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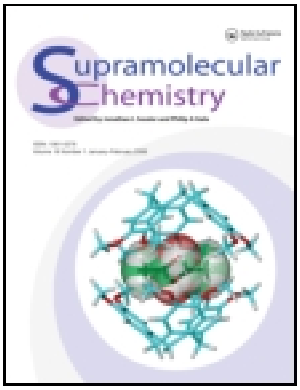

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Epoxy-based oligomer containing dithia-aza-based naphthylazobenzene pendant: a chemosensor for Hg^{2+} and Cu^{2+} ions

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Epoxy-based oligomer containing dithia-aza-based naphthylazobenzene pendant: a chemosensor for Hg^{2+} and Cu^{2+} ions

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A simple epoxy-based oligomer **1** containing naphthylazobenzene-appended dithia-aza moieties was prepared. In UV–vis measurements, the proposed oligomer showed the ion-sensing ability to Hg^{2+} and Cu^{2+} ions. The discrimination between two differently responding Hg^{2+} and Cu^{2+} ions was also realised from 'ON–OFF' type fluorescence responses of **1**.

Keywords: epoxy-based oligomer; chemosensor; Hg^{2+} and Cu^{2+} ions

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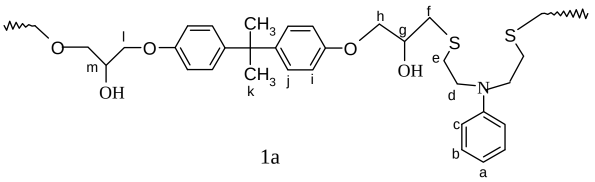
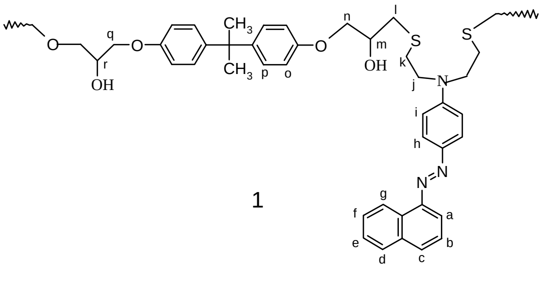
Introduction

The rational design and synthesis of efficient chemosensors capable of detecting Hg^{2+} and Cu^{2+} ions is an emerging field with potential application in industrial, environmental and biomedical monitoring (*1, 2*). Although a large number of small molecular systems have been reported (*3, 4*) to selectively recognise such metal ions, a great deal of effort continues to focus on the construction of polymeric chemosensors bearing metal ion complexing units. However, N-azo-functionalised dithia-aza linker is currently used (*5*) in the design of chemosensors owing to the relatively strong electron donor function of tertiary N-atom and S-atom for specific metal ions. We believe that if it is possible to extend the usage of such linker system, then many advantages of macromolecular structure can be utilised to develop working Hg^{2+} ion sensor. Furthermore, epoxy-based polymers are more interesting because of their attractive properties such as easy processability, good chemical resistance and dimensional stability, potential for reuse and even with the appropriate choice of design the properties of the resulting polymer can be adjusted for many applications. Very recently, we have reported the synthesis of 1-naphthylamine bearing epoxy-based polymer, which shows Fe^{3+} ion selectivity. Therefore, continuing our investigation in the field of epoxy-based metal ion sensor (*6*), we report herein a simple epoxy-based oligomeric chemosensor **1** for Hg^{2+} and Cu^{2+} ions extending the usage of dithia-aza-based naphthylazobenzene pendant. It is anticipated that fine-tuning of the chelation of Hg^{2+} and Cu^{2+} ions by dithia-aza unit can significantly alter the signalling behaviour of the naphthylazobenzene unit. It is also our further interest to examine in detail the fluorescence quenching effects of **1** with the representative metal ions. Furthermore, the oligomeric structure can induce the solubility in aqueous medium.



1a



1

Results and discussion

Synthesis and characterisation

2,2′-(Phenylazanediyl) diethanethiol was synthesised according to Scheme 1 by following the reported procedure (*5a*). This moiety has been demonstrated as an excellent entity for Hg^{2+} ion sensor utilising N-atom and S-donor.

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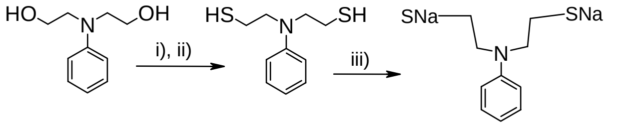


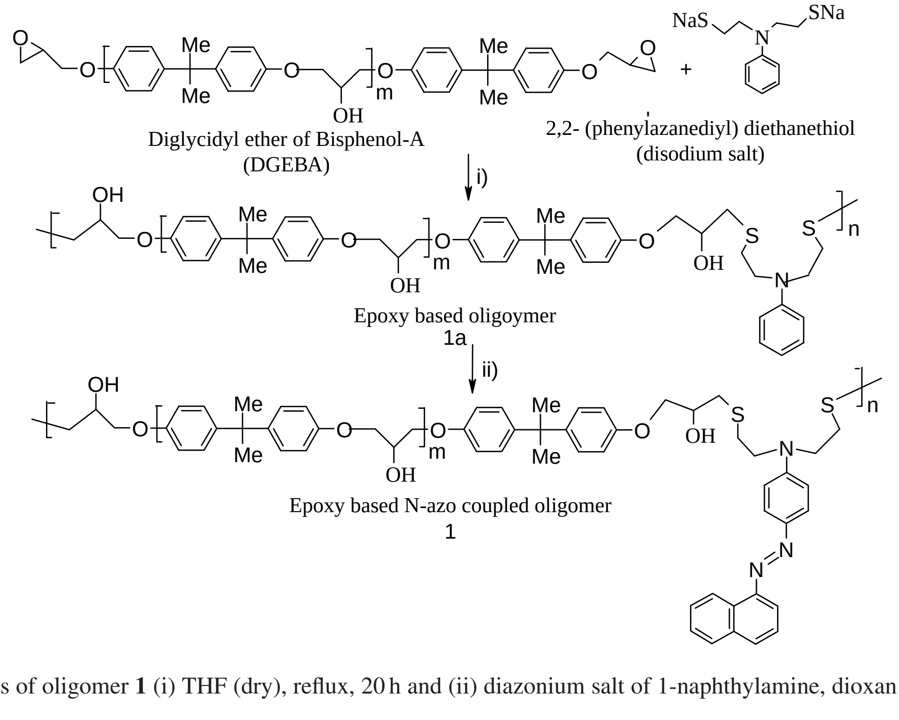
Scheme 1. (i) *p*-TsCl, pyridine, 0–5°C (80%), (ii) (a) Thiourea/EtOH, reflux, (b) $NaHCO_3/H_2O$, 80–90°C and (iii) dry THF/NaH, reflux.

Thus, in search of a macromolecular scaffold for the placement of a number of dithia-aza units, we anchored this moiety on epoxy resin scaffold as illustrated in Scheme 2. The oligomer **1a** was then reacted with diazonium salt of 1-naphthylamine to yield **1**. The titled oligomers **1a** and **1** were unequivocally characterised by FT-IR, UV–vis, NMR, GPC and elemental analyses.

Incorporation of 2,2′-(phenylazanediyl) diethanethiol unit into the oligomer was estimated to be 25% when comparing ^{1}H NMR integration of the signals for the anilinic protons with methyl protons of bisphenol-A moiety. The ^{1}H NMR analysis indicated that the resonance corresponding to the proton in the *p*-position of anilinic moiety totally disappeared on azo-coupling reaction. On azo-coupling reaction, other changes are exhibited in the chemical shifts of protons of anilinic moiety and the dithia-aza unit. The degree of azo-funtionalisation for **1a** was estimated to be about 100% from the ^{1}H NMR analysis.

Chemosensing behaviour

For the practical applicability of a chemosensor, water solubility is a matter of necessity. In this context, the oligomer **1** can maintain sufficient solubility in mixed aqueous medium. The UV–vis absorption spectrum of **1** in THF–water (8:2, v/v) ($[\mathbf{1}] = \sim 7.41 \times 10^{-5}$ (M) with respect to repeat unit) exhibited the absorption band peaked at $\lambda_{max} = 414$ nm assignable to the charge transfer between donor and weaker donor, i.e. acceptor part (D-π-D' or D-π-A) of azobenzene unit due to *push–pull* effect (*7*). Absorption titration experiments were carried out using the set of representative metal ions, such as Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (all as sulphates) and Hg^{2+}(as acetate) to evaluate the metal ion binding selectivity and sensitivity of **1**. Upon interaction with this set of metal ions, only Hg^{2+} and Cu^{2+} ions induced a progressive increase in absorption band at 414 nm with red shift ($\Delta\lambda = 4$ nm), whereas a concomitant increase in absorption peak at 318 nm was observed. Clear isosbestic point at 386 nm throughout the titration was attributed to the formation of well-defined equilibrium complexes. Figures 1 and 2 give detailed UV–vis spectral changes of **1** upon gradual titration with Hg^{2+} and Cu^{2+} ions. Other representative metal ions, except for the marginal responding Ni^{2+} and Co^{2+} ions, induced no detectable changes in the absorption spectra of **1** at 414 nm. The plot of $(A–A_0)_{414\,nm}$ vs. concentration of metal ions (Figure 3) shows unique sensitivity of **1** for Hg^{2+}/Cu^{2+} ions. It can be seen from Figure 3 that the concentrations of Cu^{2+} and Hg^{2+} ions required to reach a plateau are approximately



Scheme 2. Synthesis of oligomer **1** (i) THF (dry), reflux, 20 h and (ii) diazonium salt of 1-naphthylamine, dioxan–water, 0–5°C, 10 h.

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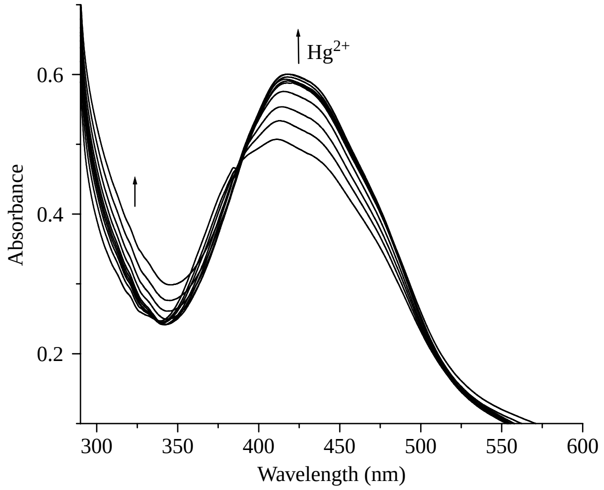

Figure 1. UV–vis titration of **1** [$\sim 7.41 \times 10^{-5}$ (M) with respect to repeat unit] with $Hg(OAc)_2$ in THF/water (8:2, v/v) solution at 25°C.

3.8×10^{-4} and 4.8×10^{-4} M, respectively, with only minor changes occurring thereafter, indicating the binding to a similar extent to **1** in the ground state in solution.

Oligomer **1** showed fluorescence centred around 523 nm in THF–water (8:2, v/v) ([**1**] = $\sim 7.41 \times 10^{-5}$ (M) with respect to repeat unit) ($\lambda_{exc} = 425$ nm) at 25°C. Azobenzenes normally have extremely low quantum yields for fluorescence due to their non-emissive nature (*8*), but hybridisation of naphthylazobenzene structure in **1** encourages the switching of fluorescence.

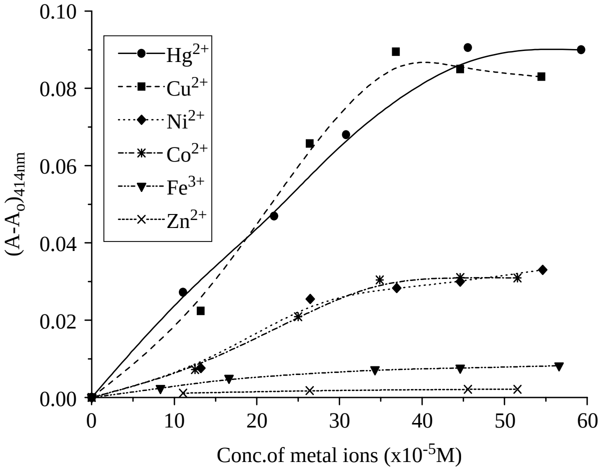

Figure 3. Variation of (A–A_0) at 414 nm as a function of metal ion concentration.

Assessment of the metal ion-sensing abilities also came from observing the extent to which the fluorescence intensity of **1** was affected in the presence of diverse metal ions [Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (all as sulphates) and Hg^{2+} (as acetate)]. Upon addition of these metal ions to the THF–water solution of **1**, a drastic quenching in fluorescence intensity (ON–OFF) at 523 nm ($\lambda_{exc} = 425$ nm) was only observed for Hg^{2+} and Cu^{2+}. Figures 4 and 5, for instance, give detailed fluorescence changes of **1** upon gradual titration with Hg^{2+} and Cu^{2+} ions. The discrimination between two differently responding Hg^{2+} and Cu^{2+} ions could be realised from the Stern–Volmer plot (Figure 6).

The plot showed the nonlinear relationship in quenching in the fluorescence intensity as a function of increasing concentration of Cu^{2+}. In contrast, Hg^{2+} showed nearly linear relationship in quenching in the fluorescence intensity. It is worth mentioning that upon interaction with Hg^{2+} and Cu^{2+} ions, the extent of fluorescence quenching by Cu^{2+} was more than Hg^{2+} up to the concentration of $\sim 2.2 \times 10^{-4}$ M beyond which extent of quenching was altered (Figure 6).

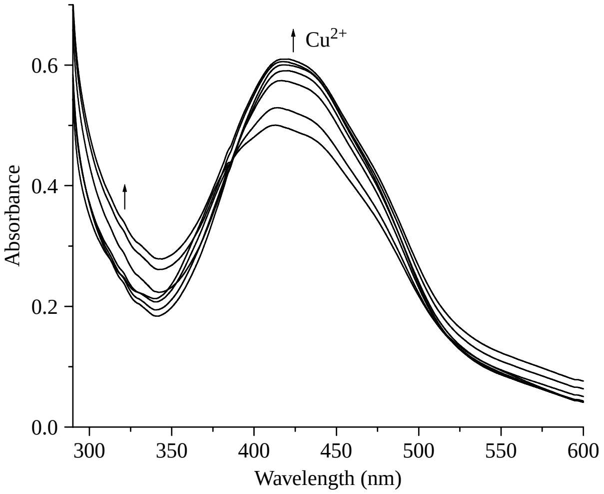

Figure 2. UV–vis titration of **1** [$\sim 7.41 \times 10^{-5}$ (M) with respect to repeat unit] with $CuSO_4$ in THF–/water (8:2, v/v) solution at 25°C.

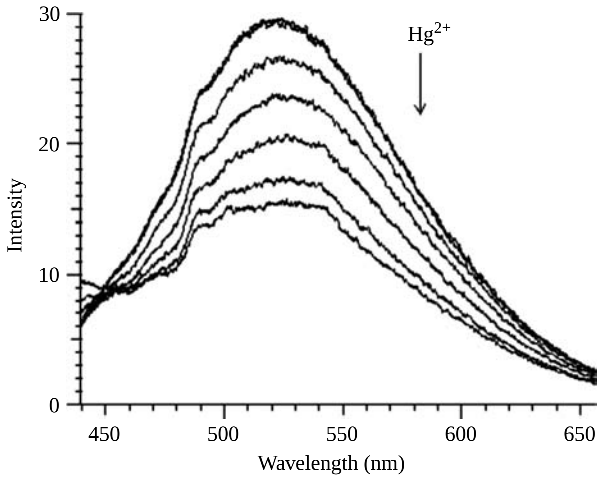

Figure 4. Fluorescence spectral changes of **1** [$\sim 7.41 \times 10^{-5}$ (M)] with different concentrations of Hg^{2+} ion in THF–water (8:2, v/v) ($\lambda_{exc} = 425$ nm).

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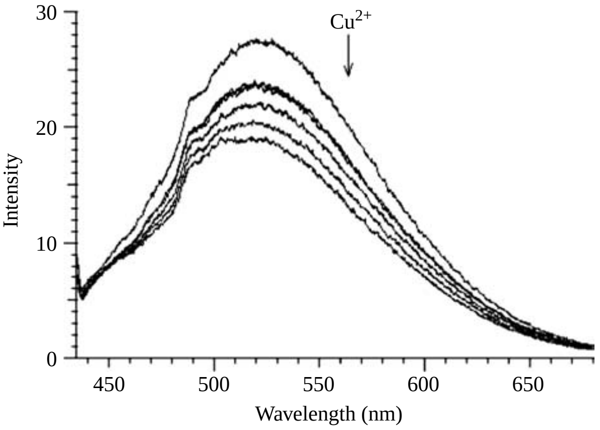


Figure 5. Fluorescence spectral changes of **1** [~7.41 × 10^{-5} (M)] with different concentrations of Cu^{2+} ion in THF–water (8:2, v/v) ($\lambda_{exc} = 425$ nm).

It is also to be remarked that **1** showed fluorescence quenching effect quite distinctively upon Fe^{3+} ion addition. But in contrast to that of Hg^{2+}/Cu^{2+} ions, UV–vis spectral enhancement of **1** was not significant upon addition of Fe^{3+} ion (Figure 2). These data thus suggest that this ensemble is unique in its ability to discriminate the sensing of these analytes of interest.

A feasible mode of metal ion-directed binding responsible for spectroscopic changes is shown in Scheme 3. The designed macromolecule **1** having a varying number of S-donors positioned at the main chain can participate in strong coordination with Hg^{2+}/Cu^{2+} ions (Scheme 3), which probably transforms the *D-π-D′*-type naphthylazobenzene moiety to *D-π-A*-type structure inducing internal charge transfer from the donor naphthyl ring to the acceptor benzene ring. Furthermore, the presence of isosbestic point in case of such metal ions in UV–vis spectral studies provides convincing clue that Hg^{2+}/Cu^{2+} ion is inserted into the dithia-aza binding pocket via M^{2+}–N interaction. This sort of binding is in accordance with the earlier report on coordination mode of N-azo coupled dithia-aza units with Hg^{2+} ion (*5a*). The fluorosensing mechanism of **1** is probably implying the presence of complexation-induced excited-state perturbations in the probe by inherent quenching Fe^{3+}, Cu^{2+} and Hg^{2+} ions.

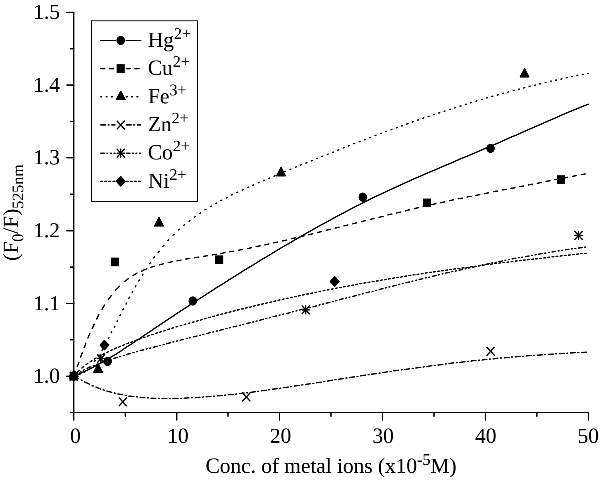
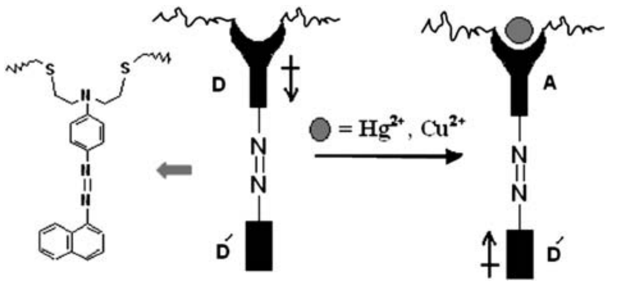


Figure 6. Stern–Volmer plot of **1** in the presence of Hg^{2+} ion in THF–water (8:2, v/v).



Scheme 3. Suggested coordination-induced sensing mechanism of **1** for Hg^{2+} and Cu^{2+} ions.

Conclusion

We demonstrated that the placing of N-azo-coupled dithia-aza units on the backbone of epoxy-based macromolecule can represent a selective chemosensor for metal ions. Oligomer **1** might be useful as a selective sensor for Hg^{2+} and Cu^{2+} ions in a dual sensing system, UV–vis spectral changes as well as the ‘ON–OFF’ type fluorescence quenching on complexation. In addition, the discrimination between two differently responding Fe^{3+} and Hg^{2+} (or Cu^{2+}) ions from ‘ON–OFF’ type fluorescence quenching of **1** is another advantage of this system. This preliminary understanding on the Hg^{2+}, Cu^{2+} and Fe^{3+} sensing would actually help to achieve further structural optimisation of thia-aza-appended precursor oligomer to tune affinities and selectivities for metal ions. Further studies in our laboratory are in progress.

Experimental

Synthesis of 1a

Under nitrogen, NaH (71 mg, 2.96 mmol) was added to a solution of 2,2′-(phenylazanediyl) diethanethiol (0.22 g, 0.74 mmol) in dry THF and refluxed for 2 h. Then, DGEBA (0.29 g, 0.74 mmol) was added and refluxed for 18 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The viscous residue was redissolved in CH$_2$Cl$_2$, washed with water, dried over *anhyd.* Na$_2$SO$_4$ and filtered. The solvent was removed *in vacuo*. The residue was redissolved in 1,4-dioxan and precipitated in petroleum ether to get the product. FT-IR (KBr): 3461, 3061, 2958, 2861, 1604, 1507, 1346, 1301, 1243, 1158, 1037, 914, 831, 760 cm^{-1}; ^{1}H NMR (CDCl$_3$,

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500 MHz) δ: 7.23 (m, H^b), 7.12 (d, $J = 10$ Hz, H^i), 6.81 (d, $J = 10$ Hz, H^j), 6.64 (m, $H^{a,c}$), 4.18–4.16 (dd, $J = 3$ Hz, H^l), 3.95 (m, $H^{m,h}$), 3.57–3.50 (m, $H^{d,g}$), 3.09 (t, $J = 7.5$ Hz, $H^{f,e}$), 1.62 (s, H^k). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 156.34, 143.65, 129.55 (unresolved), 127.77, 116.41, 114.02, 111.71 (unresolved), 111.18, 68.75, 67.09, 52.23, 51.09, 44.75, 41.72, 31.02 anal. calcd for $(C_{49}H_{61}NO_6S_2)_n$: C, 71.44; H, 7.41; N, 1.70. Found: C, 71.61; H, 7.46; N, 1.67. GPC (using polystyrene standard and THF eluent): $M_w = 1071$, MWD 2.4.

Synthesis of 1

Oligomer **1a** (0.086 g, 0.126 mmol) was dissolved in 1,4-dioxan–water (3:1, v/v, 10 ml) at 0°C. A diazonium salt of 1-naphthylamine was prepared by adding an aqueous solution of $NaNO_2$ (1.04×10^{-2} g, 0.15 mmol) into a solution of 1-naphthylamine (1.8×10^{-2} g, 0.126 mmol in 0.002 ml acetic acid). The mixture was stirred at 0°C for 2 min and then added dropwise into the solution of **1a**. The yellowish colour gradually turned into red. The solution was stirred at 0°C for 10 h. Then, the mixture was treated with water and extracted with CH_2Cl_2. The organic phase was dried over *anhyd*. Na_2SO_4 and filtered. The solvent was removed *in vacuo* to get the product. FT-IR (KBr): 3431, 2922, 2856, 1646, 1598, 1518, 1463, 1396, 1236, 1107, 1033, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.01 (bm, $H^{g,h}$), 7.90 (d, H^d, $J = 5$ Hz), 7.72–7.48 (m, $H^{e,f,b}$), 7.12 (d, H^o, $J = 10$ Hz), 7.07 (m, H^a), 6.81 (d, H^p, $J = 10$ Hz,), 4.17 (d, $H^{n,q}$, $J = 10$ Hz), 4.02–3.93 (m, H^r), 3.68–3.52 (m, $H^{j,m}$), 3.15–3.09 (m, $H^{k,l}$), 1.62 (s, $-CH_3$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 156.35, 152.25, 143.66, 134.37, 131.25, 129.80, 129.57, 128.01, 127.78, 126.22, 125.82, 125.70, 125.60 (unresolved), 123.75 (unresolved), 114.02, 111.40, 111.27, 111.18, 68.76, 66.85, 50.20, 44.79, 41.74, 31.02, 29.71, 29.44; anal. calcd for $(C_{59}H_{67}N_3O_6S_2)_n$: C, 72.46; H, 6.85; N, 4.29. Found: C, 72.35; H, 6.73; N, 4.20. GPC (using polystyrene standard and THF eluent): $M_w = 2157$, MWD 2.6.

General procedure of fluorescence and UV–vis titrations

Stock solution of **1** was prepared in THF–water (8:2, v/v) and 2 ml of the oligomer solution was taken in the cuvette. Stock solutions of cations were prepared in water, and were individually added in different amounts to the oligomer solution. For fluorescence, the solution was irradiated at the excitation wavelength of 425 nm maintaining both the excitation and emission slits at 5.0. nm upon addition of cations, the changes in emission and absorbance of the oligomer solution were noted.

Acknowledgement

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