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Hg^{2+} sensing in aqueous solutions: an intramolecular charge transfer emission quenching fluorescent chemosensors

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Abstract—Compounds **4a** and **4b**, comprising an anthracene moiety as the fluorophore and a pair of dithiocarbamate functionalities as ligating groups, were designed as fluorescent chemosensors for Hg(II). In aqueous solvent systems, upon excitation, in addition to the normal emission bands of locally excited (LE) state of anthracene, both compounds show a prominent pH-independent intramolecular charge transfer (ICT) emissive band, which can be modulated by Hg^{2+} binding. The systems can be exploited to develop a fluorescent sensitive probe for Hg^{2+}.

1. Introduction

Fluoroionophore design based on 'fluorophore–spacer–receptor' motif has been demonstrated to be an effective way of developing both anion and cation chemosensors.[1] A variety of signal transduction mechanisms are established to signify the binding event between a receptor and a guest molecule/ion.[2] Particularly, a number of cation chemosensors operated on modulation of dual fluorescence emission of electron donor–acceptor integrated systems permitting ratiometric measurement are attractive in sensory applications.[2a,3] Chemosensor exhibiting high selectivity and sensitivity toward a target analyte is in great demand due to its low cost, ability on real time monitoring, and high throughput capability. Among all metal analytes detection, mercury chemosensing has been recently attracted considerable interests. Mercury is ubiquitous and its potent neurotoxicity on human warrants the exploration of new methods for monitoring aqueous Hg^{2+} in biological, food, and environmental samples.[4]

To continue our interests in fluorescent sensor development on toxic metal monitoring,[5] we herein report acceptor–spacer–donor systems **4a** and **4b**, in which anthracene (AN) used as an electron acceptor is linked to a pair of dithiocarbamates (DTC) as both metal chelating groups and electron donors via iminophenylmethylene spacer.[6] In aqueous media, both systems display dual fluorescence emissive bands. In which the short wavelength emission bands are ascribed to the locally excited (LE) state of the anthracene moiety, and the long wavelength structureless band could be ascribed to intramolecular charge transfer (ICT) states between the DTC groups and excited AN. Interestingly, the relative intensity of these two emissions was found to be modulated by metal ion binding.

2. Results and discussion

On the outset of the investigation, we envisage that DTC is an effective ligating group for heavy metal ion's complexation and the structural environment of DTC in the system could render the sensors with discriminative binding affinities toward various metal cations. For synthesizing sensors, the requisite precursor **2** obtained from phenyliminodiethanol (**1**) and TsCl in pyridine was treated with ammonium *N*,*N*-diethyldithiocarbamate and morpholinyldithiocarbamate in CH_3CN at room temperature for 2 days, affording the corresponding bis-dithiocarbamate **3a** and **3b** in 95 and 87% yield, respectively. After building up the metal receptive site, incorporation of a fluorescent moiety on the receptor was achieved by Friedel–Crafts alkylation reaction. Thus, to complete the synthesis of sensors **4**, aluminum chloride induced Friedel–Crafts alkylation of **3** with 9-chloromethylanthracene in refluxing chloroform allowed the smooth appendage of the anthracene subunit as the fluorescent signaling handle (Scheme 1).[7]

To probe the best operative conditions for the sensors to exhibit the selective binding of metals, the choice of a proper aqueous solvent system is our first priority. In that connection, the fluorescent titration of **4a** with Hg^{2+} in aqueous acetonitrile (1:1, v/v) was first undertaken. The emission spectra of the corresponding titration curves reveal the

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Keywords: Chemosensors; Mercury probe; Dual fluorescence; Anthracene.

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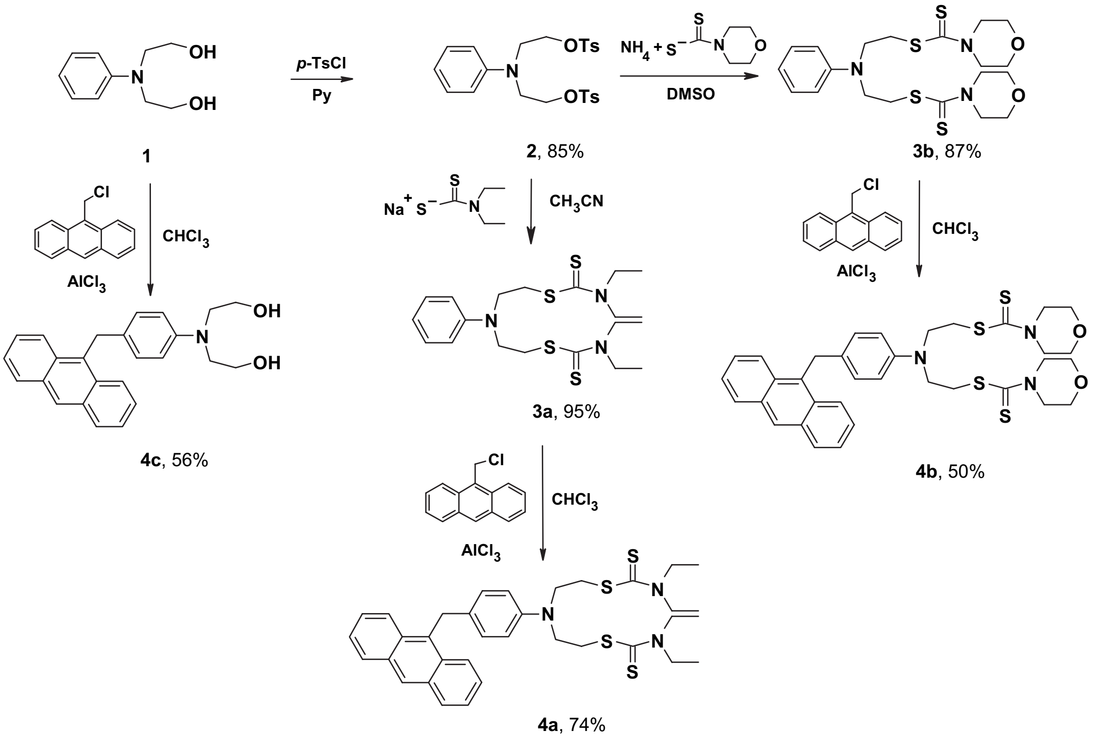

Scheme 1. Synthesis of the chemosensors.

dependence of the fluorescent behavior of the sensor on the metal concentration (Fig. 1A). Increasing the concentration of Hg^{2+} from 5×10^{-8} to 2.5×10^{-4} M, the corresponding titration curves exhibited an increase in the short wavelength emissive peaks with a concomitant decrease in the long wavelength structureless emissive peak at 525 nm. A clear isoemissive point at 455 nm was observed. The long wavelength emissive peak is conceivably arising from ICT fluorescence formed between the excited state of the anthracene moiety and DTC (vide infra). The findings provide the basis for ratiometric fluorescent determination of Hg^{2+}. The limit of detection (LOD) for Hg^{2+} is estimated to be 1×10^{-8} M with the present system. The responsive sensitivity of the sensor can be further increased by changing the solvent system to 1:1 aqueous ethanol. The more polar solvent system adopted further enhances the intensity of ICT emissive band as evidenced in the titration experiments (Fig. 1B). Interestingly, under the same conditions of the titration experiments, in contrast to that of sensor **4a**, sensor **4b** responds quite distinctively to Hg^{2+}. As shown in Figure 2, by increasing the concentration of Hg^{2+} from 5×10^{-8} to 1.0×10^{-3} M, the corresponding titration curves exhibit a decrease in ICT fluorescence with the short wavelength peaks being intact. Conceivably, the two dithiocarbamate moieties bearing morpholine ring present in **4b** could confer a more focused metal binding site for the sensor in such a way that the lone pair of the imino-nitrogen did not take part in the metal complexation. As a result, metal binding in **4b** would not interfere with the photo-induced electron transfer (PET) process. In contrast, the imino-nitrogen present in **4a** could actively participate in the metal binding; the increase of emissive peaks of LE state is attributed to the

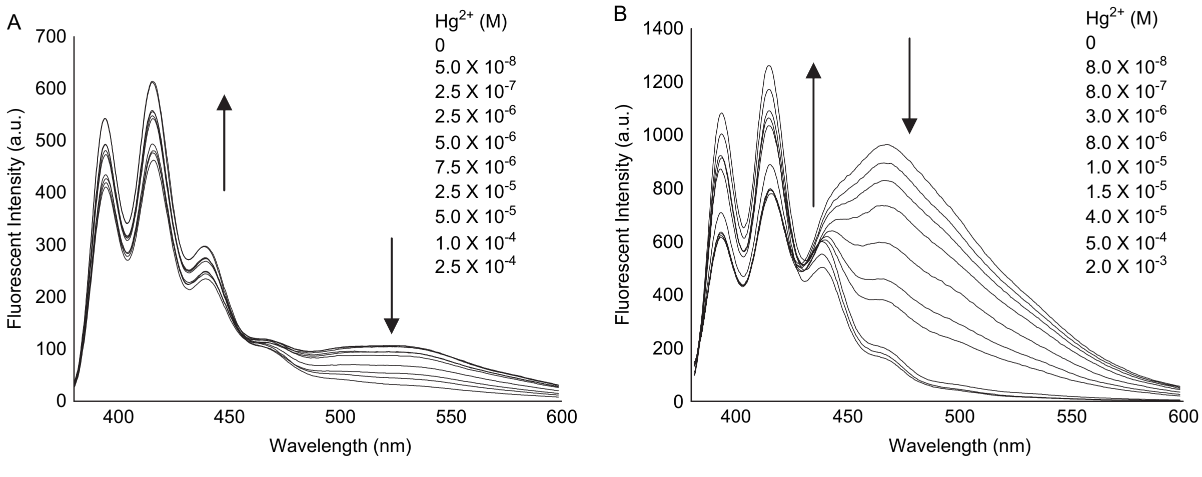

Figure 1. Fluorescence spectra of **4a** as a function of $[Hg^{2+}]$ (A) in $CH_3CN/H_2O = 1:1$, v/v; (B) in $EtOH/H_2O = 1:1$, v/v. [**4a**] $= 5.0\times10^{-6}$ M.

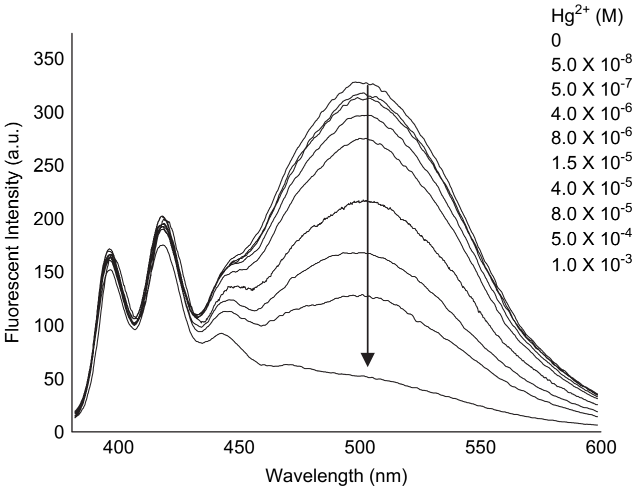

Figure 2. Fluorescence spectra of **4b** as a function of [Hg^{2+}] in EtOH/H_2O = 1:1, v/v. [**4b**] = 1.0×10^{-5} M.

reduction of the intrinsic PET process as a result of metal binding. Apparently, the fine structural environment of the binding site of sensor can be tuned by a rational design. The selectivity studies of the sensors substantiate that **4b** with more rigid binding site exhibits a better selectivity toward Hg^{2+} among other metal ions. In contrast, sensor **4a** is a less selective sensor as shown in Figure 3. Sensor **4b** in fact does not respond to other common metal cations as well as organo-mercury. Further detailed investigation reveals that sensor **4b** also responded sensitively with Ag^+. On the basis of the nonlinear fitting experiments of fluorescent titrations, the binding constant of **4b** with Ag^+ and Hg^{2+} was determined to be 32.3×10^4 and 3.9×10^4 M^{-1}, respectively. The values of binding constants revealed that the sensor forms fairly strong complexes with these metals. On the other hand, the detection sensitivity of both sensors toward Hg^{2+} is excellent with an estimated LOD at 10^{-8} M. Metal ion chemosensors often exhibit pH-dependent emission and could be problematic in practical operation. To our delight, pH fluorescent titration experiments on sensor **4b** indicated that there is no cross response of the sensor to the pH change of the sensor solution. According to Figure 4, emissions from both LE and ICT state remain constant over a wide pH range from 3.5 to 12.5. It is noteworthy that the anthracene emissive peak of the sensor exists at 'off state' when the pH of the solution is greater than 3.2. Considering the fact that Ag^+ ion is seldom found in biological and environmental samples, thus in terms of high sensitivity and selectivity and wide working pH range, sensor **4b** possesses good potential to be used for monitoring the mercury level of real samples.

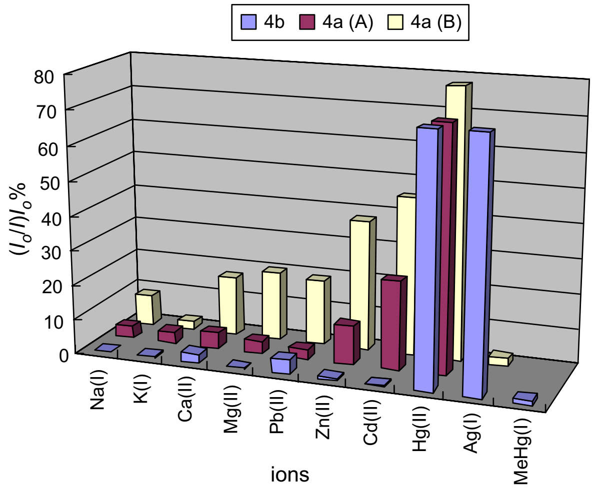

Figure 3. Quenching ratio of **4a** and **4b** with different ions. Compound **4a** (A) EtOH/H_2O = 1:1, v/v; **4a** (B) and **4b** CH_3CN/H_2O = 1:1, v/v; [**4a**] = 5.0×10^{-6} M; [ion] = 2.5×10^{-4} M; [**4b**] = 1.0×10^{-5} M.

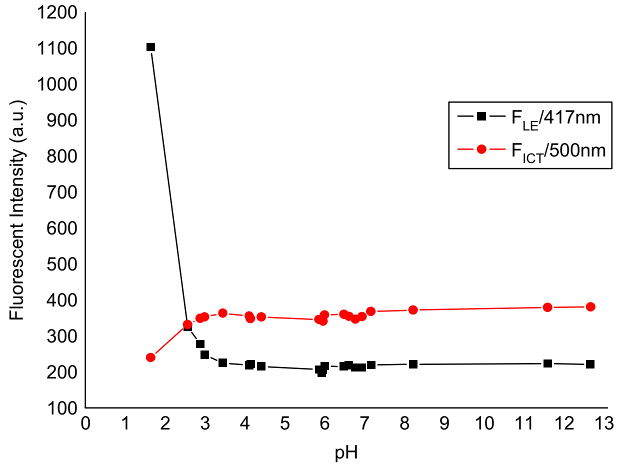

Figure 4. Effect of pH on the emission peaks of LE state (417 nm) and ICT (500 nm) peaks of **4b**.

To shed light for the response mechanism of the sensory systems, a control molecule **4c** without the DTC receptive groups was synthesized from Friedel–Crafts alkylation of phenyliminodiethanol and 9-chloromethylanthracene. No ICT fluorescence was observed in the emission spectra of **4c** in 1:1 aqueous ethanol solution. As shown in Figure 5, the fluorescent titration curves of **4c** exhibit a typical PET based chemosensor behavior. The fluorescence of the sensor was completely turned off at 10^{-3} M of Hg^{2+}. Thus, the presence of DTC moieties in sensors **4** is essential for the

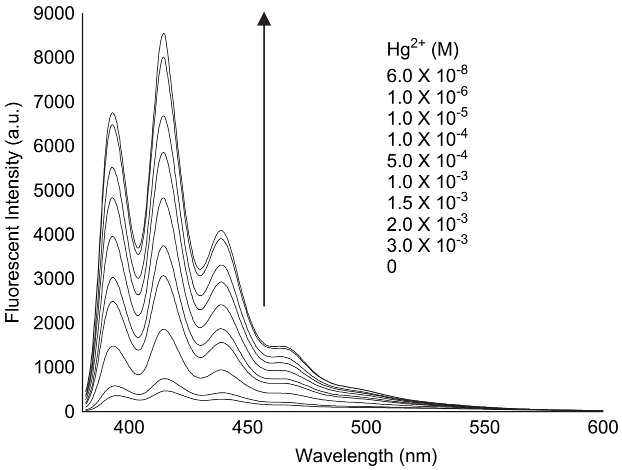

Figure 5. Fluorescence spectra of **4c** as a function of [Hg^{2+}] in EtOH/H_2O = 1:1, v/v. [**4c**] = 2.0×10^{-5} M.

Table 1. Exciplex emissive band of **4a**, **4b**, and **4c** in different solvents, excitation wavelength = 368 nm

	CH_3CN/ H_2O = 1:1 (nm)	EtOH/ H_2O = 1:1 (nm)	DMSO (nm)	DMSO/ H_2O = 0.5:99.5 (nm)
4a	525	467	—	—
4b	—	500	530	465

occurrence of dual fluorescence emission as compared with the control experiment conducted by **4c**. It is noteworthy that the fluorescence maximum of the structureless long wavelength emission of both **4a** and **4b** is highly solvent dependent (Table 1). Such an observation is consistent with the characteristics of ICT fluorescence.[3] The strong binding between Hg^{2+} and the sensors can be rationalized by the combination of electronic and steric effect. On one hand, the four sulfur atoms present in the sensors provide strong affinity to bind heavy metals while on the other hand, the bulkiness of the two morpholine moiety appended on **4b** defines a semi-rigid cavity favoring a selective binding of mercury and silver. Upon binding of metal ions by the DTC groups, the electron density of the receptive site is greatly reduced, the ICT mechanism between the 'donor–receptor' and the excited state of anthracene is retarded.

In summary, we have demonstrated that the dual fluorescence characteristics of a new Hg^{2+}-selective fluoroionophore **4b** could be modulated by its interaction with mercury ion. The excellent selectivity and sensitivity of the sensor toward Hg^{2+} and Ag^+ are attributed to the combined electronic and steric effect. The fluorescence measurements for analyzing the metal content of the solution can be conducted in un-buffered solutions.

3. Experimental

3.1. General

Melting point was determined with a MEL-TEMPII melting point apparatus (uncorrected). ^1H and ^{13}C NMR spectra were recorded on a JOEL EX 270 spectrometer (at 270 and 67.8 MHz, respectively) in DMSO-d_6 or $CDCl_3$. Chemical shifts were registered relatively to Me_4Si (in ppm). High-resolution mass spectra were recorded on a Bruker Autoflex mass spectrometer (MALDI-TOF) or electrospray ionization high-resolution mass spectra on an API Qstar Pulsari mass spectrometer. Fluorescent emission spectra were collected on a Hitachi F4500 fluorescence spectrophotometer. Unless specified, all fine chemicals were used as received.

3.1.1. Phenyliminodiethanol 1. To a THF solution (15 mL) of phenyliminodiacetic acid diethyl ester[7] (0.5 g, 1.9 mmol) in a round bottomed flask immersed in an ice bath, LAH (0.14 g, 3.6 mmol) was slowly added in two portions. The reaction mixture was allowed to stir for 10 min and then refluxed at 80 °C under N_2 for 2 h. After the reaction mixture was cooled to room temperature, the flask was soaked in the ice bath. H_2O (1 mL), NaOH (1 M, 1 mL), and again H_2O (3 mL) were added successively. White solid appeared, which was filtered off using sinter filter and washed with several portions of ethyl acetate. The filtrate was extracted by CH_2Cl_2 (3×30 mL). The combined organic layers were dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum, affording **1** as a colorless oil (0.34 g, 99% yield). δ_H (270 MHz, $CDCl_3$): 3.33 (s, 2H), 3.58 (t, *J*=4.86 Hz, 4H), 3.85 (t, *J*=4.86 Hz, 4H), 6.68–6.77 (m, 3H), 7.24 (t, *J*=7.83 Hz, 2H).

3.1.2. Phenyliminodi(ethyltosylate) 2. To a pyridine solution (5 mL) of **1** (0.5 g, 2.8 mmol), *p*-toluenesulfonyl chloride (1.6 g, 8.4 mmol) was added. The reaction mixture was stirred in an ice bath under N_2 for 5 h. Water was added (30 mL) and products were extracted by CH_2Cl_2 (3×30 mL). The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum. The crude product was recrystallized in PE to give pure **2** as white crystals (1.15 g, 85% yield). Mp 72.0–75.0 °C; HRMS *m*/*z* calcd for $C_{24}H_{27}NO_6S_2$ $(M+H)^+$: 490.1358, found: 490.1357; δ_H (270 MHz, $CDCl_3$): 2.42 (s, 6H), 3.55 (t, *J*=6.75 Hz, 4H), 4.08 (t, *J*=6.75 Hz, 4H), 6.43 (br d, *J*=8.10 Hz, 2H), 6.70 (t, *J*=8.10 Hz, 1H), 7.13 (br d, *J*=8.10 Hz, 2H), 7.28 (d, *J*=8.10 Hz, 4H), 7.71 (d, *J*=8.10 Hz, 4H); δ_C (67.8 Hz, $CDCl_3$): 21.72, 50.18, 66.57, 111.89, 117.46, 127.71, 129.34, 129.76, 132.44, 144.85, 145.55.

3.1.3. Ammonium morpholinyldithiocarbamate. Morpholine (5 mL, 57 mmol) was dissolved in CH_3OH (100 mL). CS_2 (5 mL, 83 mmol) and NH_4OH (4 mL, 28%) were added. The reaction mixture was stirred at room temperature for few minutes. Et_2O (100 mL) was added. The product was precipitated and filtered, which was dried under reduced pressure to afford a pale yellow solid (6.67 g, 70% yield). δ_H (270 MHz, DMSO-d_6): 3.48 (t, *J*=4.05 Hz, 4H), 4.27 (t, *J*=4.05 Hz, 4H); δ_C (67.8 Hz, DMSO-d_6): 49.74, 66.12.

3.1.4. Phenyliminobis(ethyldiethyldithiocarbamate) 3a. Compound **2** (1 g, 2 mmol) was dissolved in CH_3CN (40 mL). Sodium diethyldithiocarbamate (1.42 g, 6.3 mmol) was added. The reaction mixture was stirred under N_2 at room temperature for 2 days. Water (30 mL) was added and products were extracted with CH_2Cl_2 (3×30 mL). The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum, affording **3a** as white solid (0.9 g, 100% yield). Mp 77–81 °C; HRMS *m*/*z* calcd for $C_{20}H_{33}N_3S_4Na$ $(M+Na)^+$: 466.1455, found: 466.1459; δ_H (270 MHz, $CDCl_3$): 1.29 (t, *J*=6.75 Hz, 12H), 3.49–3.54 (m, 4H), 3.67–3.76 (m, 8H), 4.00–4.08 (m, 4H), 6.69 (t, *J*=8.10 Hz, 1H), 6.97 (br d, *J*=8.10 Hz, 2H), 7.24 (br d, *J*=8.10 Hz, 2H); δ_C (67.8 Hz, $CDCl_3$): 11.29, 32.96, 46.46, 49.54, 111.62, 115.91, 128.75, 146.56, 194.07.

3.1.5. Phenyliminobis(ethyldimorpholinyldithiocarbamate) 3b. Compound **2** (0.37 g, 0.8 mmol) was dissolved in DMSO (8 mL). Ammonium morpholinyldithiocarbamate (0.38 g, 2.3 mmol) was added. The reaction mixture was allowed to stir under N_2 at room temperature for 2 days. Water was added and products were extracted with CH_2Cl_2 (3×30 mL). Then, the emulsified layer was combined with satd NH_4Cl. H_2O (4×20 mL) was introduced to wash the organic portion. The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum. The crude product was purified by column chromatography, eluted with PE:EA (1:1) to give **3b** as white solids (0.31 g, 87% yield). Mp 141–143 °C; HRMS *m/z* calcd for $C_{20}H_{29}N_3O_2S_4$ $(M+Na)^+$: 494.1004, found: 494.0953; δ_H (270 MHz, $CDCl_3$): 3.53–3.59 (m, 4H), 3.68–3.70 (m, 4H), 3.76–3.79 (m, 8H), 3.96–4.00 (m, 4H), 4.30 (m, 4H), 6.73 (t, *J*=7.20 Hz, 1H), 6.92 (br d, *J*=7.20 Hz, 2H), 7.26 (br d, *J*=7.20 Hz, 2H); δ_C (67.8 Hz, $CDCl_3$): 33.37, 49.90, 50.81, 66.22, 112.07, 116.63, 129.33, 146.86, 196.71.

3.1.6. 4-(9-Methylanthracene)phenyliminobis(ethyldiethyldithiocarbamate) 4a. Compound **3a** (0.23 g, 0.5 mmol) and 9-chloromethylanthracene (0.13 g, 0.6 mmol) were added in a 50 mL round bottomed flask. Dry $CHCl_3$ was added (10 mL) and then followed by $AlCl_3$ (0.07 g, 0.5 mmol). The reaction mixture was refluxed at 70 °C under N_2 overnight. At the end of the reaction, NaOH (10 mL, 1 M) was added to the reaction mixture. The combined solution was extracted by CH_2Cl_2 (3×30 mL) and H_2O. The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum. The crude product was purified by column chromatography, eluted with PE:EA (6:1) affording the product **4a** as yellow solids (0.24 g, 74% yield). Mp 92.0–93.0 °C; HRMS *m/z* calcd for $C_{35}H_{43}N_3S_4$ (M^+): 633.2339, found: 633.2369; δ_H (270 MHz, $CDCl_3$): 1.20 (t, *J*=6.75 Hz, 12H), 3.44 (t, *J*=5.40 Hz, 4H), 3.57–3.64 (m, 8H), 3.98 (t, *J*=5.40 Hz, 4H), 4.89 (s, 2H), 6.79 (d, *J*=8.10 Hz, 2H), 6.98 (d, *J*= 8.10 Hz, 2H), 7.40–7.44 (m, 4H), 7.99 (br d, *J*=5.40 Hz, 2H), 8.24 (br d, *J*=5.40 Hz, 2H), 8.37 (s, 1H); δ_C (67.8 Hz, $CDCl_3$): 12.48, 33.48, 46.76, 49.52, 49.94, 112.16, 124.69, 124.88, 125.55, 126.00, 128.82, 128.83, 128.85, 130.28, 131.50, 132.64, 145.27, 194.70.

3.1.7. 4-(9-Methylanthracene)phenyliminobis(ethyldimorpholinyldithiocarbamate) 4b. Compound **3b** (0.15 g, 0.3 mmol) and 9-chloromethylanthracene (0.07 g, 0.3 mmol) were mixed in a 50 mL round bottomed flask. Dry $CHCl_3$ was added (11 mL) and then followed by $AlCl_3$ (0.04 g, 0.3 mmol). The reaction mixture was refluxed at 70 °C under N_2 overnight. At the end of the reaction, NaOH (11 mL, 1 M) was added to the reaction mixture. Water (30 mL) was added and CH_2Cl_2 (3×30 mL) was used for extraction. The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum. The crude product was purified by column chromatography, eluted with PE:EA (3:1) affording the product **4b** as yellow solids (0.1 g, 50% yield). Mp: 99.0–99.5 °C; HRMS *m/z* calcd for $C_{35}H_{39}N_3O_2S_4$ $(M+H)^+$: 662.2003, found: 662.2002; δ_H (270 MHz, $CDCl_3$): 3.49 (t, *J*=4.05 Hz, 4H), 3.60 (t, *J*=4.05 Hz, 4H), 3.70–3.73 (m, 8H), 3.91–3.94 (m, 4H), 4.30–4.33 (m, 4H), 4.91 (s, 2H), 6.75 (d, *J*=8.10 Hz, 2H), 7.01 (d, *J*=8.10 Hz, 2H), 7.43–7.47 (m, 4H), 8.02 (br d, *J*=5.40 Hz, 2H), 8.25 (br d, *J*=5.40 Hz, 2H), 8.41 (s, 1H); δ_C (67.8 Hz, $CDCl_3$): 32.46, 33.43, 49.92, 51.11, 62.55, 112.17, 124.76, 124.88, 125.66, 126.15, 128.88, 128.96, 129.37, 130.33, 131.56, 132.53, 145.17, 196.73.

3.1.8. 4-(9-Methylanthracene)phenyliminodiethanol 4c. Compound **1** (0.83 g, 4.6 mmol) and 9-chloromethylanthracene (1.1 g, 4.8 mmol) were mixed in dry $CHCl_3$ (10 mL). $AlCl_3$ (0.6 g, 4.6 mmol) was added. The reaction mixture was refluxed at 70 °C under N_2 overnight. At the end of the reaction, NaOH (10 mL, 1 M) was added to the reaction mixture. Water (30 mL) was added and products were extracted with CH_2Cl_2 (3×30 mL). The organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary evaporation under vacuum. The crude product was purified by column chromatography, eluted with EA to afford the product **4c** as yellow solids (0.95 g, 56% yield). Mp 46.0–47.5 °C; HRMS *m/z* calcd for $C_{25}H_{25}NO_2$ $(M+H)^+$: 372.1963, found: 372.1958; δ_H (270 MHz, $CDCl_3$): 3.34 (t, *J*=4.73 Hz, 4H), 3.61 (t, *J*=4.73 Hz, 4H), 3.74–3.77 (m, 2H), 4.86 (s, 2H), 6.42 (d, *J*=8.10 Hz, 2H), 6.91 (d, *J*=8.10 Hz, 2H), 7.38–7.42 (m, 4H), 7.95–7.99 (m, 2H), 8.19–8.22 (m, 2H), 8.36 (s, 1H); δ_C (67.8 Hz, $CDCl_3$): 32.37, 55.35, 60.66, 112.60, 114.63, 124.75, 124.79, 125.63, 126.14, 128.76, 128.94, 129.09, 130.29, 131.54, 145.86.

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