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ORIGINAL ARTICLE

Synthesis and photophysical behavior of thia-aza macrocycles with 9-anthracenylmethyl moiety as fluorescent appendage

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Abstract 1,3-Bis(bromomethyl)-2-methoxy-5-methylbenzene, 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene, 1,3- and 1,4-bis(bromomethyl)benzene undergo nucleophilic substitution with methyl mercaptoacetate to provide respective diesters **6–9**. These diesters (**6–9**) on stirring with bis(3-aminopropyl)amine and diethylenetriamine in methanol–toluene (1:1) mixture undergo intermolecular cyclization to give respective thia-aza macrocycles **10–15**. The alkylation of macrocycles **10–13** with 9-anthracenylmethyl chloride gave amine *N*-(anthracenylmethyl) substituted macrocycles **16–19**. The extraction profile of macrocycles **10–15** towards alkali (Li^+, Na^+, K^+), alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), Ag^+, Tl^+ and Pb^{2+} picrates shows preferential extraction of Ag^+ with these macrocycles. The macrocycles **16–19** show fluorescence spectrum typical of anthracene moiety and depending on their structures exhibit 0–80 times increase in fluorescence on addition of transition metal ions. Fluorescent receptors **16**, **17**, and **19** are capable of functioning as a very efficient multi input OR logic gate.

Keywords Sensor · Fluorescence enhancement · Thia aza macrocycles · OR gate · Supramolecular · Synthesis · Extraction

Introduction

The metal ion preferences of mixed donor co-ordination sites are often difficult to predict, especially when transition and other heavy metal ions are involved. Macrocycles have proved very suitable for investigating metal ion recognition phenomena since their cyclic nature tends to restrict the number of co-ordination modes possible [1]. The development of fast estimation, removal and separation techniques for Ag^+, the use of Ag^+ complexes in photographic materials and their potential use in cancer radioimmunotherapy have drawn the attention of supramolecular chemists towards Ag^+ selective receptors [2].

The ability of the Ag^+ to form stable bidentate complexes and occasionally tridentate or higher coordinate complexes in comparison with stabilization of octahedral complexes by other competing metal ions has been successfully used to design and synthesize highly Ag^+ selective receptors [1–10]. So, in addition to the presence of 2–4 appropriately placed soft ligating sites, the number of other structural features like the minimal incorporation of hard ligating sites (ether etc.), the induction of conformational and stereochemical restrictions to avoid 2:1 complexation towards interfering metal ions etc. have been used to design Ag^+ selective ionophores [1–10]. In order to attain appropriate cavity size and to restrict the coordination number <4, the non-coordinating ester and amide based spacers have been used [11]. We had earlier reported [12–16] that in case of 2-aminothiophenol based cyclic diamide macrocycles due to rigidity and steric reasons, the amide NH units fill the cavity and due to reorganization of ligating sites during complexation, their binding capacity is lowered [17]. As a continuation of our previous studies in the area of ligand design for transition metal ion recognition, now we have designed new cyclic ionophores which possess two thioether–one amine–two amide units as the common structural feature. We envisaged that the presence of three carbon spacers between nitrogen atoms and

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replacement of 2-aminophenylthio group with alkylthioether moiety would create desired flexibility in the resulting macrocycles (model II, Fig. 1).

Recently many investigations have been done on chelation enhanced fluorescence to make chemosensors [18, 19]. To improve the fluorescence intensity enhancement of a receptor upon binding of cations one needs to carefully design the receptor containing a fluorophore so that photoinduced intramolecular electron transfer (PIET) responsible for fluorescence quenching is maximized in the receptor, whereas the PIET is minimized in the cation bound state of the receptor. The PET signal process is one of the most important methods for fluorescent indication in supramolecular chemistry due to its unique advantages, "all or none" switchability, and guest induced "Off-On" and "On-Off" fluorescence [20, 21] etc. A variety of chemosensors based on fluorophore-spacer-receptor format have been developed in recent years which perform light induced simple OR [18]/AND [22] logic operations and hence may find application as photonic molecular devices in molecular information processing.

We have been also interested in the development of supramolecular luminescent chemosensors for transition metal ions, so we have appended 9-anthracenylmethyl fluorescent moiety (model III, Fig. 1) at the lower end of the segment C in model II for the direct optical estimation of transition metal ions [23]. We present here the system where transition metal ions Cu^{2+}, Fe^{3+}, Ni^{2+}, etc. cause enhancement of fluorescence. It is found that the solution of fluoroionophore **16** (CH_3CN)**,** on addition of transition metal ions, shows 70–80 times increase in emission but fluorescent macrocycles **17–19** show significantly lower fluorescence enhancement. The association constants of receptors **16–19** towards transition metal ions have been determined spectrophotometrically. These fluorescent receptors **16**, **17** and **19** are capable of functioning as a very efficient multi input OR logic gate.

Experimental

1,3-Bis(bromomethyl)-2-methoxy-5-methylbenzene [24], 1,3-bis(bromomethyl)-benzene [25], 1,4-bis(bromomethyl)benzene [25] and 1,3,5-tris(bromomethyl)-2,4,6-trimethyl-benzene [24] were prepared according to literature procedures.

Synthesis of diesters **6–9**: a general procedure

A solution of 1,3-bis(bromomethyl)-2-methoxy-5-methylbenzene (**1**) (2 g, 6.4 mmol) and methyl mercaptoacetate (**5**) (1.51 g, 14.2 mmol) in DMF (dry, 100 mL) containing K_2CO_3 anhyd. (2.55 g, 18.4 mmol) and tetrabutylammonium hydrogensulphate (TBA HSO_4) (10 mg) was stirred under N_2 atm. After completion of the reaction (tlc, 15 h), the solid suspension was filtered off and was washed with ethyl acetate (40 mL). The combined filtrate was distilled off under vacuum. The residue was column chromatographed over silica gel using hexane and its mixtures with ethyl acetate as eluents to isolate diester **6.** Similar reactions for 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene (**2**), 1,3-bis(bromomethyl) benzene (**3**) and 1,4-bis(bromomethyl) benzene (**4**) with methyl mercaptoacetate (**5**) gave diesters **7, 8** and **9,** respectively**.**

Diester 6: (75%), yellow liquid, FAB mass *m/z* 359 ($M^+ + 1$), 253 (M^+–SCH_2COOMe); ^1H NMR ($CDCl_3$): δ 2.20 (s, 3H, CH_3), 3.10 (s, 4H, $2 \times CH_2$), 3.63 (s, 6H, $2 \times OCH_3$), 3.74 (s, 7H, $2 \times CH_2$, $ArOCH_3$) , 6.97 (s, 2H, ArH); ^{13}C NMR (normal/DEPT-135) :δ 19.90 (+ve, CH_3), 30.00 (–ve, CH_2), 32.23 (–ve, CH_2), 51.41 (+ve, OCH_3), 61.55 (+ve, OCH_3), 129.90 (ab, ArC), 130.06 (+ve, ArCH), 132.76 (ab, ArC), 153.87 (ab, ArC), 169.91 (ab, C=O).

Diester 7: (80%), white solid, m.p. 53–54 °C (benzene); FAB mass *m/z* 357 ($M^+ + 1$), 251 (M^+–SCH_2COOMe); ^1H NMR ($CDCl_3$): δ 2.24 (s, 6H, $2 \times CH_3$), 2.36 (s, 3H, CH_3), 3.16 (s, 4H, $2 \times CH_2$), 3.63 (s, 6H, $2 \times OCH_3$), 3.79 (s, 4H, $2 \times CH_2$), 6.72 (s, 1H, ArH); ^{13}C NMR (normal/DEPT-135): δ 15.07 (+ve, CH_3), 19.56 (+ve, CH_3), 32.39 (–ve, CH_2), 34.18 (–ve, CH_2), 52.28 (+ve, OCH_3), 130.26 (+ve, ArCH), 131.16 (ab, ArC), 136.45 (ab, ArC), 136.72 (ab, ArC), 170.93 (ab, C=O).

Diester 8: (72%), yellow liquid, FAB mass *m/z* 315 ($M^+ + 1$); ^1H NMR ($CDCl_3$): δ 2.97 (s, 4H, $2 \times CH_2$), 3.59 (s, 4H, $2 \times CH_2$), 3.69 (s, 6H, $2 \times OCH_3$), 7.12–7.18 (m, 4H, ArH); ^{13}C NMR (normal/DEPT-135): δ 31.26 (–ve, CH_2), 35.48 (–ve, CH_2), 51.60 (+ve, OCH_3), 127.97 (+ve,

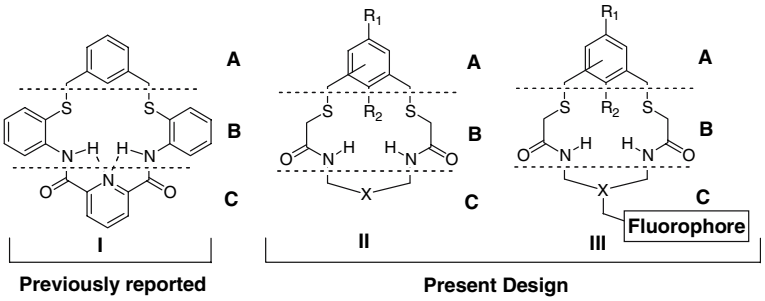


Fig. 1 The structures of models I, II, and III

ArCH), 128.39 (+ve, ArCH), 129.69 (+ve, ArCH), 137.38 (ab, ArC), 169.82 (ab, C=O)

Diester 9: (70%), white solid, m.p. 67–68 °C, FAB Mass *m/z* 315 ($M^+ + 1$), 209 (M^+–SCH_2COOMe); ^1H NMR ($CDCl_3$): δ 3.01 (s, 4H, $2 \times CH_2CO$), 3.67 (s, 6H, $2 \times OCH_3$), 3.75 (s, 4H, $2 \times CH_2Ar$), 7.23 (s, 4H, ArH); ^{13}C NMR (normal/DEPT-135): δ 31.94 (–ve, CH_2), 35.89 (–ve, CH_2), 52.25 (+ve, OCH_3), 129.24 (+ve, ArCH), 136.15 (ab, ArC), 170.67 (ab, C=O).

Synthesis of macrocycles **10–15**: a general procedure

The solution of diester **6** (2 g, 5.3 mmol) and bis(3-aminopropyl)amine (1.5 g, 6.35 mmol) in methanol–toluene mixture (1:1) was stirred for 6 days at room temperature. After completion of the reaction (tlc), the solvent was distilled off under vacuum and crude residue was chromatographed over a silica gel column using $CHCl_3$–MeOH as eluents to isolate **10**. The similar condensations of diesters **7–9** with bis(3-aminopropyl)amine gave macrocycles **11–13.** The condensation of diesters **6** and **8** with diethylenetriamine gave macrocycles **14** and **15.**

Macrocycle 10: (25%), m.p. 196–197 °C, FAB Mass MS *m/z* 426 ($M^+ + 1$); ^1H NMR ($CDCl_3$):δ 1.68 (quintet, J = 6.0 Hz, 4H, $2 \times CH_2$), 2.30 (s, 3H, CH_3), 2.69 (t, J = 6.0 Hz, 4H, $2 \times CH_2NH$), 3.15 (s, 4H, $2 \times CH_2CO$), 3.37 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.71 (s, 4H, $2 \times CH_2Ar$), 3.73 (s, 3H, $ArOCH_3$), 7.10 (s, 2H, ArH), 7.47 (t, J = 6.0 Hz, 2H, $2 \times$ CONH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135) : δ 20.74 (+ve, CH_3), 29.0 (–ve, CH_2), 30.9 (–ve, CH_2), 35.90 (–ve, CH_2), 37.86 (–ve, CH_2), 47.05 (–ve, CH_2), 62.54 (+ve, OCH_3), 130.09 (ab, ArC), 130.94 (+ve, ArCH), 134.86 (ab, ArC), 154.59 (ab, ArC), 168.73 (ab, C=O).

Macrocycle 11: (30%), m.p. 252–253 °C, FAB Mass *m/z* 424 ($M^+ + 1$); ^1H NMR ($CDCl_3$ –DMSO-d_6): δ 1.66 (quintet, J = 6.0 Hz, 4H, $2 \times CH_2$), 2.35 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 2.70 (t, J = 6.0 Hz, 4H, $2 \times CH_2NH$), 3.26 (s, 4H, $2 \times CH_2CO$), 3.31 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.85 (s, 4H, $2 \times CH_2Ar$), 6.87 (s, 1H, ArH), 7.49 (bt, J = 6.0 Hz, $2 \times$ CONH, 2H, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135): δ 15.36 (+ve, CH_3),19.26 (+ve, CH_3), 28.76 (–ve, CH_2), 32.14 (–ve, CH_2), 35.98 (–ve, CH_2), 37.56 (–ve, CH_2), 47.42 (–ve, CH_2), 129.93 (ab, ArC), 130.92 (ab, ArC), 135.10 (+ve, ArCH), 135.81 (ab, ArC), 169.0 (ab, C=O).

Macrocycle 12: (18%), m.p. 157–158 °C, FAB Mass *m/z* 382 ($M^+ + 1$); ^1H NMR ($CDCl_3$) : δ 1.74 (quintet, J = 6.0 Hz, 4H, $2 \times CH_2$), 2.69 (t, J = 6.0 Hz, 4H, $2 \times CH_2NH$,), 3.17 (s, 4H, $2 \times CH_2CO$), 3.40 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.69 (s, 4H, $2 \times CH_2Ar$), 7.07 (s, 1H, ArH), 7.23–7.37 (m, 3H, ArH) 7.53 (t, J = 6.0 Hz, $2 \times$ CONH, 2H, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135): δ 28.62 (–ve, CH_2), 35.21 (–ve, CH_2), 36.48 (–ve, CH_2), 37.15 (–ve, CH_2), 46.58 (–ve, CH_2), 127.88 (+ve, ArCH), 129.56 (+ve, ArCH), 129.83 (+ve, ArCH), 137.23 (ab, ArC), 169.13 (ab, C=O).

Macrocycle 13: (20%), m.p. 170–172 °C, FAB Mass *m/z* 382 ($M^+ + 1$); ^1H NMR ($CDCl_3$): δ 1.53 (quintet, J = 6.0 Hz, 4H, $2 \times CH_2$) 2.64 (t, J = 6.0 Hz, 4H, $2 \times CH_2NH$), 3.19 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.26 (s, 4H, $2 \times CH_2CO$), 3.77 (s, 4H, $2 \times CH_2Ar$), 7.25 (s, 4H, ArH), 7.44 (bt, 2H, $2 \times$ CONH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135): δ 28.62 (–ve, CH_2), 36.70 (–ve, CH_2), 37.80 (–ve, CH_2), 39.00 (–ve, CH_2), 48.61 (–ve, CH_2), 129.02 (+ve, ArCH), 136.92 (ab, ArC), 168.27 (ab, C=O).

Macrocycle 14: (20%), viscous liquid, FAB mass *m/z* 398 ($M^+ + 1$); ^1H NMR ($CDCl_3$): δ 2.31 (s, 3H, CH_3), 2.95 (t, J = 5.0 Hz, 4H, $2 \times CH_2NH$), 3.03 (s, 4H, $2 \times CH_2CO$), 3.52 (q, J = 5.0 Hz, 4H, $2 \times CH_2NHCO$, converts to triplet on D_2O exchange), 3.68 (s, 4H, $2 \times CH_2Ar$), 3.71 (s, 3H, OCH_3), 7.12 (s, 2H, ArH), 7.54 (t, J = 5.0 Hz, 2H, $2 \times$ CONH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135): δ 20.12 (+ve, CH_3), 29.29 (–ve, CH_2), 33.84 (–ve, CH_2), 38.63 (–ve, CH_2), 47.51 (–ve, CH_2), 62.55 (+ve, OCH_3), 129.21 (ab, ArC), 130.7 (+ve, ArCH), 134.8 (ab, ArC), 154.13 (ab, ArC), 168.65 (ab, C=O).

Macrocycle 15: (18%), white solid, m.p. 252–253 °C, FAB mass *m/z* 359 ($M^+ + 1$); ^1H NMR ($CDCl_3$): δ 2.44 (s, 6H, CH_3), 2.51 (s, 3H, CH_3), 2.89 (t, J = 5.0 Hz, 4H, $2 \times CH_2NH$), 3.21 (s, 4H, $2 \times CH_2CO$), 3.52 (q, J = 5.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.88 (s, 4H, $2 \times CH_2Ar$), 6.93 (s, 1H, ArH), 7.54 (t, J = 5.0 Hz, 2H, $2 \times$ CONH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135): δ 15.54 (+ve, CH_3),19.69 (+ve, CH_3), 31.80 (–ve, CH_2), 35.52 (–ve, CH_2), 39.61 (–ve, CH_2), 49.55 (–ve, CH_2), 130.90 (ab, ArC), 130.96 (+ve, ArCH), 135.70 (ab, ArC), 136.36 (ab, ArC), 169.12 (ab, C=O).

Synthesis of fluorescent macrocycles **16–19**: a general procedure

A 100 mL round bottom flask was charged with 9-anthracenylmethyl chloride (192 mg, 0.84 mmol), K_2CO_3 anhyd. (116 mg, 0.84 mmol) and dry chloroform (30 mL). The macrocycle **10** (300 mg, 0.7 mmol) was added in one portion. The mixture was refluxed for 36 h with stirring. After the reaction was completed (tlc, 36 h), the solid was filtered off and solvent was evaporated under vacuum. The resulting crude residue was purified through column chromatography using CH_2Cl_2 and its mixtures

with ethyl acetate to get the desired compound **16.** Similarly, macrocycles **11–13** on alkylation with 9-anthracenylmethyl chloride gave respective fluorescent macrocycles **17–19**.

Macrocycle 16: (23%), yellow solid, m.p. 162–163 °C, FAB Mass *m/z* 616 ($M^+ + 1$); ^{1}H NMR ($CDCl_3$): δ 1.76 (quintet, J = 6.0 Hz, 4H, 2 × CH_2), 2.25 (s, 3H, CH_3), 2.62 (t, J = 6.0 Hz, 4H, 2 × CH_2NH), 3.00 (s, 4H, 2 × CH_2CO), 3.12 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.62 (s, 3H, OCH_3), 3.66 (s, 4H, 2 × CH_2Ar), 4.51 (s, 2H, NCH_2), 7.06 (s, 2H, ArH), 7.20 (bt, 2H, 2 × CONH, exchanges with D_2O), 7.44–7.54 (m, 4H, ArH), 8.01 (d, J = 7.5 Hz, 2H, ArH), 8.42 - 8.45 (m, 3H, ArH); ^{13}C NMR (normal/ DEPT-135): δ 20.76 (+ve, CH_3), 26.81 (–ve, CH_2), 30.25 (–ve,CH_2), 35.26 (–ve, CH_2), 38.40 (–ve, CH_2), 51.62 (–ve, CH_2), 52.13 (–ve, CH_2), 62.45 (+ve, OCH_3), 124.70 (+ve, ArCH), 124.86 (+ve, ArCH), 125.74 (+ve, ArCH), 127.70 (ab, ArC), 129.19 (+ve, ArCH), 129.88 (+ve, ArCH), 130.27 (ab, ArC), 130.91 (+ve, ArCH), 131.40 (ab, ArC), 135.0 (ab, ArC), 154.64 (ab, ArC), 168.90 (ab, C=O).

Macrocycle 17: (15%), yellow solid, m.p. 223–225 °C, FAB mass *m/z* 614 ($M^+ + 1$); ^{1}H NMR ($CDCl_3$ – DMSO-d_6) : δ 1.77 (quintet, J = 6.0 Hz, 4H, 2 × CH_2), 2.31 (s, 6H, CH_3), 2.41 (s, 3H, CH_3), 2.63 (t, J = 6.0 Hz, 4H, 2 × CH_2NH), 2.94 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.07 (s, 4H, 2 × CH_2CO), 3.80 (s, 4H, 2 × CH_2Ar), 4.48 (s, 2H, NCH_2), 6.85 (s, 1H, ArH), 6.92 (bt, J = 6.0 Hz, 2H, 2 × CONH, exchanges with D_2O), 7.45–7.55 (m, 4H, ArH), 8.01 (d, 2H, J = 7.5 Hz ,ArH), 8.39–8.43 (m, 3H, ArH); ^{13}C NMR (normal/DEPT-135) : δ 15.98 (+ve, CH_3), 19.79 (+ve, CH_3), 26.68 (–ve, CH_2), 32.26 (–ve, CH_2), 36.34 (–ve, CH_2), 38.87 (–ve, CH_2), 45.34 (–ve, CH_2), 53.4 (–ve, CH_2), 124.32 (+ve, ArCH), 124.93 (+ve, ArCH), 126.24 (+ve, ArCH), 127.18 (+ve, ArCH), 129.37 (ab, ArC), 130.55 (+ve, ArCH), 131.30 (ab, ArC), 131.36 (ab, ArC), 131.72 (ab, ArC), 134.07 (+ve, ArCH), 136.22 (ab, ArC), 135.70 (ab, ArC), 169.07 (ab, C=O).

Macrocycle 18: (20%), yellow solid, m.p. 135–137 °C, FAB Mass *m/z* 572 ($M^+ + 1$); ^{1}H NMR ($CDCl_3$): δ 1.73 (quintet, J = 6.0 Hz, 4H, 2 × CH_2), 2.58 (t, J = 6.0 Hz, 4H, 2 × CH_2NH), 3.02 (s, 4H, 2 × CH_2CO), 3.09 (q, J = 6.0 Hz, 4H, CH_2NHCO, converts to triplet on D_2O exchange), 3.60 (s, 4H, 2 × CH_2Ar), 4.48 (s, 4H, 2 × CH_2N), 6.97 (s, 1H, ArH), 7.17–7.40 (m, 3H, ArH), 7.43–7.54 (m, 4H, ArH, 2H, 2 × CONH), 8.00 (d, J = 7.5 Hz, 2H, ArH), 8.41–8.44 (m, 3H, ArH); ^{13}C NMR (normal/DEPT-135): δ 26.84 (–ve, CH_2), 35.07 (–ve, CH_2), 36.31(–ve, CH_2), 38.27 (–ve, CH_2), 51.10 (–ve, CH_2), 51.96 (–ve, CH_2), 124.69 (+ve, ArCH), 124.88 (+ve, ArCH), 125.80 (+ve, ArCH), 127.68 (+ve, ArCH), 127.78 (+ve, ArCH), 129.19 (+ve, ArCH), 129.47 (ab, ArC), 129.70 (+ve, ArCH), 129.75 (+ve, ArCH), 137.40 (ab, ArC), 131.27 (ab, ArC), 131.39 (ab, ArC), 168.80 (ab, C=O).

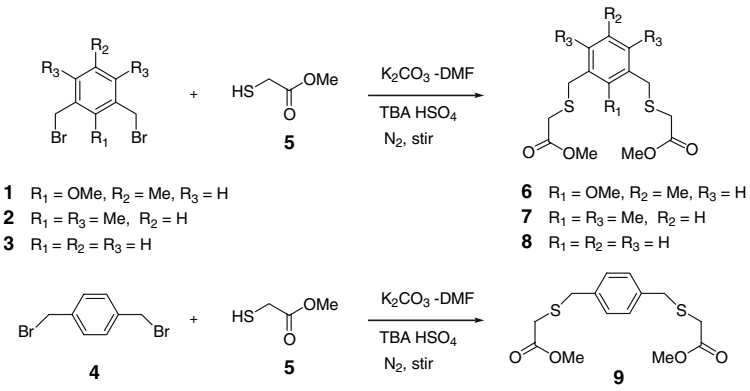
Macrocycle 19: (20%), yellow solid, m.p. 206–207 °C, FAB Mass *m/z* 572 ($M^+ + 1$); ^{1}H NMR ($CDCl_3$): δ 1.61 (quintet, J = 6.0 Hz, 4H, 2 × CH_2), 2.54 (t, J = 6.0 Hz, 4H, 2 × CH_2NH), 2.89–2.93 (m, 8H, 2 × $CH_2CONHCH_2$), 3.64 (s, 4H, 2 × CH_2Ar), 4.44 (s, 2H, NCH_2), 6.64 (bt, 2 × CONH, 2H, exchanges with D_2O), 7.02 (s, 4H, ArH), 7.46–7.58 (m, 4H, ArH), 8.04 (d, J = 9.0 Hz, 2H, ArH), 8.39 (d, J = 9.0 Hz, 2H, ArH), 8.47 (s, 1H, ArH); ^{13}C NMR (normal/DEPT-135): δ 25.91 (–ve, CH_2), 35.94 (–ve, CH_2), 37.02 (–ve, CH_2), 39.18 (–ve, CH_2), 51.38 (–ve, CH_2), 53.10 (–ve, CH_2), 124.59 (+ve, ArCH), 124.95 (+ve, ArCH), 126.04 (+ve, ArCH), 127.98 (ab, ArC), 129.08 (+ve, ArCH), 129.34 (+ve, ArCH), 131.27 (ab, ArC), 131.41 (ab, ArC), 136.75 (ab, ArC), 168.50 (ab, C=O).

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 mL) of a metal picrate (0.001 mol dm^{-3}) and a chloroform solution (2 mL) 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 mL) was withdrawn with a syringe and diluted with acetonitrile to 10 mL. 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.

UV–Vis and fluorescence experiments

UV–Vis absorption and fluorescence spectra were respectively recorded on Shimadazu UV-1601-PC spectrophotometer and Shimadazu RF1501 spectrofluorophotometer with a 1 cm quartz cell at 25 ± 0.1 °C. The solutions of **16–19** in double distilled acetonitrile and metal nitrates were prepared in double distilled water. The number of solutions containing **16–19** (1 μM) and different concentrations of metal nitrates were prepared and were kept at 25 ± 1 °C for 2 h before recording their absorption or fluorescence spectra. The spectra recorded were analyzed through curve fitting procedures by using SPECFIT 3.0.36 to determine the stability constants and the distribution of various species.



1 R_1 = OMe, R_2 = Me, R_3 = H
2 R_1 = R_3 = Me, R_2 = H
3 R_1 = R_2 = R_3 = H

4 **5** **9**

6 R_1 = OMe, R_2 = Me, R_3 = H
7 R_1 = R_3 = Me, R_2 = H
8 R_1 = R_2 = R_3 = H

Results and discussion

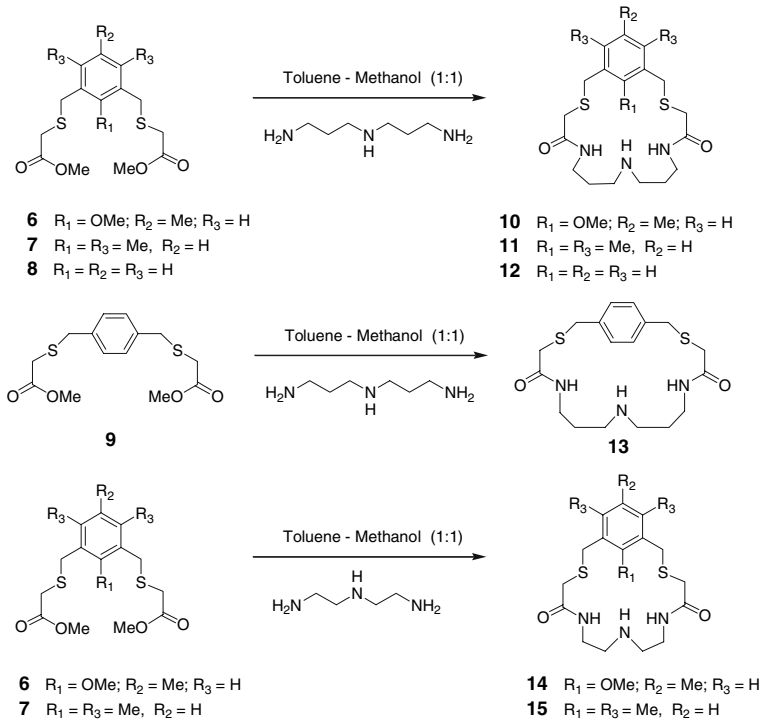
Synthesis

The phase transfer catalysed (K_2CO_3–DMF–TBA HSO_4) nucleophilic displacement of 1,3-bis(bromomethyl)-2-methoxy-5-methylbenzene (**1**) with methyl mercaptoacetate (**5**) gave diester **6** (75%). Similarly, the nucleophilic substitutions of bis(bromomethyl)benzene derivatives **2** and **3** with methyl mercaptoacetate (**5**) gave respective diesters **7** (80%) and **8** (72%). ^{1}H NMR and ^{13}C NMR data confirm their structures.

Based on the earlier reported results [15], that in 1,3-phenylene spacer based ionophores, 1,3-phenylene ring has to undergo conformational changes during complexation, but 1,4-phenylene ring in respective receptors remains perpendicular to the cavity both in the free ligand and its complex, and may undergo minimal conformational changes during complexation, the synthesis of acyclic ionophores having 1,4-phenylene spacer was planned. The phase transfer catalysed (K_2CO_3–DMF–TBA HSO_4) nucleophilic displacement of 1,4-bis(bromomethyl)benzene (**4**) with methyl mercaptoacetate (**5**) gave diester **9** (70%).

The solution of diester **6** in toluene–methanol (1:1) on stirring with bis(3-aminopropyl)amine gave macrocycle **10** (25%). Similarly, diesters **7–9** on reaction with bis(3-aminopropyl)amine gave respective macrocycles **11** (30%); **12** (18%) and **13** (20%). The diesters **6** and **7** underwent condensation with diethylenetriamine in toluene–methanol (1:1) to give macrocycles **14** (20%) and **15** (18%). The structures of these macrocycles have been confirmed by ^{1}H, ^{13}C NMR and other data.

The reaction of macrocycle **10** with 9-anthracenemethyl chloride in chloroform containing a suspension of K_2CO_3



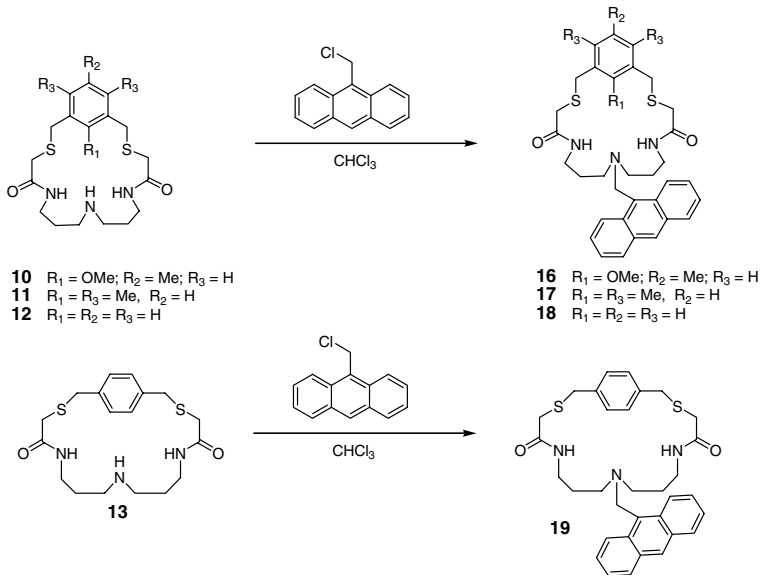
6 R_1 = OMe; R_2 = Me; R_3 = H
7 R_1 = R_3 = Me, R_2 = H
8 R_1 = R_2 = R_3 = H

10 R_1 = OMe; R_2 = Me; R_3 = H
11 R_1 = R_3 = Me, R_2 = H
12 R_1 = R_2 = R_3 = H

9 **13**

6 R_1 = OMe; R_2 = Me; R_3 = H
7 R_1 = R_3 = Me, R_2 = H

14 R_1 = OMe; R_2 = Me; R_3 = H
15 R_1 = R_3 = Me, R_2 = H



(anhyd. base) provided yellow solid **16** (23%). Similarly, macrocycles **11–13** underwent amine *N*-alkylation with 9-anthracenylmethyl chloride to give respective fluorescent macrocycles **17** (15%); **18** (20%) and **19** (20%). The structures of all these compounds have been determined on the basis of ^{1}H, ^{13}C NMR, mass and elemental analysis. Unfortunately, **14** and **15** did not undergo alkylation with 9-anthracenylmethyl chloride. The lack of alkylation of **14** and **15** could be attributed to poor basicity of amine nitrogen arising due to its intramolecular H-bonding with amide NH group [26].

The force field energy minimizations [27] by CAChe show that in compounds **10**, **12**, **16** and **18**, the 1,3-phenylene rings remain more or less in-plane with mean plane of the macrocyclic ring and two thioether and one amine units are directed towards the cavity. In **13** and **19**, the 1,4-phenylene ring remains perpendicular to the mean plane of the macrocyclic ring (Fig. 2). However, no significant effect of these conformations could be observed from ^{1}H NMR spectral data of these compounds.

Extraction and photophysical behavior of macrocycles

Macrocycles **10–13** differ from macrocycles **16–19** only by the presence of anthracenylmethyl group at amine *N* and all other ligating sites are similar. So, the binding characteristics of non-fluorescent macrocycles **10–15** have been studied through extraction of metal picrates and those of fluorescent macrocycles **16–19** through change in their fluorescence on addition of metal salts.

Extraction behavior [28]

As the process of ligand facilitated transport of cations across apolar membrane has relevance to the development of separation techniques for the cations, the extraction

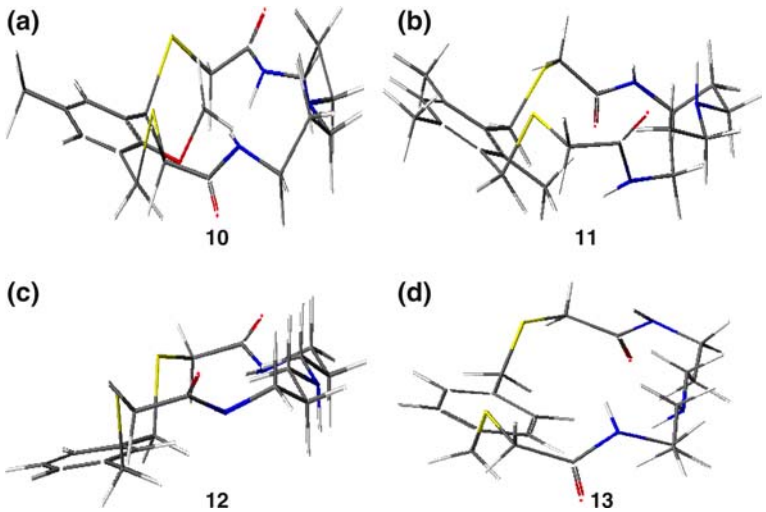


Fig. 2 The energy minimized structures of receptors **10–13**

Table 1 Extraction (%) profile of macrocycles **10–15**

M^{n+}	**10**	**11**	**12**	**13**	**14**	**15**
Li^+	22.0	20.0	20.0	14.0	4.4	9.0
Na^+	18.2	22.5	21.2	13.8	5.7	10.5
K^+	19.2	19.5	22.1	15.3	4.4	12.3
Tl^+	15.3	21.1	18.3	13.5	5.0	10.2
Mg^{2+}	14.8	14.5	14.1	9.5	4.5	6.5
Ca^{2+}	13.5	15.2	15.4	10.0	4.3	8.0
Sr^{2+}	14.2	15.8	15.8	8.8	3.5	7.5
Ba^{2+}	14.5	17.1	19.4	12.0	4.4	9.4
Pb^{2+}	53.2	8.2	31.0	16.0	2.3	4.5
Ag^+	86.5	43.0	53.0	49.0	57.0	62.0
Ag^+/Pb^{2+}	1.6	5.4	1.6	3.0	25.0	14.0

(complexation) properties of receptors **10–15** towards Ag^+, Pb^{2+}, Tl^+, alkali (Li^+, Na^+, K^+) and alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) metal picrtaes have been determined (Table 1). Macrocycles **10–15** show preferential extraction of Ag^+ picrate over extraction of alkali, alkaline earth, Pb^{2+} and Tl^+ picrates. The macrocycle **10,** possessing ether moiety pointing inward the cavity, has the largest number of binding sites and exhibited the highest extraction of Ag^+ (86.5 %) and Pb^{2+} (53.2 %) amongst all the macrocycles studied here. The absence of OMe group in macrocycle **12** resulted in considerable decrease in extraction of both Ag^+ (53%) and Pb^{2+} (31%). The increase in bulk in the cavity by the presence of methyl group in macrocycle **11** resulted in further decrease in extraction of Ag^+ to 43% but the extraction of Pb^{2+} was lowered more dramatically to only 8.2%. Similarly, the replacement of 1,3-phenylene ring in **12** with 1,4-phenylene ring in macrocycle **13** caused only a small decrease in extraction of Ag^+ (49%) but more significant decrease in extraction of Pb^{2+} (16%). Therefore, the increase in steric bulk either due to presence of methyl group in **11** and 1,4-phenylene ring in **13** lead to decrease in extraction of Pb^{2+} more dramatically than that of Ag^+ and thus causes increase in Ag^+/Pb^{2+} selectivity.

Macrocycles **14** and **15**, which possess relatively less flexible diethylenetriamine unit in comparison with bis(3-aminopropyl)amine unit in macrocycles **10–13** showed significantly lower extraction of alkali and alkaline earth and Pb^{2+} picrates and resulted in increase in Ag^+/Pb^{2+} selectivity to 25 and 14, respectively (Fig. 3). Probably, due to smaller spacer length, the carbonyl moieties of the amide units are not able to move into the cavity and thus are not able to participate in binding with all the metal ions.

The participation of amide oxygen in binding with Ag^+ is quite evident from the comparison of carbonyl absorption bands in the IR spectra of macrocycles **10–12** and their complexes with metal picrates. It was observed that the carbonyl absorption bands due to amide groups underwent lowering in frequency by 17–21 cm^{-1} on complexation with Ag^+ picrate. However, Sr^{2+} and K^+ picrates did not cause any significant shift in the carbonyl absorption frequencies. These results point to the stronger binding of these macrocycles with Ag^+ picrate in comparison with other metal picrates and is in agreement with extraction results.

Fluorescence behavior of macrocycles 16–19

The fluorescence spectra of **16**, **17** and **19** are characterized by the broad bands due to an intramolecular charge transfer

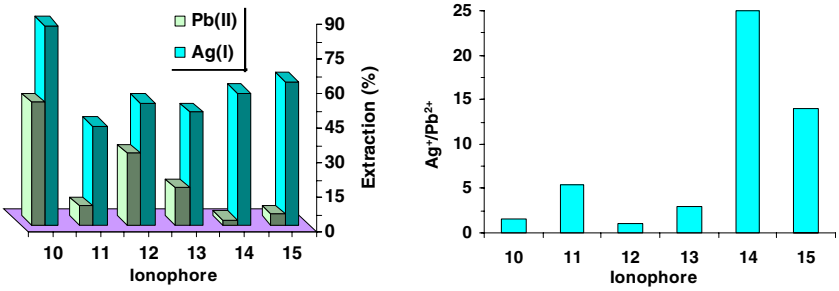


Fig. 3 (**a**) Comparison of the % extraction of the Ag^+ and Pb^{2+} by ionophores 10–15 (**b**) Ag^+/Pb^{2+} selectivity ratio observed for ionophores 10–15

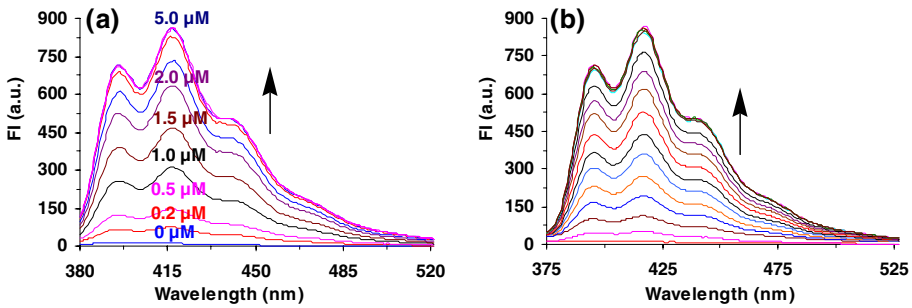


Fig. 4 The effect of (**a**) Ag^+ and (**b**) Fe^{3+} on the fluorescence spectrum of 16 (1 μM)

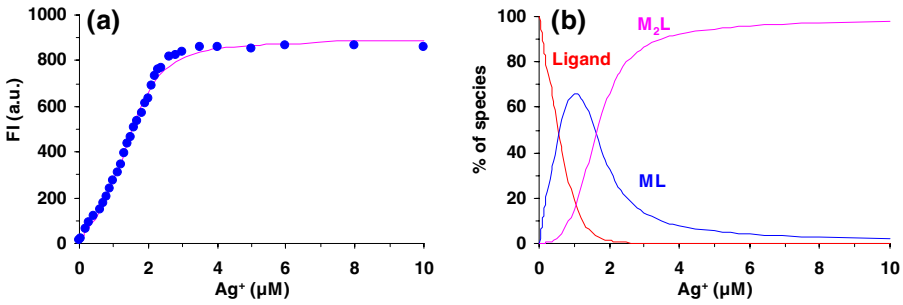


Fig. 5 (**a**) Curve fitting of change in FI of **16** (1 μM) on addition of $AgNO_3$ at 412 nm (•) experimental points, (—) fitted line (**b**) % distribution of ML and M_2L species

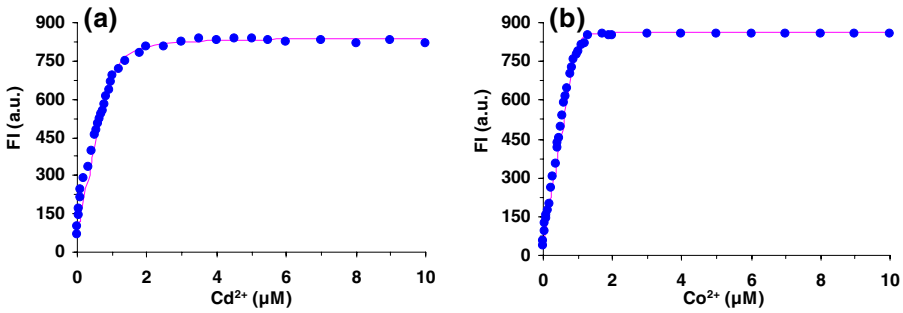


Fig. 6 Curve fitting of change in FI at 412 nm of (**a**) **17** (1 μM) on addition of $Cd(NO_3)_2$ and (**b**) **19** (1 μM) on addition of $Co(NO_3)_2$ (•) experimental points, (—) fitted line

Table 2 Stability constants and fluorescence output of **16–19** as a function of different metal ions as input[a]

Metal ion[b]	Fq/Fe[c]	ML_2	ML	M_2L	Output FE[d]
16 ± Ag^+	"OFF–ON"		7.93 ± 0.20	14.68 ± 0.19	73.0
16 ± Cd^{2+}	"OFF–ON"		6.73 ± 0.04		75.0
16 ± Co^{2+}	"OFF–ON"	15.66 ± 0.54		17.32 ± 0.45	72.0
16 ± Cr^{3+}	"OFF–ON"	11.63 ± 0.07		11.45 ± 0.07	74.0
16 ± Cu^{2+}	"OFF–ON"	13.32 ± 0.12		12.85 ± 0.10	74.0
16 ± Fe^{3+}	"OFF–ON"	12.12 ± 0.08		10.21 ± 0.32	73.0
16 ± Ni^{2+}	"OFF–ON"	12.24 ± 0.25		15.31 ± 0.13	77.0
17 ± Ag^+	"OFF–ON"			14.23 ± 0.06	8.5
17 ± Cd^{2+}	"OFF–ON"		7.13 ± 0.08		11.5
17 ± Cu^{2+}	"OFF–ON"		6.43 ± 0.03		9.8
17 ± Fe^{3+}	"OFF–ON"		6.71 ± 0.04		10.0
17 ± Pb^{2+}	"OFF–ON"	14.05 ± 0.20			10.2
17 ± Ni^{2+}	"OFF–ON"		6.36 ± 0.04		10.5
17 ± Zn^{2+}	"OFF–ON"		6.43 ± 0.09	12.33 ± 0.25	10.4
19 ± Ag^+	"OFF–ON"				19.2
19 ± Cd^{2+}	"OFF–ON"		7.73 ± 0.19		17.7
19 ± Co^{2+}	"OFF–ON"		8.36 ± 0.17		20.2
19 ± Cr^{3+}	"OFF–ON"	11.92 ± 0.15		13.02 ± 0.05	18.7
19 ± Fe^{3+}	"OFF–ON"	10.80 ± 0.05		10.73 ± 0.03	19.3
19 ± Pb^{2+}	"OFF–ON"	12.02 ± 0.15		11.8 ± 0.10	19.3
19 ± Ni^{2+}	"OFF–ON"	11.8 ± 0.20		12.8 ± 0.07	19.0
19 ± Zn^{2+}	"OFF–ON"	12.4 ± 0.24	6.69 ± 0.13		19.8

[a] Experimental conditions: 1×10^{-6} mol dm^{-3} acetonitrile solution of the compounds were used at 25 °C, λ_{ex} = 320 nm for all

[b] The salts used for experiment were nitrates of transition metals

[c] Fq = fluorescence quenching; Fe = fluorescence enhancement

[d] With reference to the fluorescence intensity of the respective compound in the absence of the metal ion

transition within the fluorophore. Attachment of the fluorophore with receptor through spacer resulted in a reduction of the fluorescence intensity of the original fluorophore in acetonitrile which is a clear indication of PET process in all cases.

The macrocycles **16–19** on excitation at $\lambda = 365$ nm gave fluorescence spectra typical of anthracene moiety and did not show aggregation of molecules in 1–10 μM concentration range. Macrocycles **16**, **17** and **19** exhibited significant "OFF–ON" switching behavior with all the transition metal ions. The fluorescence behavior of macrocycle **18** by and large remained unaffected on addition of transition metal ions. Macrocycle **16** showed 70–80 times increase in fluorescence but this emission enhancement decreases to ~20 times in case of *p*-phenylene based macrocycle **19** and to only ~10 times in case of macrocycle **17**. The highest increase in emission in case of **16** on addition of transition metal ions is in parallel with highest extraction of Ag picrate by **16**. Probably, the presence of OMe group in the cavity increases the complexation towards metal ions and thus also the change in fluorescence. The amine *N* bearing 9-anthracenylmethyl moiety coordinates with metal ions and the electron from lone pair of electrons from amine nitrogen can not be transferred to excited state of anthracene moiety which causes inhibition of PET phenomena and thus results in release of fluorescence from anthracene moiety. The illustrative examples of the effect of addition of metal ions on the fluorescence intensities of the macrocycles **16**, **17** and **19** are shown in Figs. 4–6. It is very significant that even the paramagnetic ions like Fe^{3+} and Cu^{2+} show increase in emission by the same order as shown by the diamagnetic ions (Fig. 4).

The fluorescence enhancement values of **16**, **17** and **19** with the metal ions (Table 2) are large enough to consider these simple systems as efficient fluorosensors for transition metal ions. A comparatively large FE value for **16** is due to enhanced PET in the unbound state. It is gratifying to note that a 73-fold enhancement even in the case of Fe^{3+}, reported to be most quenching transition metal ion and for which less reported fluorescence enhancement data has come to our notice.

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