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ORIGINAL PAPER

Fluorescent but 'choked' multipodands: Ag(I) complexation and NMR studies

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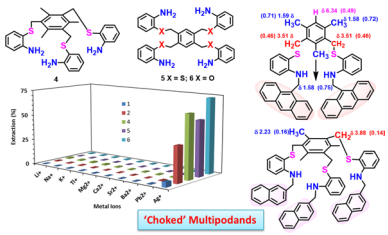
Abstract

A series of fluorescent and non-fluorescent multipodands, substituted with donor S, N, and O heteroatoms, bridged to mesitylene and benzene core at 1, 3-, 1, 3, 5-, and 1, 2, 4, 5-positions have been synthesized and characterized. The liquid–liquid extraction experiment showed that non-fluorescent podands such as mono-, di-, tri-, and tetrapod exhibited excellent complexation abilities towards Ag^+ ions. The tetrapodand (O, N) shows highest extraction of Ag^+ (73%) and tetrapodand (S, N) shows the highest Ag^+/Pb^{2+} selectivity (135). However, for fluorescent dipodands very weak complexation ability towards metal ions were observed likely due to steric crowding. Significantly, these fluorescent dipodands undergoes protonation at very low pH (ca. < 1.0), reminiscent of acid stability—a structural feature of blue copper proteins. The NMR analysis of fluorescent podands showed that amine-appended anthracene moiety(ies) almost fills the podand cavity as lid, shifting most of the protons upfield (~ 0.5 ppm), thus causing acid stability.

Graphic abstract



Keywords Transition metal compounds · NMR spectroscopy · Supramolecular chemistry · Fluorescence · Receptors

Introduction

Supramolecular chemistry has continuously progressed since the Nobel Prize to Cram, Lehn, and Pedersen in 1987 which led to great impetus to the development of new synthetic receptors for molecular recognition [1–9]. Podands, which are by definition, open chained analogues of crown compounds and cryptands, now exists in a many structural variations ranging from single chained basic compounds to multiarmed dendrimer like molecules and from highly flexible to rather rigidly preorganized molecular architectures [4–11]. From supramolecular point of view, podands can be divided into mono, di, tetra, oligo, or multipodands. These podands (branched oligo and multipodands) possess anchor group to which the podand segments are attached. Although in most cases of tripodands, three podand subunits are attached to nitrogen atom, but benzene platform, 1,3,5 triazines, calixarenes, cyclodextrins fused (aromatic) rings, steroids, or smaller molecules like glycolurils, displays interesting organization properties. Tetrapodands and

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higher polypodal structures could be constructed by considering these platforms [12–15]. Exploiting the concept of 'steric gearing' hexasubstituted benzene derivative has seen extensive use. 1,3,5-Trifunctionalised 2,4,6-(trimethyl/ethyl)benzene derivatives, in their lowest energy conformation show that the three ethyl/methyl groups and three functional groups are oriented perpendicular to the central ring in a fully alternated up-down disposition making *ababab* type arrangement of these groups [15–18]. Our group and others have reported benzene scaffold which bears different recognition units at 1,4- and 1,3,5-positions including boronic acids, ureas, thioureas, catecholates, guanidinium, imidazolium, pyrazole, oxazolines, 8-hydroxyquinoline etc., for binding of variety of anions and cations [15, 19, 20].

In nature, blue copper proteins play a key role in long range inter- and intraprotein electron transfer and are characterized by high reduction potentials, rapid transfer rates and unique spectral features compared to normal tetragonal copper complexes [21–24]. In rusticyanin the four ligating atoms (2 N + 2 S) are arranged around Cu^{2+} in a distorted tetrahedral arrangement but have high acid stability as the copper binding site is located deep within a hydrophobic region. Evidently, the potential of mixed ligating sites (S, N, O or S, N), as prevalent in nature remains more or less unexploited. The 2-aminothiophenol or 2-aminophenol which possesses N and S/O donor sites and its derivatives, have found different applications in the field of medicine, material and coordination chemistry [25–28]. We have earlier reported 2-aminothiophenol based macrocycles [29, 30] containing *para*-xylylene, and 9,10-anthracene units for Cu^{2+} coordination [31]. The 1,4-placement of ligating sites does not allow the convergence of all ligating sites towards one metal ion and these receptors result in formation of M_2L_2 or M_2L type complexes.

In continuation of our interest in multipodal and macrocyclic system [32, 33], we envisaged that 1,2- or 1,3-placement of the ligating sites on the benzene platform would encourage the convergence of these ligating sites towards one metal cation and these may be able to provide better receptors. Therefore, based on above discussed features and keeping in view the possible structural feature of the active cavity in Cu^{2+} proteins, and the additional stability provided by aromatic rings in the case of rusticyanin, we now report synthesis, complexation and NMR studies of 1,3-, 1,3,5-, and 1,2,4,5-multipodands based on 2-aminothiophenol and 2-aminophenol bridged to mesitylene (1,3,5-trimethylbenzene) and benzene platform. The presence of fluorescent moiety(ies) at one or more than one of these amine nitrogens would increase hydrophobic character as well as enables their evaluation through fluorescence spectroscopy.

Results and discussion

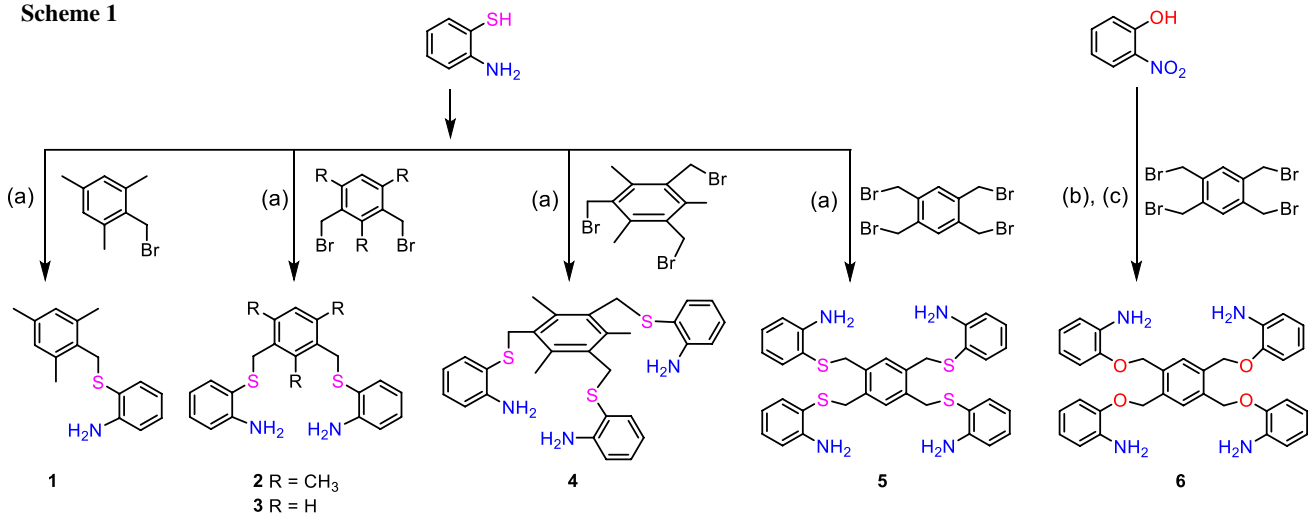
Synthesis and characterization of fluorescent multipodands

The S-alkylation of 2-aminothiophenol with 1-(bromomethyl)-2,4,6-trimethylbenzene, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene, and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, respectively in *N*,*N*-dimethylformamide (DMF), NaH (prewashed), and tetrabutylammonium hydrogensulfate as a phase transfer catalyst for 36 h followed by chromatographic (SiO_2) purification provides monopodand **1**, dipodand **2**, and tripodand **4** in excellent yields (Scheme 1). These reactions have been performed strictly in N_2 atmosphere because 2-aminothiophenol leads to the formation of disulfide bond due to oxidation in air and affects the overall yield of the reaction. We also found that using potassium carbonate as base, rather than NaH gives the comparative yields of the products. These podands showed characteristics ^{1}H NMR signals of the 2-aminophenylthio units which includes two doublets and two triplets and broad singlet of NH_2 group.

Monopodand **1** and dipodand **2** showed two singlets for methyl protons, whereas tripodand **4** showed one singlet for methyl protons which corresponds well with unsymmetrical and symmetrical nature of podands around mesitylene core. Similarly, dipodand **3** [26] and tetrapodand **5** were synthesized by reaction of 1,3-bis(bromomethyl)-benzene and 1,2,4,5-tetrakis(bromomethyl)benzene with 2-aminothiophenol under similar reaction conditions. To compare the binding ability of S with O, we also prepared tetrapodand **6** by reaction of 2-nitrophenol with 1,2,4,5-tetrakis(bromomethyl)benzene in acetonitrile using potassium carbonate as base and $TBAHSO_4$ as phase transfer catalyst in 60% yield, followed by reduction of NO_2 group with $NiCl_2/NaBH_4$ complex in methanol [36]. To distinguished between tetrapodands **5** and **6**, characteristic ^{1}H NMR signals of $-CH_2$ (methylene) was closely followed. The ^{1}H NMR peak of $-CH_2$ protons close to S-functionality showed upfield shift in compare to O-functionality.

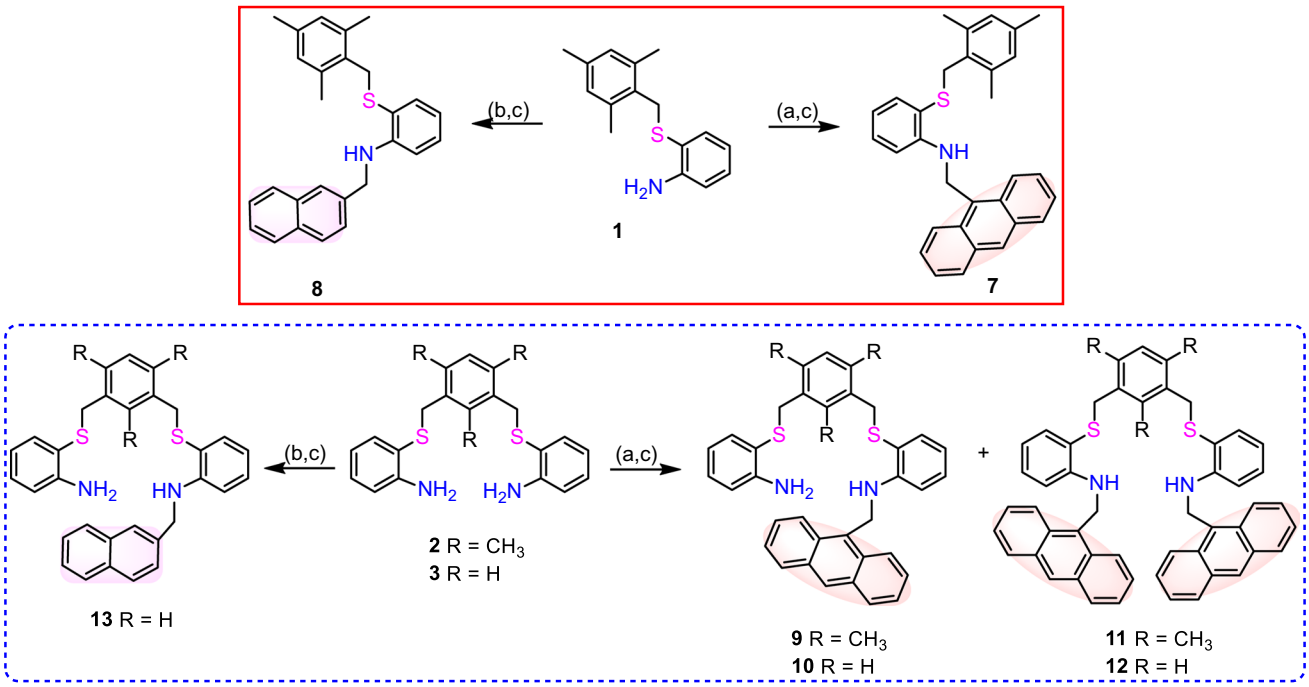
To make fluorescent multipodands, an anthracene or naphthalene fluorescent bulky group(s) were attached to the anilinyl NH_2 group by reductive amination method [37]. The presence of bulky group, either at one-, two- and three-positions as per design, would create hydrophobic pockets for metal ion complexation. Monopodand **1**, dipodand **2**, and tripodand **4** on condensation with anthracene-9-aldehyde in THF-$MgSO_4$ mixture and subsequent reduction with $NaBH_4$ in the presence of I_2 gave fluorescent

Scheme 1



a) NaH-DMF, TBA HSO_4; (b) K_2CO_3, CH_3CN, TBA HSO_4; (c) $NiCl_2/NaBH_4$, CH_3OH, $NH_2NH_2.2H_2O$

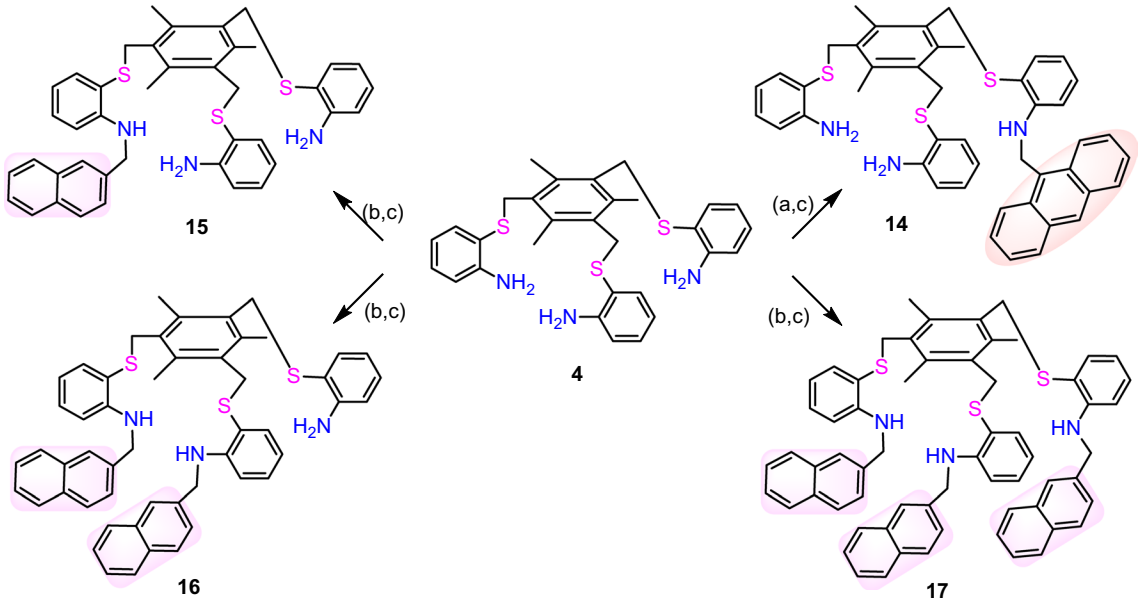
Scheme 2



(a) THF, $MgSO_4$, 9-anthracenecarbaldehyde; (b) THF, $MgSO_4$, 2-naphthaldehyde and (c) $NaBH_4$, I_2, THF

monopodand **7**, mixture of fluorescent dipodand **9** and **11**, and fluorescent tripodand **14**, respectively (Schemes 2, 3). Similarly, monopodand **1** and tripodand **4** on condensation with 2-naphthaldehyde and subsequent reduction with $NaBH_4$-I_2 gave fluorescent monopodand **8** and fluorescent tripodand **15**–**17** (Schemes 2, 3). All new compounds were characterized by ^1H and ^{13}C NMR, FAB-MS spectra, and elemental analysis. In the ^1H NMR spectra fluorescent monopodand **7** and **8** shows two singlets due to methyl groups, a singlet due to SCH_2 and doublet due to CH_2NH (converts to singlet on D_2O exchange) along with aromatic protons; fluorescent dipodand **9** exhibits three singlets due to three methyl groups, two singlets due to SCH_2, one doublet due to NCH_2 along with 2-aminophenylthio protons whereas fluorescent dipodand **11** showed two singlets for methyl protons, one singlet each for SCH_2

Scheme 3



(a) THF, $MgSO_4$, 9-anthracenecarbaldehyde; (b) THF, $MgSO_4$, 2-naphthaldehyde and (c) NaBH4, I_2, THF

and NCH_2 ($\delta = 5.18$ ppm, 4H) along with NH and aromatic H signals; fluorescent tripodand **14** exhibit two singlets for methyl group, two singlets for SCH_2 groups, a doublet due to CH_2N along with aromatic protons due to 2-aminophenylthio and anthracene moieties. Benzene based dipodand **3** on condensation with anthracene-9-aldehyde and subsequent reduction with $NaBH_4$-I_2 gave **10** (*m*/*z* peak at 542) and **12** (*m*/*z* peak at 732). Similarly, dipodand **3** on condensation with 2-naphthaldehyde followed by subsequent reduction with $NaBH_4$-I_2 gave **13** (*m*/*z* peak at 492) (Scheme 2).

Complexation studies for Ag(I) ions

As the process of ligand facilitated transport of cations across apolar membrane has relevance to the development of separation techniques for the cation, the extraction (complexation) properties of the podands towards Ag^+, Pb^{2+}, Tl^+, alkali (Li^+, Na^+, K^+), and alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations have been determined [38, 39]. Extraction profiles of these podands show that all these podands extract preferentially Ag^+ over alkali, alkaline earth, and Pb^{2+} picrates. However, the percentage extraction of the Ag^+ markedly depends on the number of 2-aminophenylthio groups present in the podands and their spatial positions. Monopodand **1** possessing only one 2-aminophenylthio group extracted only 5% Ag^+. The presence of two 2-aminophenylthio groups at 1,3-positions of dipodand **2** increased extraction of Ag^+ to 35% which was further increased to 62% in case of tripodand **4**, which possesses three 2-aminophenylthio groups at 1,3,5-positions (Fig. 1). These results clearly show that on increasing the number of aminophenylthio groups, their organization or cooperative binding with Ag^+ remarkably increases the extraction of Ag^+ from water. The cooperativity of ligating sites in tripodand **4** is also evident from the increased extraction of even alkali and alkaline earth metal ions in comparison to that of dipodand **2**. Notably, the dipodand **3** showed poor extraction (< 2%) of Ag^+ and other metal ions (< 0.5%). Therefore, probably the presence of methyl groups on benzene ring in dipodand **2** organizes the ligating sites on one plane of the

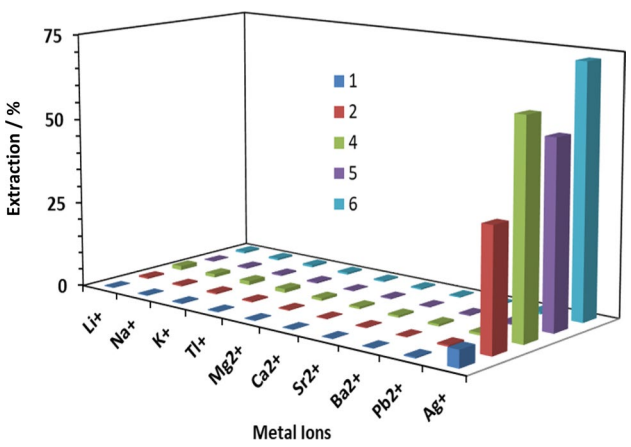


Fig. 1 Extraction (%) profile of picrate salts from water into $CHCl_3$ for podands **1**, **2**, and **4**–**6**

benzene ring and results in enhanced extraction of Ag^+ in comparison to dipodand **3** (Table S1).

On increasing the number of ligating sites to four in tetrapodand **5** in comparison to three ligating sites in tripodand **4**, the extraction of Ag^+ decreased to 54% and points to the poor organization of four ligating sites in binding with Ag^+. This can be attributed partially to the larger size of sulfur atom which does not allow the four-S-linkage on the same side of phenyl ring. However, on replacing the thioether linkages with ether linkages in tetrapodand **6**, significant increases in extraction of Ag^+ to 73% was observed. The increase in extraction of Ag^+ with increasing number of ligating sites also results in increased selectivity towards Ag^+ over similar sized Pb^{2+}. Monopodand **1** extracts Ag^+ only 12.5 times higher than Pb^{2+} but in dipodand **2** Ag^+/Pb^{2+} selectivity increases to 70 which is further increases to 89 in tripodand **4**. Tetrapodand **5** and **6** exhibit Ag^+/Pb^{2+} selectivity of the order of 135 and 121, respectively. Amongst all these podands, **6** shows highest extraction of Ag^+ (73%) and **5** shows the highest Ag^+/Pb^{2+} selectivity (135).

pH titration

The solution of **9** (50 μM, CH_3CN:H_2O, 4:1) displayed absorbance maxima at 385, 366, and 350 nm and on excitation at 366 nm it exhibited fluorescence maxima at 410 nm, with two shoulders at 390 and 437 nm, typical of anthracene unit. The fluorescent multipodands **9** and **14**, substituted with aryl/alkyl amine, are non-fluorescent due to efficient photoinduced electron transfer (PET) process from –NH to anthracene fluorophore. It was expected that addition of H^+ ions will cause the protonation of aryl/alkyl amine unit and may inhibit the PET process to revive the fluorescence of anthracene. The pH titration of **9** showed that the fluorescence intensity remained unchanged between pH ca. 14–1.0 and on lowering the pH from < 1.0, the fluorescence intensity increased progressively at very low pH and it went off scale. Similarly, fluorescence of **14** remained stable up to pH 1.0. Probably, in **9** and **14** the hydrophobic environment created by the aromatic rings makes the protonation more difficult. In the preliminary fluorescence studies, most of the transition metal ions, did not modulate the fluorescence intensity of **9** and **14**. Even on addition of excess of Cu^{2+} ions, no increase in the fluorescence intensity was observed. This is likely due to intramolecular π–π and π–CH interactions of the anthracene moiety with the rest of the molecule and as a result although multipodands **9** and **14** seem to have preorganized structures but ligating sites (N, S) have been embedded deep into the hydrophobic environment created by anthracene ring(s). This effect of hydrophobic environment is clearly manifested into the acid stability of these multipodands.

To investigate further the role of aromatic groups we look into the energy minimized structures of **9**, **14** and **20**, **21** (as control) which shows that the anthracene ring is by and large placed as a lid to the pseudocavity formed by two 2-aminophenylthio moieties and covers one half of the central aromatic ring near to it more efficiently than the second half of the central aromatic ring (Fig. S1). This leads to non-equivalency of SCH_2 and CH_3 protons. To further investigate the effect of aromatic group (anthracene) on complexation due to its over placement on the pseudo cavity, the ^{1}H NMR spectra of these fluorescent multipodands were analyzed in detail.

^{1}H NMR analysis of multipodands

The ^{1}H NMR spectra of various multipodands show that the attachment of the anthracene ring to the 1^0 aromatic amine causes significant changes in chemical shifts of different protons but attachment of the naphthalene ring to the amine does not cause any change in the chemical shift. The comparison of ^{1}H NMR spectrum of fluorescent tripodand **14** with that of its parent tripodand **4** shows that in **14**, the methyl protons are shifted up field by $\Delta\delta = 0.55$ and $\Delta\delta = 0.15$ ppm and SCH_2 singlets are shifted up field by $\Delta\delta = 0.30$ and $\Delta\delta = 0.25$ ppm. Similarly, the methyl protons in fluorescent dipodand **9** are shifted up field by $\Delta\delta = 0.58$, 0.47, and 0.14 ppm and SCH_2 signals are shifted up field by $\Delta\delta = 0.28$ and 0.21 ppm in comparison to chemical shift in dipodand **2**. The presence of two anthracene moieties in fluorescent dipodand **11**, causes enhanced up field shift of methyl ($\Delta\delta = 0.75$ ppm) and SCH_2 ($\Delta\delta = 0.46$ ppm) protons. Similar up field shift of SCH_2 and methyl protons in fluorescent monopodand **7**, in comparison with those in monopodand **1** is observed (Fig. 2). However, in case of naphthyl substituted fluorescent dipodand **13** and tripodand **15**, the upfield shift of < 0.10 ppm is observed (Fig. S2). We also observed that NCH_2 signals appeared at 5.18–5.22 ppm range in all podands where anthracene is attached at amine nitrogen which attributes that anthracene rings overlap on the cavity and shield the CH_3, SCH_2 protons whereas NCH_2 protons in these podands are present in the deshielding zone of the anthracene ring current. We observed that NCH_2 signals appeared upfield at 4.44–4.50 ppm in all podands where naphthalene is attached at amine nitrogen which possibly explains the presence of naphthalene very close to NCH_2 rather than CH_3 and SCH_2 and consequently NCH_2 showed upfield shift and negligible shift in case of CH_3 and SCH_2 protons (Table S2).

We also carried out comparison of ^{1}H NMR spectra of *p*-phenylene (1,4-linkage) based-fluorescent dipodands **20** and **21** (Fig. S3) [30] with their parent dipodands **18** and **19** which shows that the presence of anthracene ring shifts most

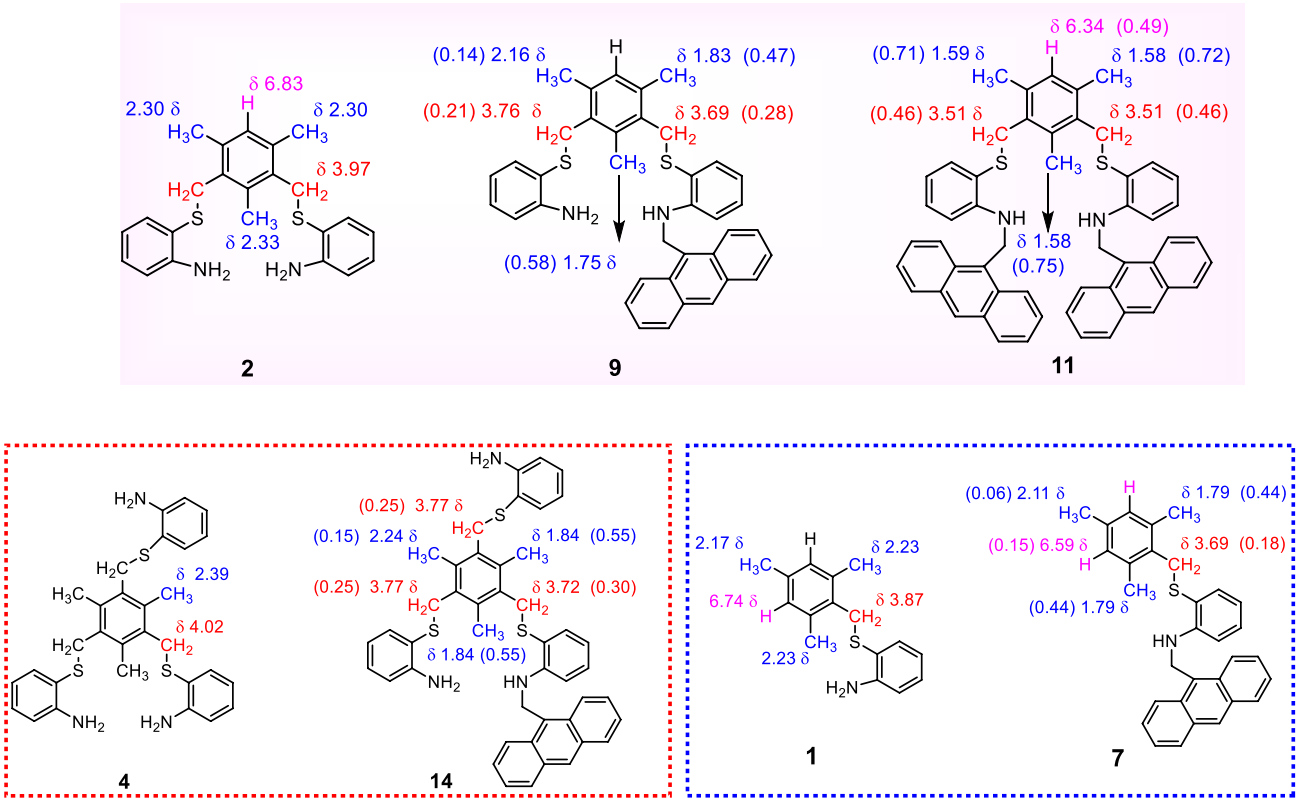


Fig. 2 The comparison of ^{1}H chemical shifts of **2** with **9** and **11**; **4** with **14**; **1** with **7**

of the protons upfield. In case of **20**, the *para*-xylene ring protons become magnetically non-equivalent and are shifted upfield by 0.17 and 0.28 ppm and SCH_2 signals are shifted up field by 0.24 and 0.07 ppm, whereas, in case of **21**, SCH_2 singlets are shifted up field by 0.22 and 0.08 ppm; the OMe singlets are shifted up field by 0.46 and 0.17 ppm; aromatic H of 2, 5-dimethoxybenzene ring are shifted upfield by 0.17 and 0.13 ppm. From these results, we observed that chemical shifts of the protons are more pronounced in case of 1,3- or 1,3,5-linked podands in compare to 1,4-linked podands.

The aromatic H of 2-aminophenylthio units in podands **7**, **9**, and **14** is also shifted downfield by 0.1–0.2 ppm. This down field shift of 2-aminophenylthio ArH in comparison to upfield shift of SCH_2 and methyl protons clearly shows that SCH_2 and central methyl protons remain in shielding zone of anthracene ring i.e. in its center, whereas 2-aminophenylthio protons are placed in deshielding zone i.e. away from the anthracene ring. The ^{1}H NMR spectra on recording between 10^{-2} and 10^{-3} M concentrations showed constant chemical shifts and point to lack of any intramolecular interactions in aggregated state. Therefore, in **7**, **9**, **10**, and **14**, the upfield chemical shifts of protons in comparison to those in their parent amines arise due to intramolecular spatial arrangement of anthracene bulky group.

Conclusion

In conclusion, multipodands possessing 2-aminophenylthio groups at 1,3-, 1,3,5-, and 1,2,4,5-positions of benzene platform have been synthesized. Tripodand and tetrapodands showed good extraction of Ag^{+} and and tetrapodand showed highest Ag^{+}/Pb^{2+} selectivity among the other podands. When anthracene groups were connected to the amine of the 2-aminothiophenol unit on dipodands and tripodands, anthracene ring(s) organized themselves on to cavity as lid which causes protonation of amine at low pH due to increased hydrophobicity around the podand. Thus, model structure for blue copper protein cavity could be achieved but at the loss of complexation ability towards Cu^{2+} ions. Further refinement in the model structure by considering stronger coordinating ligands to achieve both factors (hydrophobicity and copper complexation) simultaneously are currently in progress in our lab.

Experimental

Melting points were determined in open capillaries. For monitoring the progress of the reaction and for comparison with authentic samples, thin layer chromatography (tlc) was used. For this purpose, micro slides were

coated with silica gel 'G' containing calcium sulfate as binder or with the silica gel HF-254 (Qualigens India), by dipping a pair of slides held back to back in slurry of adsorbent in chloroform–methanol (80:20). The chromatograms were developed in iodine chamber or with UV-254 lamp. Separation of various components was carried out by column chromatography using silica gel 60–120 mesh (Qualigens, India) as adsorbent and hexane, ethyl acetate and their mixtures as eluents. All the fractions collected from column chromatography were compared with chromatograms of the reaction mixture (tlc) for checking their identity and purity. ^{1}H NMR spectra were recorded on JEOL 300 MHz instrument using $CDCl_3$ solutions containing tetramethylsilane as an internal standard. Abbreviations used for splitting patterns are s = singlet, bs = broad singlet, t = triplet, q = quartet, m = multiplet, dd = double doublet. ^{13}C NMR spectra were recorded at 75 MHz. Mass spectra were recorded at Central Drug Research Institute, Lucknow. Elemental analyses (C, H, N, S) of the samples were performed on a Thermoelectron FLASH EA1112, CHNS analyzer and their results were found to be in good agreement (± 0.3%) with the calculated values. Absorption and emission spectra were obtained respectively on Shimadzu UV-1601 spectrophotometer and on Shimadzu RF-1501 spectrofluorophotometers with 1 cm quartz cells.

2-Aminothiophenol, 2-naphthaldehyde, 1, 3, 5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, $TBAHSO_4$, and 9-anthracenealdehyde were procured from Aldrich, Spectrochem (India), Loba Chemie, and were used without further purification. 1-(Bromomethyl)-2,4,6-trimethylbenzene, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene [34], 1,3-bis(bromomethyl) benzene, and 1,2,4,5-tetrakis(bromomethyl)benzene [35] were prepared according to the published procedures and their ^{1}H NMR spectra were found to be identical with the ones described in references. Moisture-sensitive reactions were performed under N_2 atmosphere. CH_2Cl_2 was freshly distilled from CaH_2, THF from Na/benzophenone, CH_3OH from Mg wire, CH_3CN from P_2O_5, and DMF dried over 4 Å molecular sieves. Other solvents such as hexane, ethyl acetate, chloroform, and acetone were of LR grade and were distilled before use. Water was doubly distilled. Metal salts were of analytical grade. Chloroform and acetonitrile used for extraction studies were of AR grade. Compounds **1**–**4** and **6** have been already published in literature and physical properties, e.g. ^{1}H and ^{13}C NMR spectra were found to be identical with the ones described in Refs. [40–43].

General procedure for the synthesis of podands 1 and 5

In two neck round bottomed flask, 94 mg pre-washed NaH (3.95 mmol) was taken in dry DMF and 648 mg 2-aminothiophenol (5.19 mmol) was added with stirring under N_2 atm at 40 ± 2 °C. The stirring was continued for 20 min. After the hydrogen evolution ceased, TBA HSO_4 (25–30 mg) and 500 mg 1-(bromomethyl)-2,4,6-trimethylbenzene (2.35 mmol) were added and stirring was continued for additional 24–30 h. During this period reaction was completed (tlc). The suspended solid was filtered off and was washed with ethyl acetate. The combined filtrate was distilled off under vacuum. Recrystallization from $CHCl_3$–CH_3OH (1:1) produce **1**.

2-[(2,4,6-Trimethylbenzyl)thio]aniline (1, $C_{16}H_{19}NS$)

Yield 0.42 g (70%); thick liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 7.5 Hz, 1H, ArH), 7.01 (t, J = 7.5 Hz, 1H, ArH), 6.74 (s, 2H, ArH), 6.51–6.59 (m, 2H, ArH), 4.22 (s, 2H, NH_2, exchanges with D_2O), 3.87 (s, 2H, CH_2S), 2.23 (s, 6H, 2 CH_3), 2.17 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.3, 136.7, 136.1, 135.9, 130.7, 129.6, 128.7, 118.1, 117.9, 114.5, 33.8, 20.7, 19.2 ppm; MS (FAB): m/z = 257 (M^+).

2,2′,2″,2‴-[1,2,4,5-Benzenetetrayltetrakis(methylenethio)]-tetraaniline (5, $C_{34}H_{34}N_4S_4$)

Yield 0.42 g (60%); solid; m.p.: 118–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, J = 7.5 Hz, 4H, ArH), 7.11 (t, J = 7.5 Hz, 4H, ArH), 6.68 (d, J = 7.5 Hz, 4H, ArH), 6.62 (t, J = 7.5 Hz, 4H, ArH), 6.60 (s, 2H, ArH), 4.23 (bs, 8H, 4 NH_2, exchanges with D_2O), 3.78 (s, 8H, 4 CH_2S), ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 136.5, 135.1, 132.6, 130.1, 118.5, 117.1, 114.9, 36.1, ppm; MS (FAB): m/z = 626 (M^+).

General procedure for the synthesis of multipodands 7, 9–12, 14

The solution of 300 mg **2** (0.760 mmol) and 205 mg anthracenecarbaldehyde (1.0 mmol) in 30 cm^3 dry THF containing suspension of 365 mg dry $MgSO_4$ (3.04 mmol) was stirred for 48 h at room temperature. $MgSO_4$ was filtered off and washed with dry THF. The combined filtrate was recollected and to this solution of 68 mg $NaBH_4$ (1.89 mmol) and 193 mg I_2 (0.759 mmol) was added and was stirred at room temperature for additional 2 h. Then, reaction mixture was refluxed for 36 h. The reaction mixture was cooled; 20 cm^3 methanolic KOH (2%) was added and was stirred for 2 h. Then, reaction mixture was diluted with water and was extracted with CH_2Cl_2. The solvent was distilled off and the residue was purified through column chromatography over silica using CH_2Cl_2—hexane as an eluent to get **9** and **11**. Similar reactions of diamines **3**, **4**, and **1** with anthracenecarbaldehyde gave respective fluoroionophores **10** and **12**, **14**, and **7**.

2-[[3-[[(2-Aminophenyl)thio]methyl]-2,4,6-trimethylbenzyl]-thio]-*N*-(anthracen-9-ylmethyl)aniline (9, $C_{38}H_{36}N_2S_2$)

Yield 0.13 g (30%); solid; m.p.: 124–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.50$ (s, 1H, ArH), 8.28 (d, $J = 7.5$ Hz, 2H, ArH), 8.05 (d, $J = 7.5$ Hz, 2H, ArH), 7.40–7.53 (m, 6H, ArH), 7.21 (d, $J = 7.5$ Hz, 1H, ArH), 7.00–7.09 (m, 2H, ArH), 6.73 (t, $J = 7.5$ Hz, 1H, ArH), 6.58–6.63 (m, 3H, ArH), 5.36 (bs, NH, 1H, exchanges with D_2O), 5.21 (d, $J = 3.6$ Hz, 2H, CH_2NH, converts to singlet on D_2O exchange), 4.23 (bs, 2H, NH_2, exchanges with D_2O), 3.76 (s, 2H, CH_2S), 3.69 (s, 2H, CH_2S), 2.16 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.75 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 148.4, 136.6, 136.5, 136.1, 136.1, 135.9, 131.7, 131.5, 131.2, 130.7, 130.5, 129.9, 129.8, 129.1, 128.0, 126.5, 125.1, 124.1, 118.5, 118.2, 118.1, 117.1, 114.7, 109.8, 40.6, 34.8, 34.7, 19.6, 19.0, 14.5 ppm; MS (FAB): $m/z = 585$ [$(M+1)^+$].

2,2′-[[(2,4,6-Trimethyl-1,3-phenylene)bis(methylene)]-bis(sulfanediyl)]bis[*N*-(anthracen-9-ylmethyl)aniline] (11, $C_{53}H_{46}N_2S_2$)

Yield 0.06 g (10%); solid; m.p.: 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.47$ (2H, s, ArH), 8.24 (4H, d, $J = 9.0$ Hz, ArH), 8.02 (4H, d, $J = 9.0$ Hz, ArH), 7.43–7.50 (m, 8H, ArH), 7.30–7.34 (m, 4H, ArH), 6.98 (d, 2H, $J = 7.5$ Hz, ArH), 6.69 (t, $J = 7.5$ Hz, 2H, ArH), 6.34 (s, 1H, ArH), 5.29 (bs, 2H, 2 NH, exchanges with D_2O), 5.18 (bs, 4H, 2 CH_2NH), 3.51 (s, 4H, 2 CH_2S), 1.59 (s, 3H, CH_3), 1.58 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 149.3$, 136.5, 135.9, 131.5, 131.1, 130.5, 130.5, 129.7, 129.1, 128.0, 126.5, 125.1, 124.1, 118.0, 117.1, 109.7, 40.6, 34.4, 18.9, 14.0 ppm; MS (FAB): $m/z = 774$ (M^+).

2-[[3-[[(2-Aminophenyl)thio]methyl]benzyl]thio]-*N*-(anthracen-9-ylmethyl)aniline (10, $C_{35}H_{30}N_2S_2$)

Yield 0.09 g (20%); solid; m.p.: 85–87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.51$ (s, 1H, ArH), 8.26 (d, $J = 7.5$ Hz, 2H, ArH), 8.06 (d, $J = 7.5$ Hz, 2H, ArH), 7.46–7.54 (m, 4H, ArH), 7.38 (t, $J = 7.5$ Hz, 1H, ArH), 7.25 (d, $J = 7.5$ Hz, 1H, ArH), 7.14 (d, $J = 7.5$ Hz, 1H, ArH), 7.04 (d, $J = 7.5$ Hz, 1H, ArH), 7.01 (d, $J = 7.5$ Hz, 1H, ArH), 6.83–6.88 (m, 2H, ArH), 6.66–6.70 (m, 2H, ArH), 6.59 (d, $J = 7.5$ Hz, 1H, ArH), 6.56 (s, 1H, ArH), 6.55 (t, $J = 7.5$ Hz, 1H, ArH), 6.00 (s, 1H, NH, exchanges with D_2O), 5.19 (s, 2H, CH_2NH), 3.60 (s, 2H, CH_2S), 3.56 (s, 2H, CH_2S) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.1$, 148.4, 138.1, 137.7, 136.7, 136.2, 131.5, 130.6, 130.5, 129.9, 129.1, 128.1, 128.0, 127.3, 127.3, 126.5, 125.1, 124.1, 118.3, 117.3, 117.3, 117.0, 114.7, 110.0, 40.7, 39.3, 39.1 ppm; MS (FAB): $m/z = 542$ (M^+).

2,2′-[[1,3-Phenylenebis(methylene)]bis(sulfanediyl)]bis[*N*-(anthracen-9-ylmethyl)aniline] (12, $C_{50}H_{40}N_2S_2$)

Yield 0.05 g (8%); solid; m.p.: 177–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.41$ (s, 2H, ArH), 8.18 (d, $J = 8.2$ Hz, 4H, ArH), 7.96 (d, $J = 9.0$ Hz, 4H, ArH), 7.38–7.48 (m, 8H, ArH), 7.29 (t, $J = 7.5$ Hz, 2H, ArH), 7.16 (d, $J = 7.5$ Hz, 2H, ArH), 6.93 (d, $J = 7.5$ Hz, 2H, ArH), 6.69 (t, $J = 7.5$ Hz, 2H, ArH), 6.60 (t, $J = 7.5$ Hz, 1H, ArH), 6.55 (d, $J = 7.5$ Hz, 2H, ArH), 6.22 (s, 1H, ArH), 5.12 (bs, 2H, 2 NH, exchanges with D_2O), 5.06 (bs, 4H, 2 CH_2NH), 3.36 (s, 4H, 2 CH_2S) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.1$, 137.5, 136.4, 131.5, 130.4, 129.1, 128.9, 128.0, 127.1, 126.4, 125.1, 124.0, 117.3, 117.0, 109.9, 40.7, 38.9 ppm; MS (FAB): $m/z = 732$ (M^+).

2,2′-[[[5-[[[2-[(Anthracen-9-ylmethyl)amino]phenyl]thio]-methyl]-2,4,6-trimethyl-1,3-phenylene]bis(methylene)]-bis(sulfanediyl)]dianiline (14, $C_{45}H_{43}N_3S_3$)

Yield 0.09 g (23%); solid; m.p.: 187–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.50$ (s, 1H, ArH), 8.28 (d, $J = 7.5$ Hz, 2H, ArH), 8.05 (d, $J = 7.5$ Hz, 2H, ArH), 7.40–7.53 (m, 6H, ArH), 7.21–7.23 (m, 2H, ArH), 7.03–7.10 (m, 3H, ArH), 6.74 (t, $J = 7.5$ Hz, 1H, ArH), 6.60–6.66 (m, 4H, ArH), 5.35 (bs, 1H, NH, exchanges with D_2O), 5.22 (d, $J = 2.7$ Hz, 2H, CH_2NH, converts to singlet on D_2O exchange), 4.25 (bs, 4H, 2 NH_2, exchanges with D_2O), 3.77 (s, 4H, 2 CH_2S), 3.72 (2H, s, CH_2S), 2.24 (s, 3H, CH_3), 1.84 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 148.4, 136.5, 136.0, 135.8, 135.6, 132.0, 131.5, 130.7, 130.5, 129.8, 129.1, 128.0, 126.5, 125.2, 124.1, 118.6, 118.2, 118.0, 117.2, 114.8, 109.8, 40.6, 35.4, 15.7, 15.1 ppm; MS (FAB): $m/z = 721$ (M^+).

***N*-(Anthracen-9-ylmethyl)-2-[(2,4,6-trimethylbenzyl)thio]-aniline (7, $C_{31}H_{29}NS$)**

Yield 0.11 g (22%); solid; m.p.: 147–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.50$ (s, 1H, ArH), 8.28 (d, $J = 7.5$ Hz, 2H, ArH), 8.05 (d, $J = 7.5$ Hz, 2H, ArH), 7.40–7.53 (m, 6H, ArH), 7.08 (d, $J = 7.5$ Hz, 1H, ArH), 6.72 (t, $J = 7.5$ Hz, 1H, ArH), 6.59 (s, 2H, ArH), 5.38 (bt, $J = 4.2$ Hz, 1H, NH exchanges with D_2O), 5.22 (d, $J = 4.2$ Hz, 2H, CH_2NH converts to singlet on D_2O exchange), 3.69 (s, 2H, CH_2S), 2.11 (s, 3H, CH_3), 1.79 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 137.1, 136.6, 136.4, 131.6, 130.6, 130.5, 130.1, 129.1, 128.7, 128.0, 126.5, 125.1,

124.1, 118.2, 117.1, 109.8, 40.6, 33.9, 20.8, 18.8 ppm; MS (FAB): $m/z = 447$ (M^+).

General procedure for synthesis of multipodands 8, 13, 15–17

The solution of 300 mg compound **3** (0.852 mmol) and 159 mg 2-naphthaldehyde (1.0 mmol) in 30 cm^3 dry THF containing suspension of 271 mg dry $MgSO_4$ (2.25 mmol) was stirred for 48 h at room temperature. After the completion of the reaction (tlc), $MgSO_4$ was filtered off and washed with dry THF. The combined filtrate was recollected and to this solution of 77 mg $NaBH_4$ (2.12 mmol) and 143 mg I_2 (0.57 mmol) was added and reaction was stirred at room temperature for 2 h. Then reaction mixture was further refluxed for 36 h. The reaction mixture was cooled; 20 cm^3 methanolic KOH (2%) was added and stirred for additional 2 h. The reaction mixture was diluted with water and was extracted with CH_2Cl_2. The solvent was distilled off and the residue was purified through column chromatography over silica using CH_2Cl_2—hexane as an eluent to get **13**. Similar reaction of diamine **4** and **1** with 2-naphthaldehyde gave fluorescent multipodand **15**–**17** and **8**.

2-[[3-[[(2-Aminophenyl)thio]methyl]benzyl]thio]-*N*-(naphthalen-2-ylmethyl)aniline (13, $C_{31}H_{28}N_2S_2$)

Yield 0.075 g (18%); thick liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.75$–7.83 (m, 4H, ArH), 7.42–7.49 (m, 3H, ArH), 6.89–7.28 (m, 8H, ArH), 6.56–6.66 (m, 4H, ArH), 4.43 (s, 2H, CH_2NH), 3.82 (s, 2H, CH_2S), 3.76 (s, 2H, CH_2S) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.3$ 148.4, 138.3, 136.7, 136.6, 136.3, 133.4, 132.7, 130.4, 129.9, 129.3, 128.8, 128.3, 127.7, 127.6, 127.5, 127.4, 126.1, 125.7, 125.5, 118.4, 117.4, 117.1, 117.0, 114.8, 110.5, 48.1, 39.8, 39.4 ppm; MS (FAB): $m/z = 492$ (M^+).

2,2′-[[[2,4,6-Trimethyl-5-[[[2-[(naphthalen-2-ylmethyl)-amino]phenyl]thio]methyl]-1,3-phenylene]bis(methylene)]-bis(sulfanediyl)]dianiline (15, $C_{41}H_{41}N_3S_3$)

Yield 0.095 g (25%); solid; m.p.: 126–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$–7.85 (m, 4H, ArH), 7.45–7.48 (m, 3H, ArH), 7.40 (d, $J = 7.5$ Hz, 1H, ArH), 7.28 (d, $J = 7.5$ Hz, 2H, ArH), 7.19 (t, $J = 7.5$ Hz, 1H, ArH), 7.10 (t, $J = 7.5$ Hz, 2H, ArH), 6.62–6.71 (m, 6H, ArH), 4.55 (bs, 1H, NH, exchanges with D_2O), 4.49 (s, 2H, CH_2NH), 4.03 (bs, 4H, 2 NH_2, exchanges with D_2O), 4.01 (s, 2H, CH_2S), 3.93 (s, 4H, 2 CH_2S), 2.35 (s, 3H, CH_3), 2.30 (s, 6H, 2 CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 148.4, 136.6, 136.5, 136.1, 135.8, 133.5, 132.7, 132.3, 130.4, 129.9, 128.4, 127.7, 127.7, 126.2, 125.7,125.6, 118.6, 118.2, 117.9, 117.2, 114.8, 110.5, 48.2, 35.9, 35.5, 15.8 ppm; MS (FAB): $m/z = 672$ [$(M + 1)^+$].

2,2′-[[[5-[[(2-Aminophenyl)thio]methyl]-2,4,6-trimethyl-1,3-phenylene]bis(methylene)]bis(sulfanediyl)]bis[*N*-(naphthalen-2-ylmethyl)aniline] (16, $C_{52}H_{49}N_3S_3$)

Yield 0.12 g (26%); solid; m.p.: 133–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$–7.83 (m, 8H, ArH) 7.44–7.47 (m, 6H, ArH), 7.36 (d, $J = 7.5$ Hz, 2H, ArH), 7.23 (d, $J = 7.5$ Hz, 1H, ArH), 7.14 (d, $J = 7.5$ Hz, 1H, ArH), 7.10 (d, $J = 7.5$ Hz, 1H, ArH), 7.07 (d, $J = 7.5$ Hz, 1H, ArH), 6.59–6.67 (m, 6H, ArH), 5.58 (t, $J = 5.4$ Hz, 2H, 2 NH, exchanges with D_2O), 4.47 (d, $J = 5.1$ Hz, 4H, 2 CH_2NH, converts to singlet on D_2O exchange), 4.24 (bs, 2H, NH_2, exchanges with D_2O), 3.95 (s, 4H, 2 CH_2S), 3.85 (s, 2H, CH_2S), 2.28 (s, 6H, 2 CH_3), 2.26 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.3$, 148.4, 136.6, 136.4, 136.0, 135.7, 133.4, 132.7, 132.3, 132.2, 130.4, 129.8, 128.4, 127.7, 127.7, 126.2, 125.7, 125.7, 125.5, 118.6, 118.2, 117.9, 117.2, 114.8, 110.5, 103.3, 48.2, 35.8, 35.5, 15.8 ppm; MS (FAB): $m/z = 811$ (M^+).

2,2′,2″-[[(2,4,6-Trimethylbenzene-1,3,5-triyl)tris-(methylene)]tris(sulfanediyl)]tris[*N*-(naphthalen-2-ylmethyl)aniline] (17, $C_{63}H_{57}N_3S_3$)

Yield 0.11 g (20%); solid; m.p.: 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.75$–7.80 (m, 12H, ArH), 7.41–7.46 (m, 9H, ArH), 7.31 (d, $J = 7.5$ Hz, 3H, ArH), 7.12 (t, $J = 7.5$ Hz, 3H, ArH), 6.56–6.63 (m, 6H, ArH), 5.54 (bt, 3H, NH, exchanges with D_2O), 4.44 (d, $J = 4.8$ Hz, 6H, 3 CH_2NH, converts to singlet on D_2O exchange), 3.88 (s, 6H, 3 CH_2S), 2.23 (s, 9H, 3 CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.2$, 136.6, 136.3, 135.7, 133.4, 132.7, 132.3, 130.3, 128.4, 127.7, 126.2, 125.7, 125.6, 125.4, 117.9, 117.2, 110.5, 48.2, 35.8, 15.8 ppm; MS (FAB): $m/z = 952$ [$(M + 1)^+$].

N-(Naphthalen-2-ylmethyl)-2-[(2,4,6-trimethylbenzyl)thio]-aniline (8, $C_{27}H_{27}NS$)

Yield 0.14 g (30%); thick liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$–7.84 (m, 4H, ArH), 7.36–7.48 (m, 4H, ArH), 7.14 (t, $J = 7.5$ Hz, 1H, ArH), 6.76 (s, 2H, ArH), 6.58–6.63 (m, 2H, ArH), 5.62 (t, $J = 5.4$ Hz, 1H, NH, exchanges with D_2O), 4.45 (d, $J = 5.4$ Hz, 2H, CH_2NH converts to singlet on D_2O exchange), 3.96 (s, 2H, CH_2S), 2.22 (s, 6H, 2 CH_3), 2.21 (s, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.4$, 136.9, 136.6, 136.5, 133.4, 132.7, 131.0, 130.3, 128.9, 128.3, 127.7, 126.1, 125.7, 125.5, 118.1, 117.1, 110.3, 48.2, 34.5, 20.9, 19.4 ppm; MS (FAB): $m/z = 397$ (M^+).

Extraction of metal picrates

For the extraction experiments, metal picrate solutions (0.001 mol dm^{-3}) were prepared in deionised distilled water. The solutions of receptors (0.001 mol dm^{-3}) were prepared in chloroform (A.R Grade). An aqueous solution (2 cm^3) of a metal picrate (0.001 mol dm^{-3}) and a chloroform solution (2 cm^3) of a receptor (0.001 mol dm^{-3}) in a cylindrical tube closed with a septum was shaken for 5 min and kept at 27 ± 1 °C for 3–4 h. An aliquot of the chloroform layer (1 cm^3) was withdrawn with a syringe and diluted with acetonitrile to 10 cm^3. The UV absorption was measured against $CHCl_3$-CH_3CN (1:9) solution at 374 nm. Extraction of the metal picrate has been calculated as the percentage of the metal picrate extracted in the chloroform layer and values are the mean of the three independent measurements which were within ± 0.02 error.

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