Pergamon

Tetrahedron 55 (1999) 11553–11562

TETRAHEDRON

The Synthesis and Complexation Studies of Thia-Anthracene Receptors

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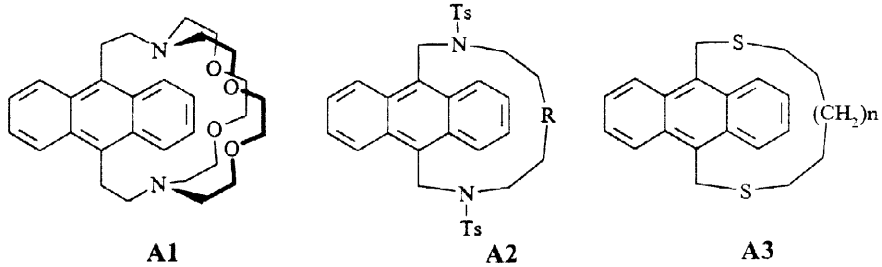
Received 21 April 1999; revised 1 July 1999; accepted 22 July 1999

Abstract: Systematic studies towards the formation of thia-anthracene receptors were performed. Anthracene podand **3** consisting of two anthryl groups connected by the $SCH_2CH_2CH_2S$ spacer group was prepared in 99% yield. The complexation properties of this compound were investigated using UV-VIS and fluorescence titration techniques. Addition of silver salts into a solution of the fluorophore strongly modifies the absorption and fluorescence spectra and the association constants were found to be $K_1 = 2 \times 10^5$ and $K_2 = 8 \times 10^4$ M^{-1} for the 1:1 and 1:2 complexes, respectively. Addition of metal ions, as Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Co^{2+}, did not lead to any change in the photophysical properties of compound **3**.

Introduction

The recent interest in the anthracene system is triggered mainly by its fluorescence properties, which are widely utilised in e.g. the design of luminescent sensors and switches based on photoinduced electron transfer processes.[1,2] Such sensors have allowed, for example, monitoring of the concentration of inorganic cations and anions in water[3], as well as neutral guests, e.g. sugars.[4] Furthermore, aromatic subunits such as the anthracene derivatives present in the receptor structure can interact with guest by π-stacking and π-cation or π-H interactions.[5,6]



A1 **A2** **A3**

Chart 1

Recently, the interaction of anthracene systems with biological polyanions (DNA, heparine) has also attracted attention.[7] It has been found that diamino anthracene derivatives intercalate CT-DNA with high affinity.[8] The chemical structure of anthracene receptors containing amino group such as cryptand **A1**[9] presented in Chart 1

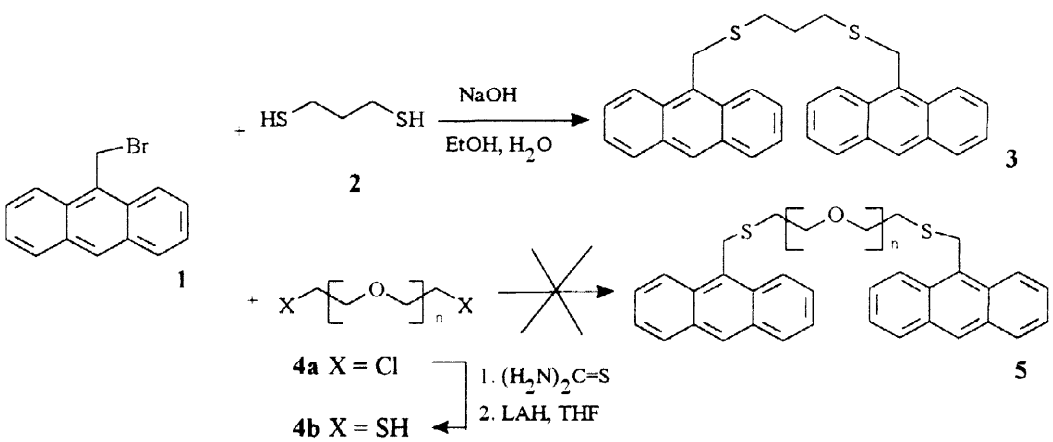
0040-4020/99/$ - see front matter
PII: S0040-4020(99)00654-7

and polyaza (9,10)anthracenophanes of structure **A2**.[10] The presence of sulfur atoms in the receptor structure strongly influences its recognition properties. Since the synthesis of dithia[n](9.10)anthracenophanes of the structure **A3** (n = 2 to 8) is well known[11], we decided to prepare a series of receptors containing additional oxygen atoms in the aliphatic bridge of cyclophane **A3**. We expected that the complexes formed by this receptor with cations would be stabilised by the π-cation interactions and that the changes of anthracene fluorescence could be used for the sensing of particular cations.

Results and Discussion

Our general strategy in the synthesis of thioanthracene ionophores was based on the formation of S-C bonds. This type of macrocyclisation reaction is commonly used in the synthesis of thiocrown ethers and thiocryptand receptors.[12] In most cases, the desired products are obtained in high yields under mild reaction conditions, without application of high-dilution techniques.

The ionophores of podand structures are a good target in the preparation of model anthracene ligands. Therefore, the functionalisation of 9-bromomethylanthracene (**1**) was performed as a model reaction. Use of 1,3-propanedithiol (**2**) as a nucleophile resulted in formation of podand **3** in 99% yield. The desired compound was prepared in a one step reaction without any synthetic problem. Since the incorporation of oxygen atoms into the aliphatic bridge may result in complex stabilisation, we decided to prepare respective α,ω-dithiols **4b** and applied them as nucleophiles in the reaction. All compounds were prepared according to the modified literature procedure. Reaction of α,ω-dichlorides **4a** derived from ethylene glycols (n = 1, 2, 3) with thiourea followed by reduction (LAH, THF) leads to the formation of α,ω-dithiols **4** in 80-90% yield. It is important to note that the reduction of thiourea salts instead of base hydrolysis gave the desired compounds in higher yields and with better purity without pollution of the laboratory atmosphere.

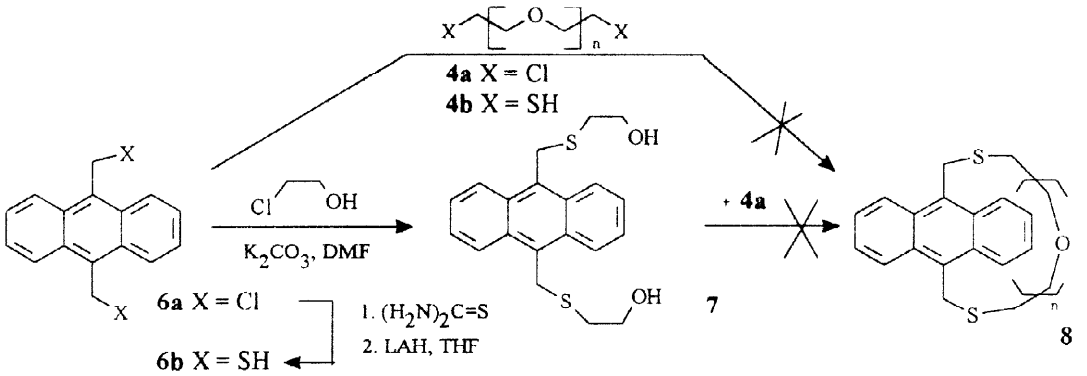


Scheme 1

The reaction of anthracene bromide **1** with α,ω-dithiol **4b** (n = 1, 2, 3) was investigated and the following observations were made: in most cases the reaction did occur but the desired products of structure **5** decomposed and finally only 9-methyl anthracene was obtained in low yield.

In the next step, the formation of anthracene receptors of general structure **A3** was investigated. The reaction of 9,10-bischloromethylanthracene (**6a**) with bisthiols **4b** (n= 1, 2, 3) was studied. The analysis of crude reaction mixtures by mass spectrometry using electron impact and L-SIMS techniques did not show evidences

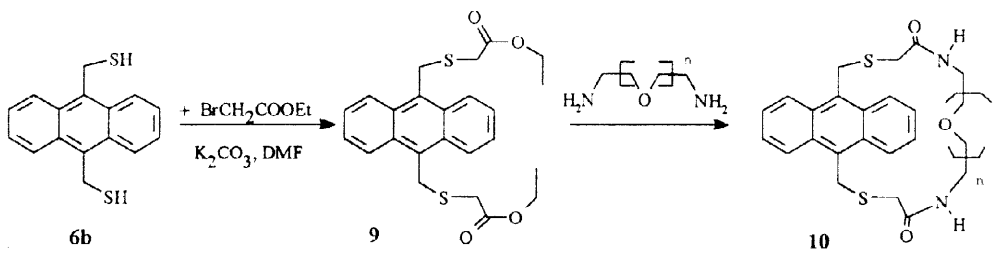
of any compound of the structure **8**. Application of caesium carbonate in DMF[13] did not allow us to prepare desired products of the structure **8** although the desired products were observed in the reaction mixtures analysed by L-SIMS techniques.



Scheme 2

Since it is possible that the reactivity of anthracene **6a** disfavours macrocyclisation reactions, we tried to perform the cyclisation based on the reaction of 9,10-bisthiamethylanthracene **6b** with compounds **4a**. The 9,10-bisthiamethylanthracene **6b** was obtained in 85% yield upon treatment of compound **6a** with thiourea followed by LAH reduction. The macrocyclisation reactions were performed under the same reaction conditions and again, none of the desired products of the structure **8** were obtained.

The unusual reactivity of bisthiol **6b** was evidenced in the reaction with 2-chloroethanol. In this case desired diol **7** was obtained in 72% yield after crystallisation. In principle, this compound can be transformed into receptor **8**. Unfortunately, attempted cyclisation reactions with chlorides **4a** (n = 1, 2, 3) failed.

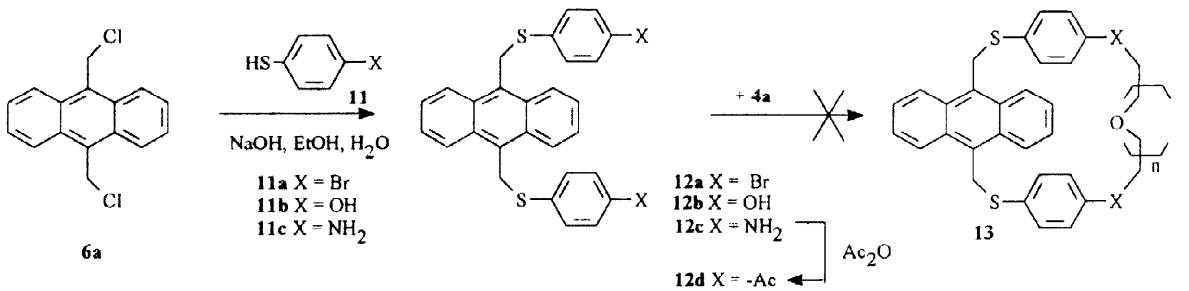


Scheme 3

Since the macrocyclisation reaction did not occur in all cases studied, we turned our attention to another method commonly used in the preparation of macrocylic receptors. This method is based on the reaction of primary amines with methyl esters of carboxylic acids.[14] Application of this method to the synthesis of macrocyclic diamides and tetraamides containing phenol[15] or pyridine[16] units was fully successful and the desired compounds were prepared in 40-80% yield. Recent studies showed that C_2-elongation of D-mannitol or L-tartaric acid with *tert*-butyl bromoacetate afforded di-*tert*-butyl ester in 80% yield. Subsequent reaction with α,ω-diamines led to formation of chiral macrocyclic diamides in 50% yield.[17]

The diester required for the macrocyclisation reaction was prepared from compound **6b** the alkylation of which with bromoacetic acid ethyl ester leads to formation of the desired compound **9** in 68% yield. The reactions of this diester with primary α,ω-bisamines derived from ethylene glycols did not proceed and bisester **9** was recovered in almost quantitative yield.

Since thiophenols are stronger bases than thiols **4b** and **6b** previously used, we tried to apply thiophenol derivatives to the functionalisation of anthracene **6a.** Direct functionalisation of 9,10-dichloromethyl anthracene **(6a)** with *p*-bromothiophenol allowed us to prepare the high-melting solid derivative **11a** in 89% yield. In the next step, *p*-hydroxythiophenol was used instead of *p*-bromothiophenol and desired compound **12b** was obtained in 92% yield. Reaction of **12b** with α,ω-dichlorides **4a** according to the method used by Pedersen for the synthesis of first benzo-crown ethers[18] did not proceed at all and starting product was recovered regardless of the conditions used.



Scheme 4

Then, another new compound **12c**, derived from **6a,** was prepared in 75% yield, which had two amino groups in the phenolic *p*-positions. Acylation of the amine functions using acetic anhydride gave diamide **12d** in 100% yield. Application of the same compound for the macrocylisation reactions with α,ω -dichlorides **4a** or diglycolic acid dichlorides failed and none of the product of the structure **13** was obtained.

The functionalization of the 9,10-methyl groups of anthracene was found to be very difficult. The desired products are chemically unstable and although observed sometimes in mass spectra of crude reaction mixture cannot be isolated. Therefore, the synthesis of thio anthracene-bridged receptors incorporating CH_2CH_2O groups cannot be performed. Functionalisation of 9-bromomethyl anthracene (**1**) was more successful and desired ionophore **3** was obtained in 99% yield. The detailed studies on the interaction of this compound with selected cations are presented below.

Absorption and luminescence spectra of 3.

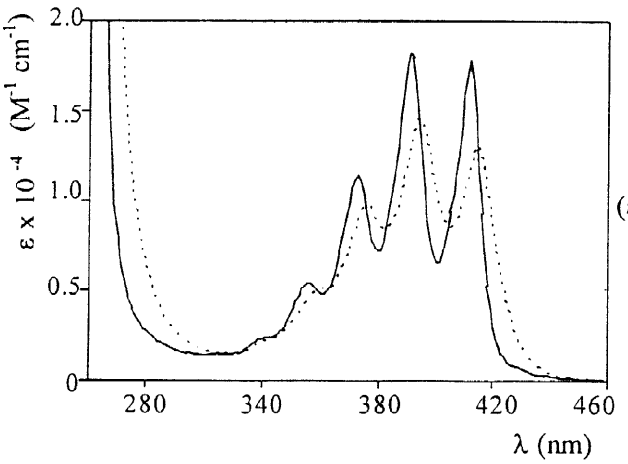


Figure 1

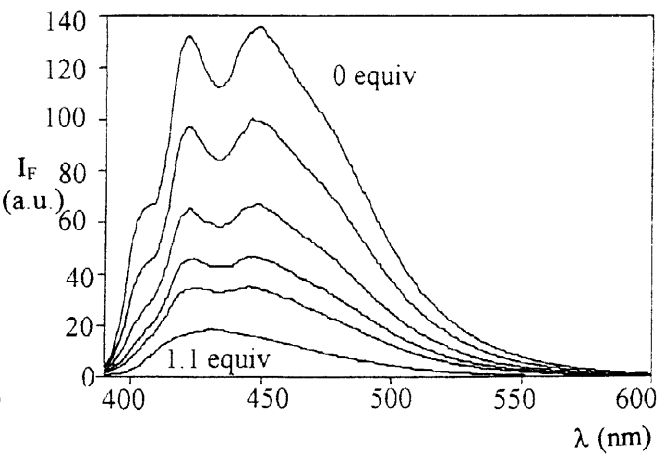


Figure 2

The absorption spectrum of **3** (in dichloromethane:methanol, 8:2, v/v) presents the typical pattern of the anthracene chromophore, with a structured band in the 330-400 nm region and an intense band at 257 nm (Fig. 1). On the contrary, the fluorescence spectrum (Fig. 2) shows some significant differences from the fluorescence spectrum of the 9-methyl-anthracene, since the spectrum can be seen as the superimposition of the structured band of the anthracene moiety and a much broader band that lies more or less in the same spectral region, but is slightly shifted towards longer wavelengths.

Its time decay profile, which can be fitted with two exponential terms only, *i.e.*, 5.5 and 0.8 ns, confirms the existence of two different luminescences. Absorption and fluorescence spectra and excited state lifetimes do not change in the concentration range between 10^{-6} and 10^{-4} M. Instead, a change in the shape of the luminescence band is observed on changing the polarity of the solvent; in particular, the contribution of the non-structured component at longer wavelength increases on going from pure dichloromethane to pure methanol.

The analysis of the pre-exponential terms obtained from fitting the excited state decay at different emission wavelengths shows that the longer term can be attributed to the higher-energy, structured band, while the shorter term can be attributed to the broader band. No differences were observed between excitation spectra recorded at different emission wavelengths, all being superimposable on the absorption spectrum. A possible explanation could be the formation of an intramolecular excimer between the two anthracene moieties of **1**, which is responsible for the broader, red shifted fluorescence band. Almost negligible effects can be observed for the ground state, as can also be seen by the nature of the excitation spectra. Similar behaviour has already been observed for a crown ether containing two 9,10-dimethoxy anthracene moieties, in which a solvent-dependent, broad fluorescence band appeared together with the characteristic fluorescence band of the isolated chromophore. This behaviour is also very common among other polycyclic aromatic hydrocarbons, e.q., pyrene.

Metal ion binding properties of 3

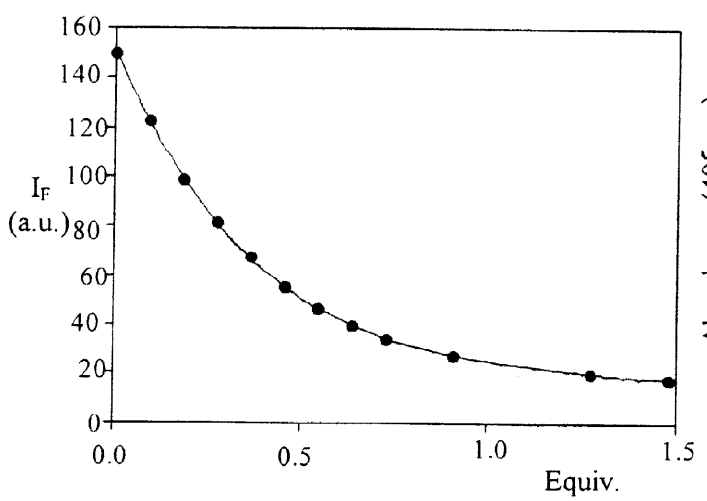


Figure 3

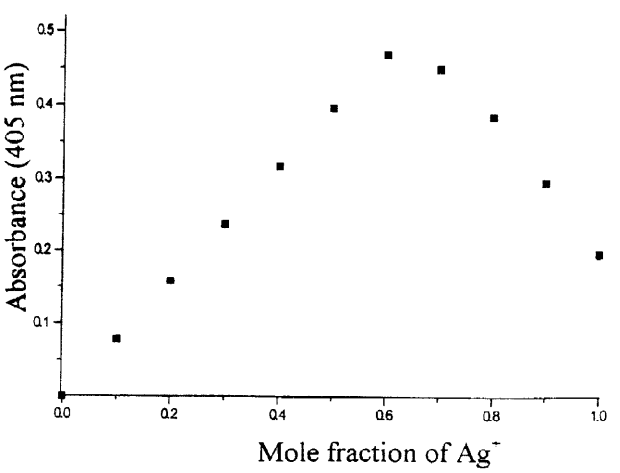


Figure 4

Addition of silver ions as perchlorate or trifluoroacetate salts to a dichloromethane: methanol (8:2, v/v) solution of **1** caused monitorable changes in the absorption spectrum (Fig. 1) and even more pronounced modifications

of the fluorescence pattern (Fig. 2). In particular, upon addition of an increasing amount of the metal ion, the fluorescence band decreases in intensity and loses its structure, while the excited state decay profile can be fitted, after addition of more than one equivalent of silver ions, with only one exponential term, indicating the occurrence of only one, quite short (0.6 ns) lifetime.

The titration profile (Fig. 3) can be fitted by assuming that the two consecutive equilibria 1 and 2 exist, and that the fluorescence properties of **1** are the same in $[Ag\cdot\mathbf{1}]^+$ and $[Ag\cdot(\mathbf{1})_2]$.

$Ag^+ + \mathbf{1} \rightleftharpoons [Ag\cdot\mathbf{1}]^+$ (1)

$[Ag\cdot\mathbf{1}]^+ + \mathbf{1} \rightleftharpoons [Ag\cdot(\mathbf{1})_2]^+$ (2)

The association constants in the experimental conditions were found to be 2×10^5 and 8×10^4 M^{-1} for equilibrium 1 and 2, respectively. The method of continuous variation allows as to identify the stoichiometry of the predominant 1:2 complex (total concentration $C = 2 \times 10^{-4}$ M, Fig.4).

In principle, different explanations can be given for the observed changes in the fluorescence spectrum: the occurrence of (i) an energy transfer process, (ii) an electron transfer process, or (iii) conformational changes upon complexation that force the two anthracene fragments of complexed **1** to lie in closer contact with respect to the free **1**. The former explanation can be ruled out, since the d^{10} silver ions do not have a low energy metal centred state, so that energy transfer from the anthracene to the metal cannot occur. The latter explanation could instead account for the presence of only a short-lived, non structured band, very similar to the excimer component of the free **1**, after the addition of one equivalent of silver ions. Moreover, the observed changes in the absorption spectrum may be explained by a stronger intramolecular interaction in the ground state. Transient absorption spectra are curently being studied in order to confirm or rule out the occurrence of electron transfer processes.

Addition of other metal ions, such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Co^{2+}, did not lead to any change in the photophysical properties. Neither changes were observed in the absorption or fluorescence spectra on addition of these metal ions to an equimolar solution of Ag^+ and **1**, indicating that this ligand shows a remarkable selectivity towards silver ions.

In summary, systematic studies on the formation of anthracene thio receptors were performed. We have found unusual reactivity of this class of compounds. In all cases, incorporation of oxygen atoms destabilised the structure of receptors. The complexation studies performed on model compounds **3** demonstrate that even such a simple chemical receptor possesses very interesting complexation properties. Futher studies will concentrate on the incorporation of anthracene unit into thia-crown ethers and detailed complexation studies of podand **3.**

Acknowledgement.

This work was supported by the Polish State Committee for Scientific Research, Grant No. 3 TO9A 050 011 and MURST and Università di Bologna (Funds for Selected Topics). We thank Prof. J. Jurczak for his kind interest and constant support.

Experimental

General. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra

were recorded using a Varian 200 Gemini spectrometer in $CDCl_3$ or $CDCl_3/C_6D_6$ with TMS as an internal standard. Liquid SIMS spectra were determined on an AMD 604 spectrometer (Cs^+, 10 keV). Ultraviolet absorption spectra were recorded with a Perkin-Elmer lambda 16. Corrected emission end excitation spectra were obtained with a Perkin-Elmer LS50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ± 5%) were obtained with an Edinburgh single-photon counting apparatus, in which the flash lamp was filled with D_2. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects and phototube sensitivity were performed. A correction for differences in the refractive index was introduced when necessary. In order to measure the binding constants with metal ions, emission spectra were run on solutions of the host in methanol (3.0 ml of 1 x 10^{-4} M at 25°C), by excitation of the solution at 270 nm. Aliquots of salt solution (10 μl of 1 x 10^{-2} M) were added and intensities recorded at the maximum of the emission band.

1,3-Di(anthrylthia)propane 3: To the mixture of 0.125 g of sodium hydroxide (3.1 mmol) and a catalytic amount of 18-crown-6 (0.011 g, 0.04 mmol) dissolved in 18 ml of ethanol and 1 ml of water, 0.151 g of 1,3-propanedithiol (1.4 mmol) was added. To this mixture stirred at room temperature, a solution of 0.765 g of 9-bromomethylanthracene (2,8 mmol) in 25 ml of dioxane was added and the reaction mixture was refluxed for 4 hours, cooled to room temperature and the solvents were evaporated. Crystallisation of crude product from chloroform - methanol mixture (1:1, v/v) gave 0.680 g (99 % yield) of pure compound **3** as a yellowish powder.

^{1}H NMR ($CDCl_3$) δ 1.86-2.06 (2H,m, $-SCH_2CH_2-$), 2.69 (4H,t, J=7.2, $-SCH_2-$), 4.62 (4H, s, $-ArCH_2S$), 7.38-7.55 (8H, m, ArH), 7.95 (4H, brd, J_1=8.3, ArH), 8.24 (4H, brd, J_1=8.3, ArH), 8.35 (2H, s, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 29.0, 29.9, 32.0, 124.1, 124.9, 126.1, 127.3, 129.2, 129.9, 131.5; IR (KBr): ν_{max} 3049, 2910, 1622, 15234, 1444, 1345, 1154, 881, 839, 732; L-SIMS m/z 489 ($[M+H]^+$, 0.3%), 460 (0.7%), 325 (15%), 191 (100%); EI-MS m/z 383 (9%), 191 (100%); Anal. Calcd. for $C_{33}H_{28}S_2$: C 81.10; H 5.77; S 13.12. Found: C 80.93; H 6.02; S 13.14.

Synthesis of α,ω-dithiaethylene glycols 4b, General Procedure: 0.5 mole of the respective ethylene glycol was mixed with 79.9 g (1.05 mole) of thiourea in 150 ml of ethanol and refluxed for 2 hours, then cooled to 0°C and the solid product was filtered off and washed with 10 ml of cold ethanol. These salts were reduced in THF solution using $LiAlH_4$ in usual way and purified by vacuum distillation.

1,5-Dithia-3-oxapentane 4b; n=1 b.p. 60-65 °C / 1.0 mm Hg (Kugelrohr, lit.[19] b.p. 83-85 °C / 8 mm Hg), ^{1}H NMR ($CDCl_3$) δ 1.55 (2H, brs, -SH), 2.50-2.65 (4H, m, $-SCH_2-$), 3.35-3.50 (4H, m, $-OCH_2-$).

1,8-Ditha-3,6-dioxaoctane 4b; n=2 b.p. 90-94 °C / 0.8 mm Hg (Kugelrohr, lit.[20] b.p. 125-131 °C / 5 mm Hg), ^{1}H NMR ($CDCl_3$) δ 1.55 (2H, t, J=8.0, -SH), 2.50-265 (4H, m, $-SCH_2-$), 3.35-3.50 (8H, m, $-OCH_2-$).

1,11-Dithia-3,6,9-trioxadodecane 4b; n=3 : b.p. 130-135 °C / 0.9 mm Hg (Kugelrohr, lit.[20] b.p. 168-169 °C / 7 mm Hg), ^{1}H NMR ($CDCl_3$) 1.58 (2H, t, J=8.0, -SH), 2.55-2.73 (4H, m, $-SCH_2-$), 3.40-3.65 (12H, m, $-OCH_2-$).

9,10-Dithiamethyl-anthracene 6b: This compound was prepared according to the procedure used for preparation of α,ω-dithiaethylene glycols **4b** in 85 % yield after crystallisation from DMF. M.p. 206-208 °C (lit.[21] m.p. 217-218 °C); IR (KBr): ν_{max} 3343, 3066, 163, 1621, 1444, 1372, 1231, 753, 631.

9,10-Di(2-hydroxyethylthiamethyl)anthracene 7: To the suspension of potassium carbonate (2.0 g, 14.4 mmol) in 40 ml of DMF, 9,10-dithiamethyl-anthracene (1.114 g, 4.1 mmol) and 2-chloroethanol (0.905 g, 11.2 mmol) were added. The reaction mixture was heated at 100 °C for 5 hours, then cooled to room temerature, and water (35 ml) was added. The precipitated product was filtered off, washed with water (3 ml) and ethanol (3 ml). Crystallisation of crude product from DMF-ethanol gave 1.058 g (72 % yield) of pure compound **6** as a yellow powder. ^{1}H NMR ($CDCl_3$-DMSO-d_6, 1:1, v/v) δ 2.87 (4H, t, J_1=6.4, OCH_2CH_2SH), 3.85 (4H, dt, J_1=6.4, J_2=5.5, OCH_2CH_2SH), 4.39 (2H, t, J_2=5.5, OCH_2CH_2SH), 4.79 (4H, s, -$ArCH_2S$), 7.56 (4H, dd, J_3=3.2, J_4= 7.0, ArH), 8.39 (4H, J_3=3.2, J_4= 7.0, ArH); ^{13}C NMR ($CDCl_3$) δ 29.9, 35.5, 61.2, 124.5, 125.2, 129.1, 129.4; IR (KBr): ν_{max} 3245, 2922, 2869, 1939, 1665, 1444, 1293, 1220, 1172, 1065, 1010, 779; L-SIMS *m/z* 358 ([M]$^+$, 98%), 281 (100%) 235; EI-MS *m/z* 358 ([M]$^+$, 35%), 281 (100%), 235 (43%), 204 (695); HR-MS *m/z* 358.1066 ([M]$^+$; $C_{24}H_{26}O_4S_2$ requires 358.1061); Anal. Calcd. for $C_{24}H_{26}O_4S_2$: C 67.00; H 6.19. Found: C 66.68; H 6.19.

Diester 9: To the suspension of potassium carbonate (1.0 g, 7.2 mmol) in 20ml of DMF, 9,10-dithiamethyl-anthracene (0.691 g, 3.6 mmol) and ethyl bromoacetate (0.914 g, 4.47 mmol) were added. The reaction mixture was heated at 100 °C for 5 hours, then cooled to room temperature and water (20 ml) was added. The precipitated product was filtered off, washed with water (3 ml) and ethanol (3 ml). Crystallisation of the crude product from dioxane gave 0.770 g (68 % yield) of pure compound **9** as a yellowish powder melting at 121-122 °C. ^{1}H NMR ($CDCl_3$) δ 1.35 (6H, t, J_1=7.1, -OCH_2CH_3), 3.34 (4H, s, $COCH_2$), 4.28 (4H, q, J_1=7.1, -OCH_2CH_3), 4.91 (4H, s, -$ArCH_2S$), 7.55 (4H, dd, J_2=3.2, J_3= 6.9, ArH), 8.41 (4H, J_2=3.2, J_3= 6.9, ArH); ^{13}C NMR ($CDCl_3$) δ 14.2, 29.8, 34.4, 61.5, 124.9, 125.9, 129.1, 130.0, 170.7; IR (KBr): ν_{max} 2975, 2778, 1729, 1620, 1444, 1263, 1205, 1153, 1122, 1094, 1025, 769, 710.3; L-SIMS *m/z* 465 ([M+ Na]$^+$, 7%), 442 ([M]$^+$, 32%), 323 (100%); EI-MS *m/z* 442 ([M]$^+$, 17%), 323 (100%), 235 (55%); HR-MS *m/z* 442.1273 ([M]$^+$; $C_{24}H_{26}O_4S_2$ requires 442.1272); Anal. Calcd. for $C_{24}H_{26}O_4S_2$: C 65.13; H 5.92; S 14.49. Found: C 65.50; H 6.07; S 13.92.

Synthesis of 9,10-di(phenylthiamethyl)-anthracenes 12: General Procedure: To the solution of sodium hydroxide (0.193 g, 4.8 mmol) and a catalytic amount of 18-crown-6 (0.011 g, 0.04 mmol) dissolved in 10 ml of ethanol and 1 ml of water, the respective thiophenol **11** was added (4.5 mmol) and the reaction mixture was stirred at room temperature for 10 minutes. To this mixture, a solution of 1,9-dichloromethylanthracene (0.653 g, 2.4 mmol) in 25 ml of benzene was added and reaction mixture was refluxed for 8 hours, cooled to room temperature and solvents were evaporated. Crude products were purified by crystallisation.

Anthracene 12a; R = Br; yield 89%, m.p. 247-249 °C (dioxane): ^{1}H NMR (DMSO-d_6) δ 5.14 (4H, s, -$ArCH_2S$), 6.53, (2H, d, J_1=8.5, ArH), 7.45 (2H, d, J_1=8.8, ArH), 7.55 (4H, dd, J_3=3.2, J_4= 6.8, ArH), 8.33 (4H, J_3=3.2, J_4= 6.8, ArH); IR (KBr): ν_{max} 3025, 1470, 1444, 1386, 1219, 1089, 1004, 807, 771, 716, 629; EI-MS *m/z* 580 ([M]$^+$, 0.2%), 393 (45%), 391 (44%), 204 (100%), 108 (7%); HR-MS *m/z* 579.9347 (579.9353 $C_{24}H_{20}Br_2S_2$ calcd, [M]$^+$); Anal. Calcd. for $C_{28}H_{20}S_2Br_2$: C 57.93; H 3.47. Found: C 57.64; H 3.31.

Anthracene 12b; R=OH; yield 92%, m.p. 155-159 °C (dioxane): ^{1}H NMR (DMSO-d_6) δ 3.36 (2H, s, O*H*), 5.04 (4H, s, -ArCH_2S), 6.73, (2H, d, J_1=8.2, ArH), 7.33 (2H, d, J_1=8.2, ArH), 7.55 (4H, dd, J_3=3.2, J_4= 6.8, ArH), 8.33 (4H, J_3=3.2, J_4= 6.8, ArH); ^{13}C NMR ($CDCl_3$) δ 33.5, 116.0, 124.0, 125.0, 125.7, 129.2, 129.3, 133.9, 157.3; IR (KBr): ν_{max} 3382, 2964, 1644, 1583, 1492, 1429, 1362, 1261, 1089, 1030, 813, 753, 719, 644; EI-MS *m/z* 454 ([M]$^+$, 0.5%), 329 (15%), 250 (83%), 205 (100%), 126 (72%); Anal. Calcd. for $C_{28}H_{22}O_2S_2$+0.5H_2O: C 72.54; H 5.00. Found: C 72.25; H 4.65.

Anthracene 12c; R=NH_2; yield 62%, m.p. 186-190 °C (dioxane/MeOH): ^{1}H NMR (DMSO-d_6) δ 3.63 (4H, s, NH_2), (4H, s, -ArCH_2S), 6.73, (2H, d, J_1=8.5, ArH), 7.33 (2H, d, J_1=8.8, ArH), 7.55 (4H, dd, J_3=3.2, J_4= 6.8, ArH), 8.33 (4H, J_3=3.2, J_4= 6.8, ArH); ^{13}C NMR ($CDCl_3$) δ 33.5, 116.0, 124.0, 125.0, 125.7, 129.2, 129.3, 133.9, 157.3; IR (KBr): ν_{max} 3377, 3311, 3206, 3023, 2867, 1621, 1593, 1493, 1445, 1256, 1216, 1124, 826, 768, 718; EI-MS *m/z* 454 ([M]$^+$, 0.5%), 329 (15%), 250 (83%), 205 (100%), 126 (72%); Anal. Calcd. for $C_{28}H_{24}N_2S_2$+0.5 $C_4H_8O_2$(dioxane): C 72.56; H 5.69; N 5.64 Found: C 72.76; H 5.15; N 5.10.

Anthracene 12d; R=NHAc, 0.061 g of anthracene amine **12c** (0.13 mmol) was suspended in 2 ml of acetic anhydride and refluxed for 0.5 hour. Evaporation of solvent yielded 0.071 g of pure product. Yield 99.9%, ^{1}H NMR (DMSO-d_6) δ 2.08 (6H, s, $COCH_3$), 5.11 (4H, s, -ArCH_2S), 7.43, (2H, d, J_1=8.6, ArH), 7.55 (4H, dd, J_3=3.1, J_4= 7.0, ArH), 7.60 (2H, d, J_1=8.6, ArH), 8.35 (4H, J_3=3.1, J_4= 7.0, ArH), 9.95 (2H, s, NH); ^{13}C NMR ($CDCl_3$-DMSO-d_6, 1:1, v/v) δ 23.8, 32.4, 119.4, 124.7, 125.6, 128.6, 129.1, 129.5, 130.9, 138.3, 168.0; IR (KBr): ν_{max} 3407, 3300, 3179, 3093, 1660, 1591, 1526, 1495, 1395, 1369, 1313, 1289, 1256, 1093, 1015, 822, 772, 722; EI-MS *m/z* 536 ([M]$^+$, 0.4%), 370 (22%), 204 (100%), 12 (78%); HR-MS *m/z* 536.1583 (536.1592 $C_{32}H_{28}N_2S_2O_2$ calcd, [M]$^+$).

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