M) in dry THF solution at 298 K (a–j) upon addition of 0, 1, 2, 3, 4, 5, 10, 50, 100, and 500 equiv of Cu(II).

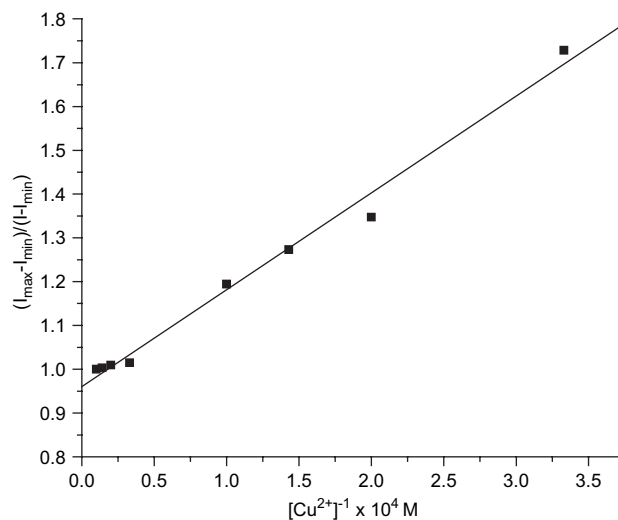


Figure 4. Fluorescence intensity of L_5 (in THF) at each concentration of Cu^{2+} added, normalized between the minimum fluorescence intensity, found at 0 equiv of Cu^{2+} and the maximum fluorescence intensity, found at $[Cu^{2+}] = 3 \times 10^{-4}$ M.

The influence of alkali metal ions Na(I), K(I), Rb(I), Cs(I) and alkaline earth metal ions like Mg(II), Ca(II), Ba(II) in their hydrated form has also been studied on L_2 as well as L_5 under the same experimental conditions. In both cases, there is no effect on fluorescence output with the above mentioned input metal ions. These results indicate that electron rich N4 donor sets of L_2 and L_5 are not suitable for binding alkali/alkaline earth metal ions in THF medium.

To find out the effect of electron withdrawing moiety attached to the nitrogen atoms of PET center we have synthesized L_3 bearing three *p*-nitro benzyl units. L_3 does not show any appreciable change in fluorescence in the presence of Ni(II)/Cu(II)/Zn(II) or H^+ (Table 1),¹⁵ which indicates that L_3 is not susceptible for protonation or complex formation with the above metal ions.

The metal perchlorate salts are hydrated and can generate protons in organic solvents. The generated protons can engage the lone pairs of nitrogen through protonation causing fluorescence enhancement. To probe that the fluorescence quantum yield enhancement by Cu(II) in the case of L_5 is not due to the protons generated, following control experiments are carried out. When no Cu(II) is added in THF/ H_2O (9:1 v/v) medium, fluorescence output is same as observed in the case of dry THF medium. When the input is a hydrated Cu(II) salt (10^{-4} M) in THF/ H_2O (1:1) medium fluorescence intensity (Fig. 5, trace b) is about 4.5 times lower compared to the case when dry THF is used (Fig. 5, trace a). This could be due to partial protonation of the nitrogens in the receptor unit as a result of generation of protons upon addition of a transition metal ion in aqueous THF medium. Further, when 0.5 and 1.0 mL polar solvent like H_2O is added in to 9.5 and 9.0 mL of fully Cu(II) titrated dry THF solution, respectively (final ligand and Cu(II) concentrations are maintained 10^{-6} and 10^{-4} M, respectively), in both the cases fluorescence intensity reduced to the value close to the intensity which is observed in the case of b. This could be due to partial protonation of nitrogen centers of the

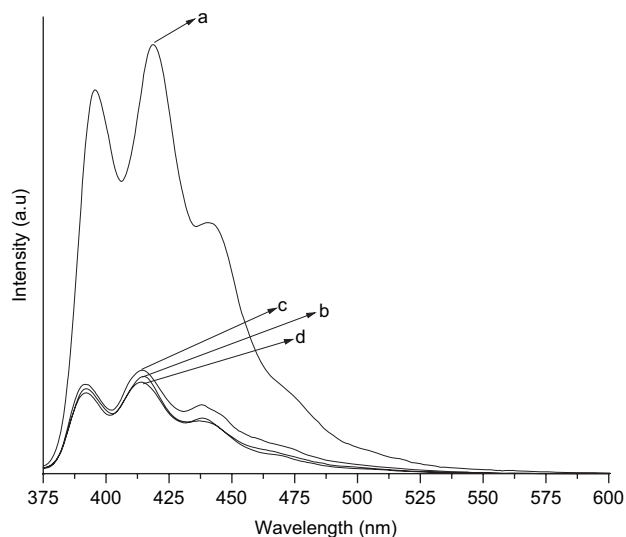


Figure 5. Fluorescence spectra of L_5 ($c=1 \times 10^{-6}$ M) in the presence of 100 equiv Cu(II) in dry THF solution (a) and THF/H₂O (1:1) (b), addition of H₂O in fully Cu(II) titrated THF solution THF/H₂O (19:1) (c) and (9:1) (d); at 298 K ($\lambda_{\text{exc}}=368$ nm).

receptor followed by demetalation in the presence of polar solvent.

2.3. Electrochemical studies

Further, we have performed cyclic voltammetry (CV) experiments with L_5 and L_5 in the presence of Ni²⁺/Cu²⁺/Zn²⁺ to ascertain the different behavior of Cu²⁺ and Ni²⁺ toward the fluorescence output of L_5 (Fig. 6). The CV of the receptor L_5 showed an irreversible oxidation wave at ca. +1.47 V which may be assigned to the oxidation of the anthracenyl groups

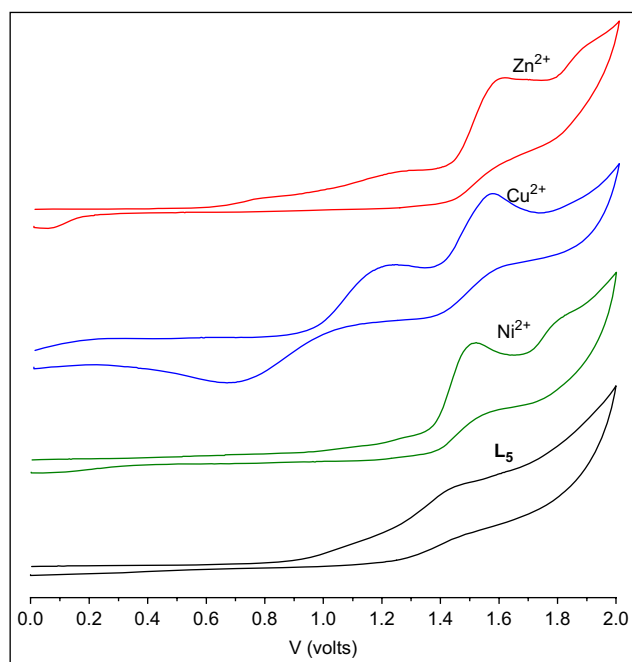


Figure 6. Cyclic voltammogram changes observed for the oxidation wave of compound L_5 , in acetonitrile, after addition of 10 equiv of Ni²⁺, Cu²⁺, and Zn²⁺ as perchlorate salts.

and is comparable with the oxidation potential of anthracene (+1.56 V vs NHE). The addition of Ni²⁺ caused no significant perturbation in the oxidation potential (+1.46 V) compared to the free receptor. But the oxidation wave of anthryl moiety is anodically shifted with respect to the free receptor after the addition of Cu²⁺ ($\Delta E_{1/2}=110$ mV) or Zn²⁺ ($\Delta E_{1/2}=100$ mV), which might support the formation of the complexed species $[L_5 \cdot Cu]^{2+}$ or $[L_5 \cdot Zn]^{2+}$. In the case of Cu²⁺ an additional redox process is observed with $E_{1/2}=+1.19$ V, which is quasi-reversible. Since this is not observed in the case of Zn²⁺, this seems to be metal based.

3. Conclusion

In conclusion, the present study demonstrates that L_5 bearing three *p*-methoxy benzyl units attached to the nitrogen centers of PET units is a viable candidate for fluorescence enhancement with Cu(II) in THF. This study also shows that L_5 has a preference in binding toward Cu(II) over other metal ions like Ni(II) and Zn(II) and has a lower detection limit of 3 μ M of Cu(II) in THF. We have also synthesized a number of tripodal ligands with different coordination sites and substituted aryl moieties in close proximity to the fluorophores to probe binding and sensing with transition/inner-transition metal ions.

4. Experimental section

4.1. Materials

Tris-(2-aminoethyl)amine (tren), 9-anthraldehyde, *p*-anisaldehyde, *p*-nitro benzylbromide, 9-anthracene methanol, anhydrous sodium sulfate, bromine, triphenyl phosphine, Cr(ClO₄)₃·6H₂O, Mn(ClO₄)₂·H₂O, Fe(ClO₄)₂·H₂O, Co(ClO₄)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(ClO₄)₂·6H₂O, Zn(ClO₄)₂·6H₂O, NaClO₄·H₂O, KClO₄·H₂O, CsClO₄·H₂O, RbClO₄·H₂O, Mg(ClO₄)₂·H₂O, Ca(ClO₄)₂·4H₂O, and Ba(ClO₄)₂·H₂O were purchased from Aldrich chemicals Co. and used without further purification. Triethylamine was purified with calcium hydride prior to use. Chloroform, methanol, dichloromethane, acetonitrile, and tetrahydrofuran were also procured from SD Fine (India) Ltd. and were purified prior to use following standard procedures. Tetrahydrofuran (THF) was dried under a nitrogen atmosphere from potassium benzophenone ketyl.

4.2. Measurements

¹H NMR and ¹³C NMR spectra were recorded on a Bruker 200 MHz and 50 MHz FT-NMR spectrometers. The chemical shifts are reported in parts per million on the scale using tetramethyl silane (TMS) as a reference. MS (ESI) measurements were carried out on a Qtof Micro YA263 HRMS instrument. The absorption spectra were recorded with a Cary Varian UV–vis–NIR scanning spectrophotometer at 298 K. The fluorescence spectra were recorded using Perkin Elmer luminescence spectrophotometer at 298 K. Electrochemical measurements were carried out with a Princeton Applied Research potentiostat/Glavanostat Model 273A. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting of platinum

working and auxiliary electrodes and a Ag/Ag⁺, NaCl (satd) reference electrode. The experiments were carried out with a 10⁻³ M solution of sample in acetonitrile containing 0.1 M *n*-tetrabutylammonium perchlorate as supporting electrolyte. Deoxygenation of the solutions was achieved by bubbling nitrogen gas for at least 5 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate of 100 mV S⁻¹. The guest under investigation was then added as a 10⁻² M solution.

4.3. Syntheses of L₁ and L₂

A solution of tris-(2-aminoethyl)amine (0.71 mL, 4.72 mmol) in 25 mL of dry CH₃CN was added dropwise to a solution of 9-anthraldehyde (97%) (3.0 g, 4.16 mmol) in dry CH₃CN (50 mL). The reaction mixture was stirred vigorously under N₂ atmosphere at rt for 6 h. The yellow precipitate formed was removed by filtration, washed several times with cold CH₃CN, and dried under vacuum. Schiff base L₁ was obtained in 95% yield as yellow solid. Mp 210 °C, FTIR (cm⁻¹, KBr): 1637.45 (s, -C=N, str). ¹H NMR (CDCl₃, TMS, 200 MHz) δ: 3.39 (t, 6H, -NCH₂, J=6 Hz), 4.21 (t, 6H, -NCH₂CH₂, J=6 Hz), 7.39 (m, 12H, ArH), 7.88 (d, 12H, ArH, J=8.72 Hz), 8.32 (s, 3H, ArH), 9.34 (s, 3H, -CH=N). ¹³C NMR (CDCl₃, 50 MHz) δ: 56.4 (NCH₂), 61.9 (NCH₂CH₂), 125.7, 127.2, 128.7, 129.4, 129.8, 130.5, 131.8 (Ar), 161.9 (-CH=N). HRMS (positive ESI): *m/z* 711.2412 [L₁⁺] 100%.

About 600 mg of L₁ was dissolved in 150 mL of dry methanol in 250 mL round bottom flask. Excess NaBH₄ was added portionwise over a period of 30 min to the stirring solution at about 5 °C. Resulting solution was stirred at rt for 12 h and finally refluxed for 2 h. Methanol was evaporated under vacuum. To the evaporated mass, 100 mL distilled water was added and extracted with chloroform (3×30 mL). The combined organic phases were dried with anhydrous Na₂SO₄, and the solvent was evaporated to obtain the desired product (tris-((2-anthracen-9-ylmethylamino)ethyl)amine), L₂: yield: 80% as brown oil. FTIR (cm⁻¹, KBr): 1672.17 (s, -NH, ben), 3053.11 (br, -NH, str). ¹H NMR (CDCl₃, TMS, 200 MHz) δ: 2.44 (t, 6H, -NCH₂, J=6 Hz), 2.61 (t, 6H, -NCH₂CH₂, J=6 Hz), 4.44 (s, 6H, ArCH₂), 7.34 (m, 12H, ArH), 7.92 (d, 6H, ArH, J=7 Hz), 8.11 (d, 6H, ArH, J=7 Hz), 8.30 (s, 3H, ArH), 1.94 (br, NH). ¹³C NMR (CDCl₃, 50 MHz) δ: 45.9 (NCH₂), 48.5 (NCH₂CH₂), 55.5 (ArCH₂), 124.8, 125.5, 126.6, 127.7, 129.7, 130.9, 132.1 (Ar). HRMS (positive ESI): *m/z* 716.9083 [L₂⁺] 100%.

4.4. Synthesis of L₃

Compound L₂ (1.052 g, 1.46 mmol) was dissolved in 60 mL of dry THF and slight excess of dry Et₃N (0.5 mL, ~5.0 mmol) was added. The mixture was stirred at rt under Ar atmosphere. After half an hour, a solution of *p*-nitro benzyl bromide (0.952 g, 4.4 mmol) in 20 mL of dry THF was added to the reaction mixture for a period of 1 h and stirring was continued for another 6 h at rt. Finally, the reaction mixture was refluxed for 2 h. The precipitated triethylamine hydrobromide was removed by filtration. The filtrate containing the desired product was evaporated under vacuum. The residue was dissolved in 25 mL of CHCl₃ and washed

with water (3×30 mL) to remove unreacted triethylamine. The organic layer collected was dried with anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified using column chromatography (EtOAc/DCM 4:1) to isolate the desired product L₃ as yellow solid in 60% yield. Mp 135 °C, FTIR (cm⁻¹, KBr): 1560.32, 1384.79 (s, -NO₂, str), 3053.11 (m, C-H, str). ¹H NMR (CDCl₃, TMS, 200 MHz) δ: 2.23 (br, 12H, NCH₂CH₂), 3.17 (s, 6H, ArCH₂), 3.99 (s, 6H, ArCH₂), 6.94 (d, 6H, ArH, J=7 Hz), 7.32 (m, 12H, ArH), 7.71 (m, 12H, ArH), 8.03 (s, 3H, ArH), 8.13 (d, 6H, ArH, J=9 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 51.5 (NCH₂CH₂), 52.6 (ArCH₂), 58.5 (ArCH₂), 114.7, 123.3, 127.3, 128.2, 129.5, 130.5, 133.6, 148.1, 148.6 (Ar). HRMS (positive ESI): *m/z* 1122.0074 [L₃+H⁺] 100%.

4.5. Syntheses of L₄ and L₅

A solution of tris-(2-aminoethyl)amine (1.7 mL, 11 mmol) in dry methanol (40 mL) was added to the 100 mL of methanolic solution of *p*-methoxy benzaldehyde (4 mL, 33 mmol). The mixture was stirred at rt in N₂ atmosphere for 6 h and the progress of the reaction was monitored by TLC on silica, ethyl acetate/chloroform 4:6. Stirring the mixture at elevated temperature (60 °C) for another 2 h was allowed the completion of the condensation reaction. Then the reaction mixture was cooled to 5 °C and a slight excess of solid NaBH₄ was added in portion and the reaction mixture was slowly allowed to warm at rt with constant stirring for 3 h. Reduction of Schiff base was monitored by TLC on neutral alumina, CH₃COOC₂H₅/CHCl₃ 1:1. After complete reduction the solvent was removed under reduced pressure. The solid was dissolved in 100 mL of dichloromethane and the organic solution was washed with water (3×100 mL) and dried over anhydrous Na₂SO₄. The crude yellow oily material obtained after the evaporation of the solvent was finally purified by column chromatography (alumina, CH₃COOC₂H₅/CHCl₃ 2:8) to obtain the tripodal amine L₄ as yellow oil: yield: 65%. FTIR (cm⁻¹, KBr): 1033.77, 1245.93 (s, -C-O, str), 1610.45 (s, -NH, ben), 3298.05 (br, -NH, str). ¹H NMR (CDCl₃, TMS, 200 MHz) δ: 2.14 (t, 6H, NCH₂, J=6 Hz), 2.61 (t, 6H, NCH₂CH₂, J=6 Hz), 3.66 (s, 6H, ArCH₂), 3.781 (s, 9H, -OCH₃), 6.82 (d, 6H, ArH, J=8.74 Hz), 7.13 (d, 6H, ArH, J=8.74 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 48.8 (NCH₂), 50.4 (NCH₂CH₂), 54.3 (ArCH₂), 57.1 (-OCH₃), 115.2, 130.4, 132.6, 158.7 (Ar). HRMS (positive ESI): *m/z* 507.2061 [L₄+H⁺] 78%.

The tripodal amine L₄ (0.54 g, 1.1 mmol) was dissolved in 75 mL of dry THF and a slight excess of dry triethylamine (4 mmol, 0.4 mL) was added to the above solution. The mixture was stirred at rt under N₂ atmosphere for 30 min. Then a solution of 9-bromomethyl anthracene¹³ (0.87 g, 3.2 mmol) in 25 mL dry THF was added dropwise for a period of 1 h to the above solution and the mixture was stirred at rt for 5 h and then at ~65 °C for another 2 h. After completion of the reaction, triethylammonium bromide formed as a precipitate was filtered off. The filtrate was evaporated under vacuum and the resulting light yellow liquid was redissolved in 10 mL CH₂Cl₂. The organic layer was washed with distilled water (3×100 mL) and the combined organic layers were dried over anhydrous Na₂SO₄. After the removal

of solvent a yellowish semi-solid was obtained. The crude product was finally purified by column chromatography (silica gel, CH₃COOC₂H₅/CHCl₃ 1:1) to obtain the desired product **L**₅ as a yellow solid: yield: 80%, Mp 110 °C, FTIR (cm⁻¹, KBr): 1099.35, 1299.93 (s, –C–O, str), 1444.58, 1670.24 (m, C=C, str), 3049.84 (m, C–H, str). ¹H NMR (CDCl₃, 200 MHz) δ: 2.14 (br, 6H, –NCH₂), 2.19 (br, 6H, –NCH₂CH₂), 3.12 (s, 6H, ArCH₂), 3.56 (s, 9H, –OCH₃), 3.98 (s, 6H, ArCH₂), 6.58 (d, 6H, ArH, *J*=8.7 Hz), 6.68 (d, 6H, ArH, *J*=8.7 Hz), 7.28 (m, 12H, ArH), 7.74 (d, 6H, ArH, *J*=7 Hz), 8.14 (s, 3H, ArH), 8.20 (d, 6H, ArH, *J*=7.4 Hz). ¹³C NMR (CDCl₃, 50 MHz) δ: 51.4 (NCH₂), 52.7 (NCH₂CH₂), 53.3 (ArCH₂), 55.5 (ArCH₂), 58.8 (–OCH₃), 114, 125.4, 126.1, 127.9, 129.5, 130.9, 132.0, 159.1 (Ar). HRMS (positive ESI): *m/z* 1077.1470 [**L**₅⁺] 100%.

4.6. Quantum yield

The emission quantum yields (Φ_F) were obtained by comparing the areas under the curve (375–500 nm) of the sample and the standard (anthracene in ethanol, $\Phi_F=0.297$) using the following equation.

$$\text{Quantum yield, } \Phi_F = \Phi_s(A_s/A_u)(F_u/F_s)(\eta_u^2/\eta_s^2)$$

Whereas, A_s and A_u are absorbances of standard and unknown solutions, respectively. F_s and F_u are the peak areas under the curve of standard and unknown, respectively. η_s and η_u are the refractive indexes of the solvents for standard and unknown solution, respectively. Φ_s is the quantum yield of the standard.

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Supplementary data

Characterization data (¹H NMR, ¹³C NMR, and HRMS spectra) and UV–vis and fluorescence data of **L**₂, **L**₃, and **L**₅ in the presence of different inputs. This material is available free of charge via the internet at <http://sciencedirect.com>. Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.tet.2007.10.041](https://doi.org/10.1016/j.tet.2007.10.041).

References and notes

- (a) Amendola, V.; Fabbri, L.; Foti, F.; Licchelli, M.; Mangano, C.; Pallavicini, P.; Poggi, A.; Sacchi, D.; Taglietti, A. *Coord. Chem. Rev.* **2006**, *250*, 273–299; (b) Bharadwaj, P. K. *Prog. Inorg. Chem.* **2003**, *51*, 251–331; (c) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccaroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59–83; (d) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3–40; (e) Ramachandram, B.; Saroja, G.; Sankaran, N. B.; Samanta, A. *J. Phys. Chem. B* **2000**, *104*, 11824–11832; (f) de Silva, A. P.; Gunaratne, H. Q. N.;

Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566; (g) *Fluorescent Chemosensors for Ion and Molecule Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1997.

- (a) Linder, M. C.; Hazegh-Azam, M. *Am. J. Clin. Nutr.* **1996**, *63*, 797S–811S; (b) Beyersmann, D. *Metals and Their Compounds in Environment*; Merian, E., Ed.; VCH: Weinheim, 1991.
- (a) Mei, Y.; Bentley, P. A.; Wang, W. *Tetrahedron Lett.* **2006**, *47*, 2447–2449; (b) Mokhir, A.; Kiel, A.; Hertel, D.-P.; Krämer, R. *Inorg. Chem.* **2005**, *44*, 5661–5666; (c) Kaur, S.; Kumar, S. *Tetrahedron Lett.* **2004**, *45*, 5081–5085; (d) Roy, B. C.; Chandra, B.; Hromas, D.; Mallik, S. *Org. Lett.* **2003**, *5*, 11–14; (e) Boiocchi, M.; Fabbri, L.; Licchelli, M.; Sacchi, D.; Vázquez, M.; Zampa, C. *Chem. Commun.* **2003**, 1812–1813; (f) Zheng, Y.; Orbulescu, J.; Ji, X.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. *J. Am. Chem. Soc.* **2003**, *125*, 2680–2686; (g) Li, Y.; Yang, C. M. *Chem. Commun.* **2003**, 2884–2885; (h) Brasola, E.; Mancin, F.; Rampazzo, E.; Tecilla, P.; Tonellato, U. *Chem. Commun.* **2003**, 3026–3027; (i) Zheng, Y.; Cao, X.; Orbulescu, J.; Konka, V.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. *Anal. Chem.* **2003**, *75*, 1706–1712; (j) Zheng, Y.; Gattás-Asfura, K. M.; Konka, V.; Leblanc, R. M. *Chem. Commun.* **2002**, 2350–2351; (k) Zheng, Y.; Huo, Q.; Kele, P.; Andreopoulos, F. M.; Pham, S. M.; Leblanc, R. M. *Org. Lett.* **2001**, *3*, 3277–3280; (l) Klein, G.; Kaufmann, D.; Schürch, S.; Reymond, J.-L. *Chem. Commun.* **2001**, 561–562; (m) Bodenant, B.; Weil, T.; Businelli-Pourcel, M.; Fages, F.; Barbe, B.; Pianet, I.; Laguerre, M. *J. Org. Chem.* **1999**, *64*, 7034–7039; (n) Grandini, P.; Mancin, F.; Tecilla, P.; Scrimin, P.; Tonellato, U. *Angew. Chem., Int. Ed.* **1999**, *38*, 3061–3064; (o) Bolletta, F.; Costa, I.; Fabbri, L.; Licchelli, M.; Montalti, M.; Pallavicini, P.; Prodi, L.; Zaccaroni, N. *J. Chem. Soc., Dalton Trans.* **1999**, 1381–1385; (p) Krämer, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 772–773; (q) Torrado, A.; Walkup, G. K.; Imperoali, B. *J. Am. Chem. Soc.* **1998**, *120*, 609–610; (r) Yoon, J.; Ohler, N. E.; Vance, D. H.; Aumiller, W. D.; Czarnik, W. *Tetrahedron Lett.* **1997**, *38*, 3845–3848; (s) Sasaki, D. Y.; Shnek, D. R.; Pack, D. W.; Arnold, F. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 905–907; (t) Fabbri, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Sacchi, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1975–1977; (u) Rurack, K.; Resch, U.; Senoner, M.; Daehne, S. *J. Fluoresc.* **1993**, *3*, 141–143; (v) Kemlo, J. A.; Shepherd, T. M. *Chem. Phys. Lett.* **1977**, *47*, 158–162; (w) Varnes, A. V.; Dodson, R. B.; Whery, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 946–950.
- (a) Fabbri, L.; Licchelli, M.; Parodi, L.; Poggi, A.; Taglietti, A. *Eur. J. Inorg. Chem.* **1999**, 35–39; (b) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccaroni, N. *Eur. J. Inorg. Chem.* **1999**, 455–460; (c) DeSantis, G.; Fabbri, L.; Licchelli, M.; Poggi, A.; Taglietti, A. *Angew. Chem., Int. Ed.* **1996**, *35*, 202–204.
- (a) Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh, S. *J. Am. Chem. Soc.* **1996**, *118*, 1553–1554; (b) Ghosh, P.; Bharadwaj, P. K.; Roy, J.; Ghosh, S. *J. Am. Chem. Soc.* **1997**, *119*, 11903–11909.
- Wu, Q.; Anslyn, E. V. *J. Am. Chem. Soc.* **2004**, *126*, 14682–14683.
- (a) Ramachandram, B.; Samanta, A. *Chem. Commun.* **1997**, 1037–1038; (b) Ramachandram, B.; Samanta, A. *J. Phys. Chem. A* **1998**, *102*, 10579–10587.

8. Rurack, K.; Kollmannsberger, M.; Resch-Genger, U.; Daub, J. *J. Am. Chem. Soc.* **2000**, *122*, 968–969.
9. (a) Kaur, S.; Kumar, S. *Chem. Commun.* **2002**, 2840–2841; (b) Wen, Z.-C.; Yang, R.; He, H.; Jiang, Y.-B. *Chem. Commun.* **2006**, 106–108.
10. (a) Martinez, R.; Zapata, F.; Caballero, A.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Lett.* **2006**, *8*, 3235–3238; (b) Martinez, R.; Espinosa, A.; Tárraga, A.; Molina, P. *Org. Lett.* **2005**, *7*, 5869–5872.
11. (a) Park, S. M.; Kim, M. H.; Choe, J.-I.; No, K. T.; Chang, S.-K. *J. Org. Chem.* **2007**, *72*, 3550–3553; (b) Youn, N. J.; Chang, S.-K. *Tetrahedron Lett.* **2005**, *46*, 125–129; (c) Sarkar, M.; Banthia, S.; Samanta, A. *Tetrahedron Lett.* **2005**, *47*, 7575–7578; (d) Fabbri, L.; Licchelli, M.; Taglietti, A. *Dalton Trans.* **2003**, 3471–3479; (e) Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S. K.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 2348–2351; (f) Chae, M. Y.; Czarnik, A. W. *J. Am. Chem. Soc.* **1992**, *114*, 9704–9705; (g) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590–3593; (h) Huston, M. E.; Engleman, C.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 7054–7056; (i) Konopelski, J. P.; Kotzyba-Hibert, F.; Lehn, J.-M.; Desvergne, J.-P.; Fagès, F.; Castellán, A.; Bouas-Laurent, H. *J. Chem. Soc., Chem. Commun.* **1985**, 433–436.
12. (a) Fischmann, A. J.; Warden, A. C.; Black, J.; Spiccia, L. *Inorg. Chem.* **2004**, *43*, 6568–6578; (b) Thaler, F.; Hubbard, C. D.; Heinemann, F. W.; Eldi, R. V.; Schindler, S.; Fàbiàn, I.; Dittler-Klingemann, A.; Hahn, F. E.; Orvig, C. *Inorg. Chem.* **1998**, *37*, 4022–4029; (c) Herrera, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M.; Mathonière, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5468–5471; (d) Schatz, M.; Becker, M.; Walter, O.; Liehr, G.; Schindler, S. *Inorg. Chim. Acta* **2001**, *324*, 173–179.
13. Bullpitt, M.; Kitching, W.; Doddrell, D.; Adcock, W. *J. Org. Chem.* **1976**, *41*, 760–766.
14. Ghosh, P.; Shukla, A. D.; Das, A. *Tetrahedron Lett.* **2002**, *43*, 7419–7422.
15. See [Supplementary data](#).
16. (a) Mallick, A.; Chattopadhyay, N. *Photochem. Photobiol.* **2005**, *81*, 419–424; (b) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.