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PAPER

Thiacalix[4]arene based reconfigurable molecular switches: set-reset memorized sequential device†

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The fluorescent chemosensors **3**, **5** and **7** based on thiacalix[4]arene bearing naphthyl groups have been designed and synthesized. The optical chemosensor **3** based on a thiacalix[4]arene of *cone* conformation behaves as "turn-on" optical chemosensor for Fe^{3+} and F^- ions. However, chemosensors **5** and **7** based on a thiacalix[4]arene of 1,3-*alternate* conformation demonstrate "turn-on" optical behaviour for Hg^{2+}, F^- ions (with receptor **5** as turn-on for K^+ ions also) and "turn-off" behaviour for Fe^{3+} ions. The simultaneous presence of Fe^{3+} and Hg^{2+} or K^+ or F^- ions results in formulation of reversible "on-off" switches. Various molecular logic gates developed in response to molecular switching between these chemical inputs have been integrated into sequential logic circuits with memory function in a feedback loop which mimics "set-reset" molecular level information processing device.

Introduction

The development of fluorogenic chemosensors for transition-metal ions[1] and anions[2] is of particular interest because of their applications in chemical, biological and environmental systems. Among the transition metal ions, mercury[3] is particularly important due to its high toxic impact on living beings. Mercury and its compounds easily penetrate skin, respiratory, and gastrointestinal tissues which produces various immunotoxic and neurotoxic effects.[4] The short or long-term exposure to mercury leads to various brain and kidney disorders.[5] Mercury ion contamination can be attributed to anthropogenic sources and natural sources like oceanic and volcanic emission,[6] combustion of fossil fuels[7] and gold mining.[8] Despite its acute toxicity, mercury ions are used in many industries such as electrical, paints and mining.[9] On the other hand, iron, an essential element in human body, provides the oxygen-carrying capacity of heme and plays an important role in many biological processes at the cellular level ranging from oxygen metabolism and electron-transfer processes to DNA and RNA synthesis.[10] The deficiency and excess of iron causes imbalance in iron transport and its storage[11] which results in various pathological disorders,[12] organ malfunction and mortality.[13] Further, among the biologically important anions, fluoride plays a significant role in preventing dental caries,[14] and in the treatment for osteoporosis.[15] Furthermore, F^- ions are also used in hypnotics and psychiatric drugs, in the analysis of drinking water and the refinement of uranium used in nuclear weapon manufacture.[16] An excess of fluoride can result in immune system disruption, thyroid activity depression and fluorosis.[17] Thus, the diversity of their functions, both beneficial and otherwise, makes the detection of mercury, iron and fluoride ions important. Considerable efforts have been devoted to the development of fluorogenic chemosensors for Fe^{3+},[18] Hg^{2+}[19] and F^-[20] ions over the last few years. However, there have been few reports for fluorogenic sensors for Fe^{3+} ions[18] and "turn-on" chemosensors for Hg^{2+}[21] and F^-[22] ions.

Recently, the development of molecular logic gates[23] and photonic devices[24] based on the optical sensing of specific analytes has emerged as an attractive research area of unconventional computing. The chemically encoded information was converted into fluorescent signals as output which results in development of molecular level logic gates such as AND, OR, NOR, INHIBIT, XOR, YES, NOT, and XNOR logic gates. The integration of these molecular logic gates at the molecular level is related to the integration and processing of binary data of conventional microprocessor systems.[25] Conventional silicon based devices have the limitation of their miniaturization down to the nanoscale.[26] Therefore, the development of materials for information storage and retrieval at the molecular level is a promising choice to overcome this limitation.[27] The sequential integration of molecular logic gates is an important step for the realization of information storage processes (memory devices).[28] Sequential logic circuits, which are the function of both past and present inputs, operate through the feedback loop in which one of the outputs of the device operates as input and is memorized as "memory function". Boom *et al.*[29] reported molecular level random access memory (RAM) using "set-reset"/"flip-flop" function based on surface-confined osmium polypyridyl complexes using chemical reagents as inputs. Chemical devices such as molecular keypad locks[30] and set reset logic devices[28,29,31] have been mimicked by sequential integration

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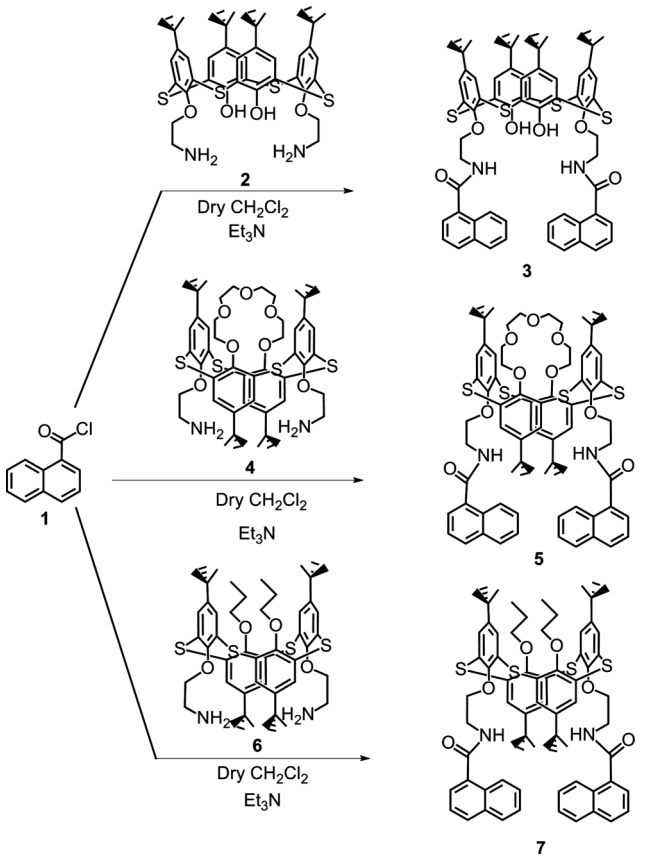
† Electronic supplementary information (ESI) available: $^1H/^{13}C$ NMR, FAB and ESI mass spectra, ^1H NMR spectrum of compounds **3** and **5** with Hg^{2+} and F^- ions, UV-vis and fluorescence titrations of compound **7**, Job's plot of compounds **3**, **5** and **7** with Fe^{3+}, Hg^{2+}, F^-, On-Off switching process between Fe^{3+} and Hg^{2+}/K^+ and selectivity graphs for Fe^{3+} ion. See DOI: 10.1039/c1ob06273e

of molecular logic gates. Recently, Pischel[31c] highlighted the importance of sequential logic circuits with memory function in molecular computing. Thus, intelligent molecules which are capable of producing sequential logic operations are extremely interesting. However there are only a few reports about "set-reset" logic devices[28,29,31] where the memorized unit[32] has been mimicked by sequential integration of molecular logic gates.

Thiacalix[4]arene[33] possessing four bridging sulfur atoms has superior binding properties toward transition metal ions than conventional calix[4]arene. Thus, there is much more potential in investigating the chemistry of thiacalix[4]arenes towards transition metal ions as artificial receptors, enzyme mimics or molecular level devices. Our research programme involves the design, synthesis and evaluation of novel artificial receptors selective for soft metal ions[30a,b,31a,b] and anions,[34] and the development of molecular logic devices based on (thia)calix[4]arenes. Recently, in a preliminary communication,[31a] we reported a thiacalix[4]arene based optical chemosensor bearing two pyrene groups which demonstrates ratiometric sensing with Ag^+ and fluorescence quenching with Fe^{3+} ions in mixed aqueous media. The '*in situ*' prepared Ag^+ and Fe^{3+} complexes showed high selectivity toward cysteine. The molecular switching between three chemical inputs (Ag^+, Fe^{3+}, cysteine) results in various molecular logic gates which have been integrated sequentially to generate a sequential information processing device. In continuation of this work, in the present manuscript, we have designed and synthesized naphthalene-appended chemosensors **3**, **5** and **7** based on thiacalix[4]arenes of *cone* and 1,3-*alternate* conformations. The chemosensor **3** based on a thiacalix[4]arene of *cone* conformation shows high selectivity toward Fe^{3+} and F^- ions with increases in excimer and monomer emission (turn-on) of naphthalene rings. However, chemosensors **5** and **7** based on thiacalix[4]arene of 1,3-*alternate* conformation demonstrate "turn-on" optical behaviour for Hg^{2+}, K^+ and F^- ions and "turn-off" behaviour for Fe^{3+} ions at 364 nm. The presence of Fe^{3+} and Hg^{2+} or K^+ or F^- ions results in formulation of reversible "on-off" switch. Various molecular logic gates developed in response to molecular switching between these chemical inputs have been integrated into sequential logic circuits which generate memory element in a feedback loop of "set-reset" logic function.

Results and discussion

The condensation of 5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-dihydroxythiacalix[4]arene **2**/5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-tetraethylenecrown-5-thiacalix[4]arene **4**/5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-dipropoxythiacalix[4]arene **6**, with 2.0 mol equiv of 1-naphthoyl chloride **1** in dry dichloromethane in the presence of Et_3N furnished **3** (24%)/**5** (32.9%)/**7** (38%) (Scheme 1). The structures of all these receptors **3**, **5** and **7** were confirmed from their spectroscopic and analytical data. The IR spectra of receptors **3**, **5** and **7** showed stretching bands between 1675–1682 cm^{-1} due to NHC═O groups. The FAB and ESI mass spectra of compounds **3**, **5** and **7** showed parent ion peaks corresponding to 1 : 2 condensation products. In general, the ^1H NMR spectra of **3**, **5** and **7** showed two singlets (18H each) for the *tert*-butyl protons, triplets (4H each) for the OCH_2 protons, two singlets (4H each) for the aromatic protons



Scheme 1 Synthesis of thiacalix[4]podands **3**, **5** and **7**.

and a singlet for (2H) for the amide protons of **3** and a triplet (2H) for the amido protons of **5** and **7**. In addition, compound **3** showed one triplet for NCH_2 protons and compound **5** showed one multiplet for NCH_2 and OCH_2 protons, two broad signals (4H, each) for OCH_2 protons while compound **7** showed one quartet (4H) for NCH_2, one triplet (4H) for CH_3 protons.

Cation binding studies of compounds 3, 5 and 7

The UV-vis spectrum of compound **3**/**5**/**7** exhibits an absorption band at λ 293 nm/290 nm/290 nm due to the π–π^* transitions of the naphthalene moiety. The addition of increasing amounts of Fe^{3+} ion (1.0 to 70 equiv for receptor **3** and 1.0 to 50 equiv for receptors **5** and **7**) to the solutions of compounds **3**, **5** and **7** results in an increase in absorption at λ 293 nm and 290 nm and formation of a new red shifted absorption band at 341 nm which indicates the interaction of Fe^{3+} ions with receptors **3**, **5** and **7** (Fig. 1, Supporting Information, Fig. S10†). The red shift in the absorbance spectra of receptors **3**, **5** and **7** upon binding with Fe^{3+} ions is attributed to a photo-induced charge transfer mechanism.[35]

The fluorescence spectrum of compounds **3**/**5**/**7** exhibits fluorescence emission at 352 nm (ϕ_f = 0.159 for **3**, ϕ_f = 0.134 for **5** and ϕ_f = 0.067 for **7**, Supporting Information, page S12†)[36] when excited at 310 nm (Fig. 2, Supporting Information, Fig. S12†). Among all the metal ions tested, the receptor **3** showed high selectivity towards Fe^{3+} ions while receptors **5** and **7** show high selectivity toward Fe^{3+} and Hg^{2+} ions in contrasting modes. Upon addition of increasing amounts of Fe^{3+} ion (0.01–10 μM) as its perchlorate salt to the solution of compound **3**, there was

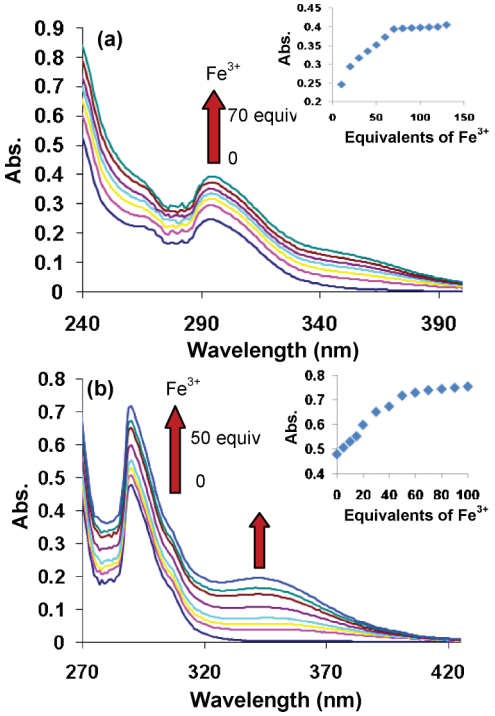


Fig. 1 Absorption spectra of (a) compound **3** (10 μM) and (b) compound **5** on addition of Fe^{3+} (0–70 equiv and 0–50 equiv, respectively) in THF. Inset; Change in absorbance with different equivalents of Fe^{3+} ions.

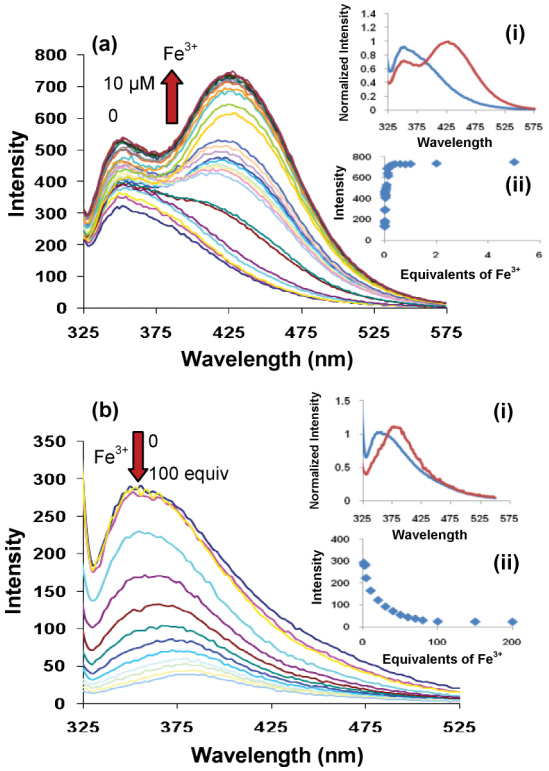


Fig. 2 Fluorescence emission spectra of (a) receptor **3** (10 μM) and (b) receptor **5** upon various additions of Fe^{3+} (0–10 μM and 0–100 equiv, respectively) in THF. Inset; normalized fluorescence intensity with Fe^{3+} ions (2a–i and 2b–i) and fluorescence intensity changes with different equivalents of Fe^{3+} ions (2a–ii and 2b–ii).

small increase in fluorescence emission at 352 nm but a significant emission band is formed at 428 nm (ϕ_f = 0.447, Fig. 2a). The formation of red shifted emission band at 428 nm (Fig. 2a) of compound **3** with Fe^{3+} ions was attributed to intramolecular excimer formation between two naphthalene rings (Supporting Information, Fig. S11†). The intermolecular binding interactions between Fe^{3+} ions and oxygen atoms of **3** moieties trigger the intramolecular π–π interactions of naphthalene rings which lead to excimer formation.[37] The "off-state" of free ligand **3** at 428 nm turns to "on-state" with the addition of Fe^{3+} ions. On the other hand, the addition of increasing amounts of Fe^{3+} ions (1–100 equiv) to the solutions of receptors **5** and **7**, results in significant quenching in the fluorescence emission (ϕ_f = 0.011 for **5**.$\mathbf{Fe^{3+}}$ and ϕ_f = 0.007 for **7**.$\mathbf{Fe^{3+}}$, Fig. 2b, Supporting Information, Fig. S12†). The fluorescence quenching induced by Fe^{3+} is attributed to reverse photo-induced electron transfer (reverse-PET) from naphthalene units to carbonyl oxygens[38] which turn inward from outward orientation and the electron density diminished upon iron binding (Supporting Information, Fig. S13†). However, the addition of Hg^{2+} ions (200 equiv) to the solutions of **5** and **7** leads to an increase in fluorescence emission at 364 nm with a red shift of 12 nm (ϕ_f = 0.263 for **5**.$\mathbf{Hg^{2+}}$ and ϕ_f = 0.227 for **7**.$\mathbf{Hg^{2+}}$, Fig. 3a, Supporting Information, Fig. S14†). The increase in fluorescence emission at 364 nm induced by Hg^{2+} ions is due to binding of Hg^{2+} ions with amide moiety resulting in suppression of photo-induced electron transfer from amide to naphthalene moiety. The binding modes of receptor **5** with mercury ions were evaluated by ^{1}H NMR spectroscopy. It was found that on addition of a small amount of Hg^{2+} ions to receptor **5**, a significant downfield shift of 0.77, 0.17 and 0.55 ppm was observed for protons of NCH_2, OCH_2 and CH_2NH groups of naphthyl arms, respectively (Supporting Information, Fig. S15†) which indicates that Hg^{2+} is interacting with nitrogens of naphthyl arms of receptor **5**. In addition, compound **5** also shows fluorescence enhancement with K^+ ions (ϕ_f = 0.220 for **5**.$\mathbf{K^+}$, Fig. 3b). This enhancement in fluorescence emission is different from the **5**.Hg^{2+} complex and is due to complexation of K^+ with crown-5 ring which suppresses the photo induced electron transfer from polyether chain to naphthalene rings. The complexation of K^+ with crown-5 ring is further supported by the ^{1}H NMR spectrum of compound **5** with potassium perchlorate which shows significant downfield shifts of 0.14, 0.27, 0.12 and 0.22 ppm for protons of OCH_2 (c, d, e, f) of crown-5 moiety, respectively (Supporting Information, Fig. S16†). Under the same conditions as used above for Fe^{3+}, Hg^{2+} and K^+ ions, we also tested the fluorescence response of compounds **3**, **5** and **7** to other metal ions such as Li^+, Na^+, Ba^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, Co^{2+} besides Fe^{3+}, Hg^{2+} and K^+, no significant fluorescence change of **3**, **5** and **7** occurred in the presence of these cations (Fig. 4 and 5). The binding constants (log β_{11}) of compounds **3**, **5** and **7** toward different metal ions calculated from fluorescence titration experiments by means of the SPECFIT programme (global analysis system V3.0 for 32-bit Window system),[39] are shown in Table 1 which clearly indicates the high binding affinity of compound **3** towards Fe^{3+} ions and compounds **5** and **7** toward Fe^{3+} and Hg^{2+} ions. In addition, compound **5** also showed good binding affinity towards K^+ ions. The method of continuous variation (Job's plot) was used to find

Table 1 Stability constants (log β_{11}) values of **3**.M^{n+} **5**.M^{n+}, **7**.M^{n+} complexes

	Metal ion (M^{n+})													
Receptor	Li^+	Na^+	K^+	Ba^{2+}	Mg^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Hg^{2+}	Pb^{2+}	Co^{2+}	Fe^{2+}	Fe^{3+}
3	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	7.8 ± 0.09
5	—[a]	—[a]	5.56 ± 0.35	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	4.96 ± 0.37	—[a]	—[a]	—[a]	4.63 ± 0.08
7	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]	4.68 ± 0.18	—[a]	—[a]	—[a]	4.38 ± 0.64

[a] Not available because of minor spectral changes.

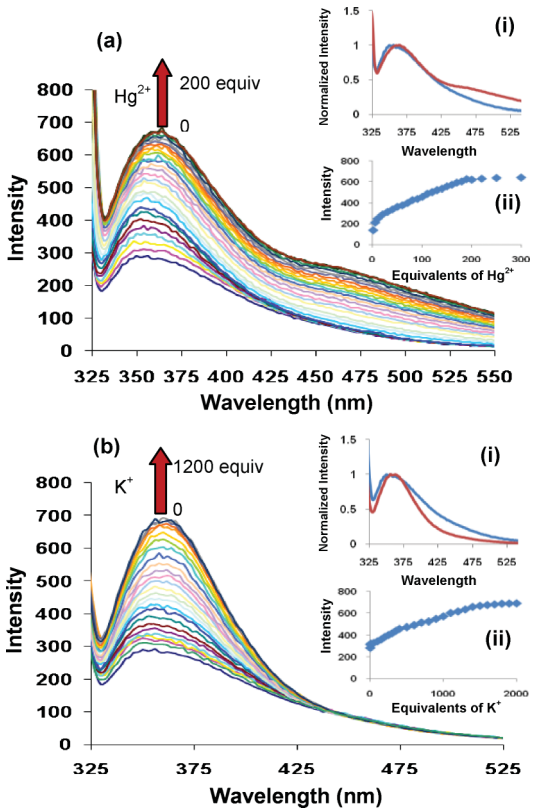


Fig. 3 Fluorescence emission spectra of receptor **5** (10 μM) upon various additions of (a) Hg^{2+} (0–200 equiv) and (b) K^+ (0–1200 equiv) in THF. Inset; normalized fluorescence intensity with Hg^{2+} (3a–i)/K^+ ions (3b–i) and fluorescence intensity changes with different equivalents of Hg^{2+} (3a–ii)/K^+ ions (3b–ii).

the 1 : 1 stoichiometry of **3**.Fe^{3+}, **5**.G and **7**.G complexes (G = Fe^{3+}, Hg^{2+} and F^-) (Supporting Information, Fig. S17–S19†).

Anion binding studies of compounds 3, 5 and 7

Since the receptors **3**, **5** and **7** contain amide units which are known to interact with anions through hydrogen bonding with the proton of the amide group,[40] we investigated the binding behaviour of compounds **3**, **5** and **7** toward different anions like F^-, Cl^-, Br^-, I^-, CN^-, OAc^-, HSO_4^-, $H_2PO_4^-$ and NO_3^- as their tetrabutylammonium salt. The anion binding studies were carried out in tetrahydrofuran. Among all the anions studied, the receptors **3**, **5** and **7** showed high selectivity toward F^- ions. The addition of increasing amounts of F^- ions (1–500 equiv, each) to the solutions of compounds **3**, **5** and **7** results in an increase in fluorescence emission at 352 nm (ϕ_f = 0.330 for **3**.F^-, ϕ_f = 0.220 for **5**.F^- and ϕ_f = 0.294 for **7**.F^-, Fig. 6, Supporting Information, Fig. S20†). The enhancement in fluorescence emission is probably due to charged hydrogen bonding between amide NH protons and fluoride ions which increase the rigidity of the receptor and thereby disfavouring the non-radiative vibrational/rotational decay processes and hence reduction of photo-induced transfer (PET) process.[41] Earlier, Tarr *et al.*[41a] and Zhu *et al.*[41b] reported similar enhancement in fluorescence emission with fluoride ions. Further, the intermolecular interactions between compound **3**/**5**, and F^- ions were also studied using ^{1}H NMR spectroscopy. It was found that on addition of small amounts of tetrabutylammonium fluoride to a solution of compound **3**/**5**, the weakening of signal due to NH protons takes place which indicates that interaction of these protons is taking place with fluoride ions. On adding one equivalent of tetrabutylammonium fluoride to a solution of compound **3**/**5**, the NH protons completely disappeared (Supporting Information, Fig. S21 and S22†). This indicates the

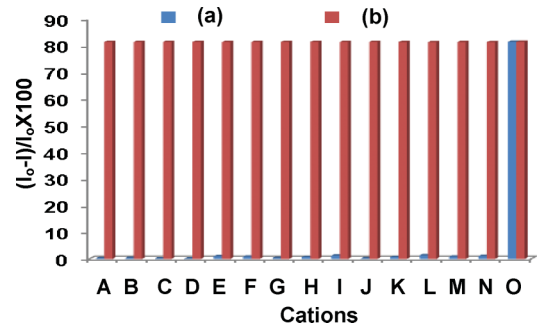


Fig. 4 (a) Selectivity of **3** (10 μM) towards Fe^{3+} upon addition of different cations and (b) Competitive selectivity of **3** (10 μM) towards Fe^{3+} in the presence of different cations in THF. A = Li^+, B = Na^+, C = K^+, D = Ba^{2+}, E = Mg^{2+}, F = Ni^{2+}, G = Cu^{2+}, H = Zn^{2+}, I = Ag^+, J = Cd^{2+}, K = Hg^{2+}, L = Pb^{2+}, M = Co^{2+}, N = Fe^{2+}, O = Fe^{3+}.

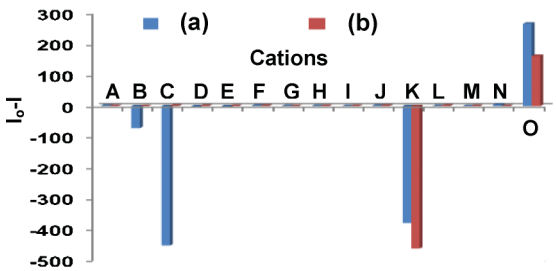


Fig. 5 (a) Selectivity of **5** (10 μM) toward Fe^{3+}, Hg^{2+} and K^+ ions (b) Selectivity of **7** (10 μM) toward Fe^{3+} and Hg^{2+} upon addition of different cations in THF. A = Li^+, B = Na^+, C = K^+, D = Ba^{2+}, E = Mg^{2+}, F = Ni^{2+}, G = Cu^{2+}, H = Zn^{2+}, I = Ag^+, J = Cd^{2+}, K = Hg^{2+}, L = Pb^{2+}, M = Co^{2+}, N = Fe^{2+}, O = Fe^{3+}.

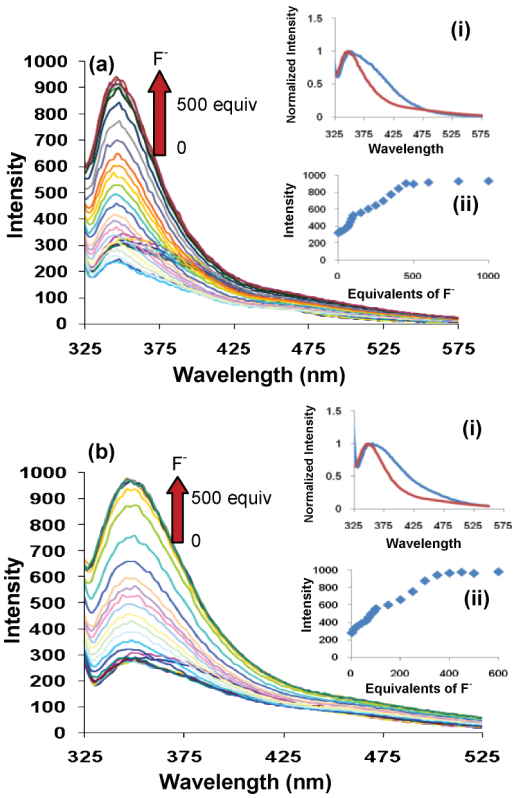


Fig. 6 Fluorescence emission spectra of (a) receptor **3** (10 μM) and (b) receptor **5** upon various additions of F^- (0–500 equiv) in THF. Inset; normalized fluorescence intensity with F^- ions (6a–i and 6b–i) and fluorescence intensity changes with different equivalents of F^- ions (6a–ii and 6b–ii).

fast exchange of protons between amide NH and fluoride ions which results in charged hydrogen bonding. We also tested the fluorescence response of compounds **3**, **5** and **7** in the presence of other anions like Cl^-, Br^-, I^-, OAc^-, CN^-, HSO_4^-, NO_3^- besides F^-, no significant fluorescence change of compounds **3**, **5** and **7** occurred in the presence of these anions (Supporting Information, Fig. S23†).

Molecular switching behaviour of compounds 3, 5 and 7

Since compound **3** shows optical sensing toward Fe^{3+} and F^- ions and the compounds **5** and **7** toward Fe^{3+} and Hg^{2+}, F^- (and K^+ for compound **5**) ions in contrasting modes, we investigated the "on-off" switching process and sequence dependence emission output between these chemical inputs. For receptor **3**, the addition of 1.0 equiv of Fe^{3+} results in excimer formation at 428 nm ($\phi_f = 0.447$) and with further addition of 3.0 equiv of F^- ions, the fluorescence emission restored to free ligand ($\phi_f = 0.162$, Fig. 7) which is due to complexation of F^- with Fe^{3+} ions. Further, addition of Fe^{3+} ions (5.0 equiv) to the above solution results in excimer formation at 428 nm (Supporting Information, Fig. S24†). Thus, compound **3** behaves as a reversible "off-on" switch at 428 nm with two chemical inputs of Fe^{3+} and F^- ions.

Further, we have investigated the switching behaviour of receptor **5** between Fe^{3+}, $Hg^{2+}/K^+/F^-$ ions and between Fe^{3+} and Hg^{2+}/F^- ions for receptor **7**. The addition of Hg^{2+} ions to the solutions of **5**.Fe^{3+} and **7**.Fe^{3+} complexes *i.e.* "off-state", results in

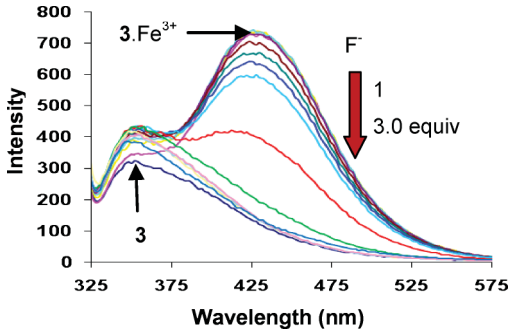


Fig. 7 Fluorescence emission spectra of **3**.Fe^{3+} upon various additions of F^- (0–3.0 equiv) in THF.

revival of fluorescence emission ($\phi_f = 0.110$ and 0.139, respectively) at 364 nm *i.e.* "on-state" (Fig. 8, Supporting Information, Fig. S25†). The revival of fluorescence emission indicates that Fe^{3+} ion interacting with carbonyl oxygens of naphthyl arms is pushed out of receptors **5** and **7** due to an electrostatic repulsion between the two metal ions and a negative allosteric effect (Supporting Information, Fig. S26†). Further, fluorescence emission at 364 nm gets quenched with addition of Fe^{3+} ions (Supporting Information, Fig. S27 and S28†) which shows that receptors **5** and **7** behave as a reversible "on-off" switch with Fe^{3+} and Hg^{2+} ions. In addition, compound **5** showed similar molecular switching behaviour between Fe^{3+} and K^+ ions. The addition of K^+ ions to the solution of **5**.Fe^{3+} complex *i.e.* "off-state", revive the fluorescence emission at 364 nm ($\phi_f = 0.044$) *i.e.* "on-state" (Fig. 9a) due to an electrostatic repulsion between the two metal ions and a negative allosteric effect (Supporting Information, Fig. S29†). Further addition of Fe^{3+} ions to **5**.Fe^{3+}.K^+ complex quenches the fluorescence emission indicating its reversibility. The **7**.Fe^{3+} complex showed no change in fluorescence emission with the addition of K^+ ions indicating the crown-5 ring is must for K^+ binding.

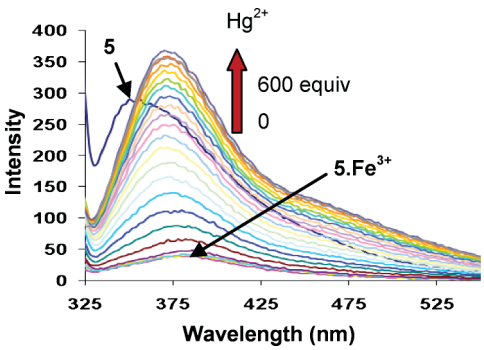


Fig. 8 Fluorescence emission spectra of receptor **5**.Fe^{3+} upon various addition of Hg^{2+} (0–600 equiv) in THF.

The "on-off" molecular switching behaviour was also observed with Fe^{3+} and F^- ions in the case of compounds **5** and **7**. The addition of Fe^{3+} ions to the solution of receptors **5** and **7** leads to fluorescence quenching *i.e.* "off state". The addition of F^- ions to the solution of **5**.Fe^{3+} complex or **7**.Fe^{3+} complex results in revival of fluorescence emission ($\phi_f = 0.072$ and 0.088, respectively) *i.e.* "on state" (Fig. 9b, Supporting Information, Fig. S30†). The revival of fluorescence emission with the addition of F^- ion is due to a higher affinity of Fe^{3+} ions for F^- ions than with the receptors **5**

Table 2 Truth table for the INHIBIT gate of compound **3** with chemical inputs of Fe^{3+} and F^- ions

Entry	*In* 1 (Fe^{3+})	*In* 2 (F^-)	Output 1 (λ 352 nm)	Output 2 (λ 428 nm)
1	0	0	0	0
2	1	0	0	1
3	0	1	1	0
4	1	1	0	0

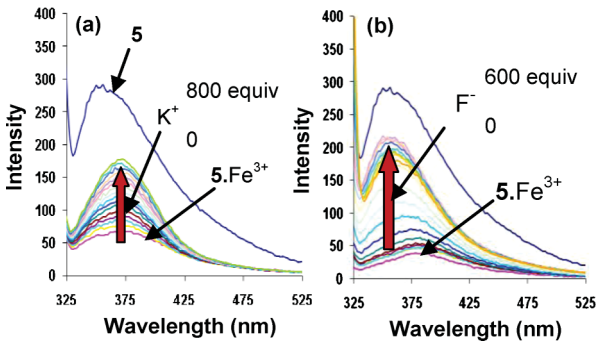


Fig. 9 Fluorescence emission spectra of receptor **5**.Fe^{3+} upon various addition of (a) K^+ (0–800 equiv) and (b) F^- (0–600 equiv) in THF.

and **7**. The fluorescence is quenched again *i.e.* "off state" when Fe^{3+} ions were titrated into the solution of **5**.Fe^{3+}.F^- and **7**.Fe^{3+}.F^- complexes (Supporting Information, Fig. S31 and S32†). This reversible "on-off" switching process of receptors **5** and **7** could not be observed with other anions indicating the high selectivity of **5**.Fe^{3+} and **7**.Fe^{3+} complexes toward fluoride ions.

Development of molecular logic gates and device

The reversible "on-off" switching behaviour of compounds **3**, **5** and **7** can be demonstrated with the help of binary logic. Binary digits (0 or 1) can be used to represent the two states "off or on" of each signal and the chemical inputs of Fe^{3+}, F^-, Hg^{2+}, and K^+ are designated as *In*1, *In*2, *In*3 and *In*4 respectively and considered as "1" when they are present and "0" if they are absent. For receptor **3**, the output signals were measured as the fluorescence emissions at 352 nm and 428 nm, being "1" when fluorescence emission is above 300 a.u. and "0" when it is below. However for receptors **5** and **7**, the output signals were measured as the fluorescence emissions at 352 nm/364 nm and considered as "0" when the emission intensity is below 50 a.u. and "1" when it is above.

In case of receptor **3**, for the chemical inputs of Fe^{3+} (*In*1) and F^- (*In*2), the input and output strings corresponding to fluorescence responses are illustrated in Table 2. The output at 352 nm (*out* 1) and 428 nm (*out* 2) of receptor **3** with chemical inputs of Fe^{3+} (*In*1) and F^- (*In*2) is activated through an INHIBIT gate (Fig. 10).

However, for receptor **5**, three reversible "on-off" switches operate with *i.e.* Fe^{3+}-Hg^{2+}, Fe^{3+}-K^+ and Fe^{3+}-F^-, and for receptor **7**, two reversible "on-off" switches operate *i.e.* Fe^{3+}-Hg^{2+} and Fe^{3+}-F^-. The input and output signals for these reversible "on-off" switches of receptors **5** and **7** are shown in truth Table 2. The logic operations are represented by two inputs: set (*In*2 = F^- or *In*3 = Hg^{2+} or *In*4 = K^+) and reset (*In*1 = Fe^{3+}) as a function of memory element (Table 3). The sequential logic circuit constructed for these switches demonstrate the memory effect of receptors **5** and **7** in

Table 3 Truth table for memory unit for two input signals set and reset, where 0 and 1 indicates that the corresponding signals is off or on

Reset *In*1	Set *In*2/*In*3/*In*4	*Output* (352/364 nm)
0	0	1
1	0	0
0	1	1
1	1	1

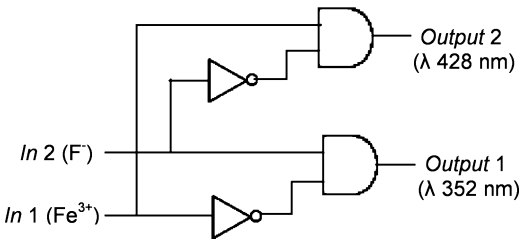


Fig. 10 The logic circuit of receptor **3** with chemical inputs of Fe^{3+} and F^- ions mimicking an INHIBIT gate.

the feedback loop in which one of the outputs of the device acts as input (Fig. 11).[31a] This behaviour is the basis of memory elements of integrated logic circuits used in microprocessors. The reversible and reconfigurable sequences of set/reset logic operations in a feedback loop demonstrate the memorized state of system with "write-read-erase-read" functions with optical output signal at 352 nm/364 nm (Fig. 12). When "set input" is high (set = 1), the system "writes" and saves "logic state 1" with the strong emission at 352 nm/364 nm. This encoded information is "read" out optically as strong emission at 352 nm/364 nm. The stored information was "erased" by "reset input" (*In*1 = 1) with quenching in emission at 364 nm and system write and save "logic state 0". Many write-erase cycles were conducted on compounds **5** and **7** considering their "on-off" states with good rewritable characteristics and no fluorescence emission degradation is observed for both the "on" state and "off" state during the state transition.

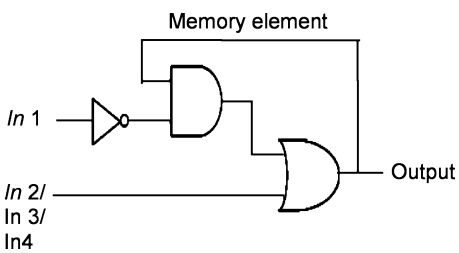


Fig. 11 Sequential logic circuit which displays the memory unit with two input strings set (*In* 1) and reset (*In*2/*In*3/*In*4) at output of λ 352/364 nm.

Conclusions

In conclusion, we synthesized and evaluated the fluorescence behaviour of chemosensors **3**, **5** and **7** based on thiacalix[4]arenes of *cone* and 1,3-*alternate* conformations bearing naphthyl groups. The optical chemosensor **3** based on a thiacalix[4]arene of *cone* conformation behaves as an "off-on" optical chemosensor for Fe^{3+} and F^- ions. However, chemosensors **5** and **7** based on thiacalix[4]arenes of 1,3-*alternate* conformation demonstrate "turn-on" optical behaviour for Hg^{2+}, F^- ions (also receptor **5** as

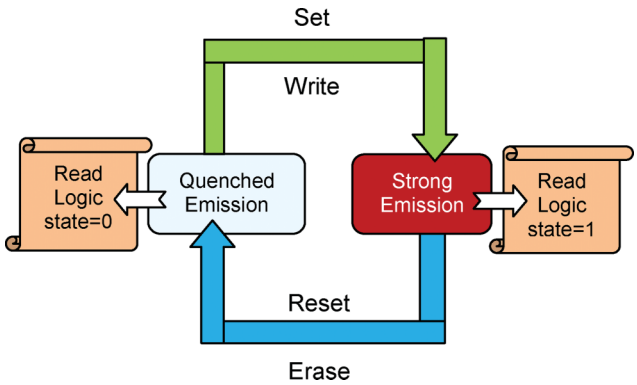


Fig. 12 The feedback loop showing reversible logic operations for memory element with two inputs (set and reset) possessing "write-read--erase-read" functions with optical output signals.

turn-on for K^+ ions) and "turn-off" behaviour for Fe^{3+} ions. The simultaneous presence of Fe^{3+} and Hg^{2+} or K^+ or F^- ions results in the formulation of reversible "on-off" switches. Various molecular logic gates developed in response to molecular switching between these chemical inputs have been integrated into sequential logic circuits with memory function in a feedback loop which mimics the "set-reset" molecular level information processing device.

Experimental

General information

The ^1H and ^{13}C NMR spectra were recorded on a JEOL 300 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent. FAB Mass spectra were recorded on a JEOL XS102/DA-6000 mass spectrometer using xenon (6 kV, 10mA) as FAB gas. Infrared spectra were recorded on a Pye Unicam SP3-3 Infrared spectrophotometer. The UV/vis and fluorescence spectra were recorded with a Shimdzu UV-2450 spectrophotometer and a CARY-varian 100 spectrofluorophotometer, respectively. Stock solutions (0.1 M) of metal perchlorate salts and tetrabutylammonium anion salts were prepared in tetrahydrofuran. Stock solutions (0.1 mM) of compounds **3**, **5** and **7** were prepared in tetrahydrofuran. The fluorescence spectra were performed by using 10 μM of compounds **3**, **5** and **7** in THF with varying concentration of guests (cations and anions) and excitation wavelength was at 310 nm and slit width of 10.

General procedure for synthesis of compounds 5–7

1-Naphthoyl chloride **1** (53 mg, 0.27 mmol) was added to a solution of 5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-dihydroxythiacalix[4]arene **2** (100 mg, 0.12 mmol), 5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-tetraethylenecrown-5-thiacalix[4]arene **4** (100 mg, 0.11 mmol)/5,11,17,23-tetra-*tert*-butyl-*syn*-25,27-bis(2-aminoethoxy)-26,28-dipropoxythiacalix[4]arene **6** (100 mg, 0.11 mmol) and Et_3N (0.22 mmol) in dry CH_2Cl_2 (30 ml). The reaction was stirred at room temperature for 48 h. After completion of reaction (TLC), the reaction mixture was diluted with CH_2Cl_2 (50 ml), washed thrice with water (50 ml), dried over anhydrous sodium sulphate and distilled under reduced pressure to give crude product which was recrystallized from dichloromethane and methanol (1 : 4, v/v) to give the corresponding product **3**/**5**/**7**.

Compound 3

Yield: 34 mg (24%): off white solid; m. p. 195–197 °C; IR (KBr pallet, cm^{-1}) 1677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.90 (18H, s, $C(CH_3)_3 \times 2$), 1.27 (18H, s, $C(CH_3)_3 \times 2$), 3.88 (4H, t, J = 4.8 Hz, $NCH_2 \times 2$), 4.39 (4H, t, J = 4.2 Hz, $OCH_2 \times 2$), 7.08–7.15 (6H, m, ArH × 6), 7.37–7.42 (4H, m, ArH × 4), 7.47 (4H, s, ArH × 4), 7.67–7.72 (6H, m, ArH × 6), 8.05 (2H, s, OH × 6), 8.17 (2H, br, NH × 2), 8.46 (2H, t, J = 4.2 Hz, ArH × 2).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 30.8 $(CH_3)_3$, 31.4 $(CH_3)_3$, 34.1 $(C(CH_3)_3)$, 34.2 $(C(CH_3)_3)$, 40.3 (NCH_2), 75.7 (OCH_2), 120.8 (ArC), 124.3 (ArC), 125.5 (ArC), 125.8 (ArC), 126.0 (ArC), 126.8 (ArC), 127.9 (ArC), 128.3 (ArC), 130.1 (ArC), 130.2 (ArC), 133.4 (ArC), 134.1 (ArC), 134.5 (ArC), 134.8 (ArC), 143.0 (ArC), 148.8 (ArC), 155.7 (ArC), 156.2 (ArO), 170.2 (CO); FAB-MS: m/z 1115 (M^+); Anal. Calcd for $C_{66}H_{70}N_2O_6S_4$: C, 71.06; H, 6.32; N, 2.51; S, 11.50, Found: C, 70.97; H, 6.21; N, 2.33; S, 11.29%.

Compound 5

Yield: 46 mg (32.9%); off white solid; m. p. 210–212 °C; IR (KBr pallet, cm^{-1}) 1675; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.09 (18H, s, $C(CH_3)_3 \times 2$), 1.35 (18H, s, $C(CH_3)_3 \times 2$), 2.98–3.09 (8H, m, $NCH_2 \times 2$, $OCH_2 \times 2$), 3.38 (4H, br, $OCH_2 \times 2$), 3.59 (4H, br, $OCH_2 \times 2$), 3.90 (4H, t, J = 7.5 Hz, $OCH_2 \times 2$), 4.14 (4H, t, J = 6.6 Hz, $OCH_2 \times 2$), 6.66 (2H, t, J = 5.4 Hz, NH × 2), 7.30 (4H, s, ArH × 4), 7.34–7.38 (6H, m, ArH × 6), 7.40–7.52 (6H, m, ArH × 6), 7.82–7.89 (4H, m, ArH × 4), 8.30 (2H, t, J = 5.4 Hz, ArH × 2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 30.6 $(CH_3)_3$, 31.0 $(CH_3)_3$, 33.7 $(C(CH_3)_3)$, 33.9 $(C(CH_3)_3)$, 39.2 (NCH_2), 69.7 (OCH_2), 72.3 (OCH_2), 72.9 (OCH_2), 73.0 (OCH_2), 73.8 (OCH_2), 124.1 (ArC), 124.6 (ArC), 125.2 (ArC), 125.9 (ArC), 126.4 (ArC), 126.5 (ArC), 126.8 (ArC), 126.9 (ArC), 127.2 (ArC), 127.7 (ArC), 129.8 (ArC), 130.2 (ArC), 133.3 (ArC), 133.7 (ArC), 146.3 (ArC), 155.1 (ArC), 156.0 (ArC), 168.9 (CO); ESI-MS: m/z 1295 (M + Na^+); Anal. Calcd for $C_{74}H_{84}N_2O_9S_4$: C, 69.78; H, 6.65; N, 2.20; S, 10.07, Found: C, 69.53; H, 6.39; N, 2.07; S, 9.86%.

Compound 7

Yield: 52 mg (38.6%); off white solid; m. p. 208–210 °C; IR (KBr pallet, cm^{-1}) 1676; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.71 (6H, t, J = 7.5 Hz, $CH_3 \times 2$), 1.06 (18H, s, $C(CH_3)_3 \times 2$), 1.10–1.28 (22H, m, $C(CH_3)_3 \times 2$, $CH_2 \times 2$), 3.41 (4H, q, J = 5.4 Hz, $NCH_2 \times 2$), 3.80 (4H, t, J = 7.5 Hz, $OCH_2 \times 2$), 4.26 (4H, t, J = 5.7 Hz, $OCH_2 \times 2$), 7.15 (2H, t, J = 5.4 Hz, NH × 2), 7.28 (4H, s, ArH × 4), 7.34–7.42 (8H, m, ArH × 8), 7.47–7.51 (4H, m, ArH × 4), 7.81–7.90 (4H, m, ArH × 4), 8.34 (2H, t, J = 3.3 Hz, ArH × 2). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 10.1 (CH_3), 22.3 (CH_2), 31.0 $(CH_3)_3$, 31.2 $(CH_3)_3$, 34.1 $(C(CH_3)_3)$, 34.2 $(C(CH_3)_3)$, 39.8 (NCH_2), 70.4 (OCH_2), 71.8 (OCH_2), 124.5 (ArC), 125.0 (ArC), 125.7 (ArC), 126.3 (ArC), 126.9 (ArC), 127.3 (ArC), 127.9 (ArC), 128.2 (ArC), 128.9 (ArC), 129.8 (ArC), 130.3 (ArC), 130.6 (ArC), 145.4 (ArC), 146.2 (ArC), 156.7 (ArO), 157.6 (ArC), 169.3 (CO); ESI-MS: m/z 1221.5 (M + Na^+); Anal. Calcd for $C_{72}H_{82}N_2O_9S_4$: C, 72.08; H, 6.89; N, 2.34; S, 10.69, Found: C, 71.89; H, 6.72; N, 2.11; S, 10.38%.

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