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Study on the synthesis and molecular recognition of new receptors for selective complexation of carboxylic acids

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ABSTRACT

A new synthetic method based on the synthesis of unsymmetrical thioureas followed by double S-alkylation reaction by xylylene dibromides was used to obtain isothiouronium receptors. Their binding abilities to acetate, succinate and maleate anions were evaluated by UV–vis spectroscopic titrations in such solvents as water, acetonitrile, methanol and mixtures of acetonitrile/methanol (1:1, v/v). For simple receptor **4** with one isothiouronium group, no selectivity was observed in the complexation of the anions studied. Receptors (R) **5a–c** with two thiouronium groups are able to form with all the anions studied (A) not only stable complexes of 1:1 stoichiometry but also other possessing structure of the type A_nR_m. The most reliable values of stability constants are for systems of the type maleate anion-receptor **5** and acetate-receptor **5b**. However, the best selectivity in the mixed solvents is demonstrated by anion-**5c** system. The study indicates also that particularly **5c** is preferred as a chemosensor for the maleate anion. The obtained results suggest that subtle changes in the receptor structure lead to different binding modes towards anions.

1. Introduction

The great interest devoted by chemists to chemical sensors is comprehensible taking into account that these species can offer the possibility to monitor in situ, in real time and real space, the concentrations of analytes for many different purposes. They have important applications in environmental monitoring,[1] process control,[2] food and beverage analyses,[3] medical diagnosis[4] and so on. A fruitful approach to the design and synthesis of efficient sensor device is the development of molecular entities, referred to as chemosensors, able to recognise the target analyte with desire affinity and selectivity, and presenting an efficient signal transduction mechanism.[5]

Nowadays, among different target analytes, organic carboxylic and dicarboxylic acids are points of interest. When designing the structure of a chemosensor for anions, one has to take into account not only some photophysical parameters but also a type of hydrogen bonding structure involved in the anion-ligand complex in order to achieve the best sensitivity and selectivity.

The selective recognition of carboxylic acid oxoanions takes place by a combination of hydrogen bonds and electrostatic interactions.[6–8] Using these binding forces as well as others, some synthetic receptors for oxoanions in strongly solvating solvents have recently been developed by several research groups.[7] Many years ago thiouronium salts have been used as reagents for the identification of organic acids.[8] Yeo and Hong[9] showed that the thiouronium group generated by S-alkylation of the thiourea group possesses a relatively larger dipole moment and enhances acidity of thiourea NH residues and therefore could function as a carboxylic acid anion binder better than the thiourea group.

For efficient complexation of dicarboxylic acid anions, special receptors are required. In the chemical structure of these receptors, two thiouronium groups should be present in precisely defined positions as already discussed in the literature.[10] Therefore, the synthesis of receptors should give the possibility to define the distance between thiouronium groups. This type of receptor showed UV–vis spectral changes on complexation with dicarboxylic acid anions in spite of lacking conjugation between the chromophore and the binding sites, in polar organic solvents such as acetonitrile. It is also important to compare the complexation

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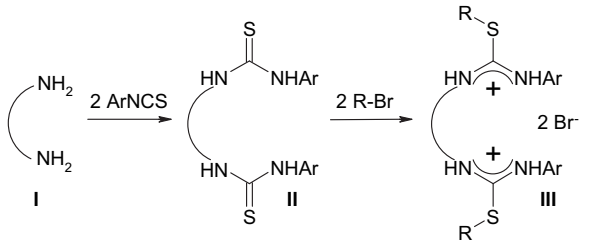
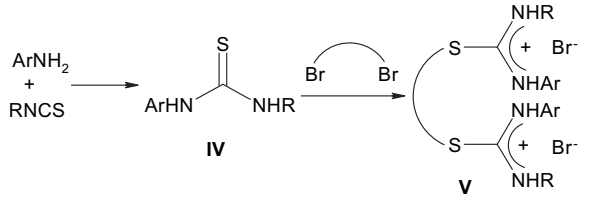
properties of receptors prepared for mono- and dicarboxylic acid anions in order to find receptors selective towards dicarboxylic acid anions.

A common problem in the synthesis of new receptors and further complexation studies is associated with existing synthetic procedures. Therefore, simple and efficient synthetic methods are of great importance for the scientific community. In most cases, the synthesis of bis-thiouronium receptors **III** is based on reaction of diamines and arylisocyanates (Scheme 1).[9,11] Products **II** are key elements in this synthesis. Double S-alkylation of these bifunctional receptors **II** with alkyl bromides leads to respective thiouronium salts **III**, which can be used for complexation studies.



Scheme 1. The synthesis reactions of the bis-thiouronium salt III.

Here we propose a new method based on the reaction of aryl amines with alkyl or arylisocyanates (Scheme 2). In the reaction of primary aromatic or aliphatic amines and isothiocyanates, asymmetric thioureas **IV** can be obtained, which might be used as substrates for subsequent reaction with α,ω-dibromides leading to target structures **V**. Aromatic amines can be used for the synthesis of new receptors, commercially available or prepared according to standard synthetic procedures.



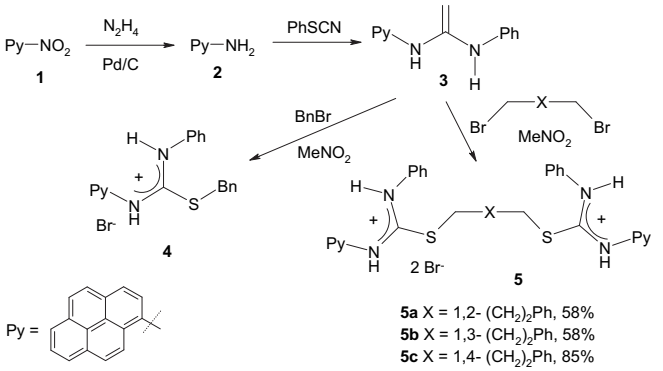
Scheme 2. Proposal of the synthesis of the bis-thiouronium salts **V**.

For our studies, aminopyrene was chosen as a good fluorescent substrate readily available in large quantities. Thus, we report here the synthesis of pyrene chemosenors and their complexation studies with carboxylic (acetate, succinate and maleate) anions in water, acetonitrile (MeCN), methanol (MeOH) or MeCN/MeOH (1:1, v/v).

2. Results and discussion

The method used for the synthesis of receptors is based on two reactions: formation of unsymmetrical thioureas followed by double S-alkylation of the products obtained. Since a very large number of aromatic amines is available this approach opens a convenient way for the synthesis of receptors of general structure **V** (Scheme 2).

The key compound in the synthetic strategy is thiourea **3** that was prepared in a three-step synthesis (Scheme 3). Nitration of pyrene gave 1-nitropyrene (**1**) as yellow crystals in 51% yield. Reduction (Pd/C) of this compound using hydrazine monohydrate led to 1-aminopyrene (**2**) in 56% yield. Both reactions can be readily performed on large scale. The product obtained was used as a substrate for next reaction with phenyl isothiocyanate, which lead to compound **3** in 74% yield.



Scheme 3. Synthesis of bis-thiouronium salts based on xylylene structures.

In the model reaction between thiourea **3** and benzyl bromide, the product isothiouronium salt **4** was obtained in 95% yield. The product precipitates from reaction mixture what simplifies the experimental procedure. In the next step of our studies the reaction with dibromides was performed. As the substrates, compound **3** and *o*-, *m*- and *p*-xylylene dibromides were used. Xylylene dibromides are readily available and offer full control of the structure of receptors with precisely increasing distances between isothiouronium groups. In nitromethane solution, at 80 °C, the bis-thiouronium receptors **5a**, **b** and **c** were obtained in 58, 58 and 85% yields, respectively. Again, we observed precipitation of the products from reaction mixtures. A strong electrostatic interaction between thiouronium groups lowers the yields of reaction for *o*- and *m*-xylylene dibromides. Longer distances between functional groups diminished the electrostatic interaction and increased the yield up to 85% for compound **5c**.

In the next steps of our studies, the complexation of acetate, succinate and maleate anions (as their tetrapropylammonium salts) with the receptors obtained was investigated by UV–vis spectroscopic titrations in water, aprotic MeCN, MeOH and mixed MeCN/MeOH (1:1, v/v). In the case of aqueous solutions no distinct changes in absorption spectra of receptors studied are observed, while in MeOH solutions the spectral changes are more distinct but remain ambiguous. An increase of the anion concentration in each of the receptor–anion systems in MeCN/MeOH solutions up to [anion]/[receptor]=5 causes an increase of the absorption bands at 282, 357, 367 and 386 nm as well as a decrease at about 243, 277, 328 and 345 nm with isosbestic points at 279, 309 and 350 nm (Fig. 1). The well-defined red shift of the charge transfer bands (at 243 and 344 nm) is probably a result of the electron density transfer to the thiouronium moiety, which makes the intensity of the dipole

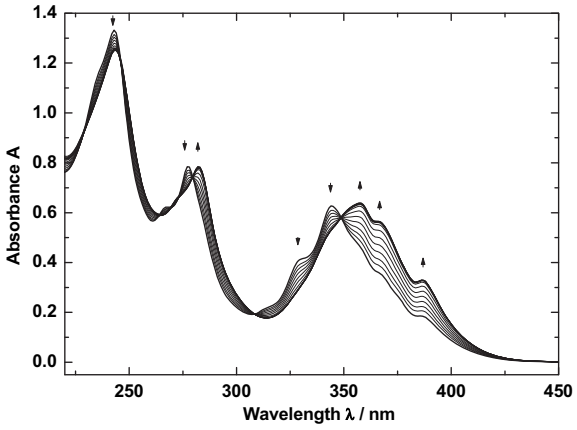


Figure 1. UV–vis spectral changes of the receptor upon the addition of acetate, maleate or succinate anion in MeCN/MeOH (1:1, v/v).

increase and shifts the charge transfer band to longer wavelength. The presence of sharp isosbestic points indicate that some authentic H-bonded complexes of different stoichiometry co-exist in the solution. This is additionally confirmed by the absorbance–absorbance (*A*–*A*) and absorbance-[anion]/[receptor] plots in MeCN or MeCN/MeOH solutions.

For the three selected anions and receptors **5** in the mixture of MeCN and MeOH, the *A*–*A* plots (Fig. S1, Supplementary data) exhibit distinct two linear intersecting segments, indicating that the system involves two titration steps.[12] Unfortunately, the results obtained for receptors **4** are unresolved.

The absorbance vs [anion]/[receptor] plots (Fig. 2) for the above-mentioned complex systems are composed of two linear segments, which intersect at about 1.5 M ratio for [maleate]:[**5a**] and [acetate]:[**5b**] as well as about 1.0 M ratio for [succinate]:[**5c**]. In all cases, a small inflection is also observed for higher molar ratio. These effects confirm the results shown in Figure S1 (Supplementary data) and indicate on the presence of complexes with various stoichiometries.[12] Contribution of the complexes with various stoichiometries to the absorption spectra is sufficient enough for the calculation of stability constants of each complex formed in the anion-**5a–c** systems (Table 1).

The stability constants calculated for each of the studied complex systems are collected in Table 1.

A relatively low standard deviation of the calculated binding constants is a result of the fact that the formation of higher order complex, the presence of which is suggested in the plots (Fig. 2), has been considered in calculations. Thus, the maleate-**5a** system is characterized in practice by the 1:1 and 3:1 complexes, while acetate or succinate anions with the same receptor form complexes of stoichiometry 1:1 and 2:1 or 1:1 and 1:2, respectively. The changes of the concentration of the complexes with different stoichiometries during titration for the selected complex systems are presented in Figure S2 (Supplementary data). The standard deviations of the higher order complexes are higher than those of 1:1 complexes. However, the stability constants of the 1:1 species are over the reliability limit for the UV–vis spectroscopy equal to 7 (cf. in Table 1).

Acetate anion with receptor **5b** forms a 1:1 complex where log β is reliable because its value is lower than 7 and has low confidence interval (entry 5 in Table 1). Equally valuable are the stability constants of the complexes with maleate anion. It is interesting to note that log β value is near the same, within experimental error, for maleate complexes 1:1 with the receptors, while the stability of the 2:1 complexes with **5b** and **c** slightly decreases with the distance between thiouronium groups in the receptor (entries 7 and 10 in Table 1). The higher constant value the more effective is charge compensation of the receptors by succinate anions. However, too high stability constants (above 7) of the 1:1 complexes in the systems acetate-**5a** and succinate-**5a–c** are not reliable enough to compare the charge compensation in those systems with others. Then, for succinate-**5b** system log β of both complexes is charged with rather high experimental error (entry 5 in Table 1).

As observed, the acetate anion can form with receptors **5a** or **5b** complexes of 2:1 or 3:2 stoichiometries besides the 1:1 species. On

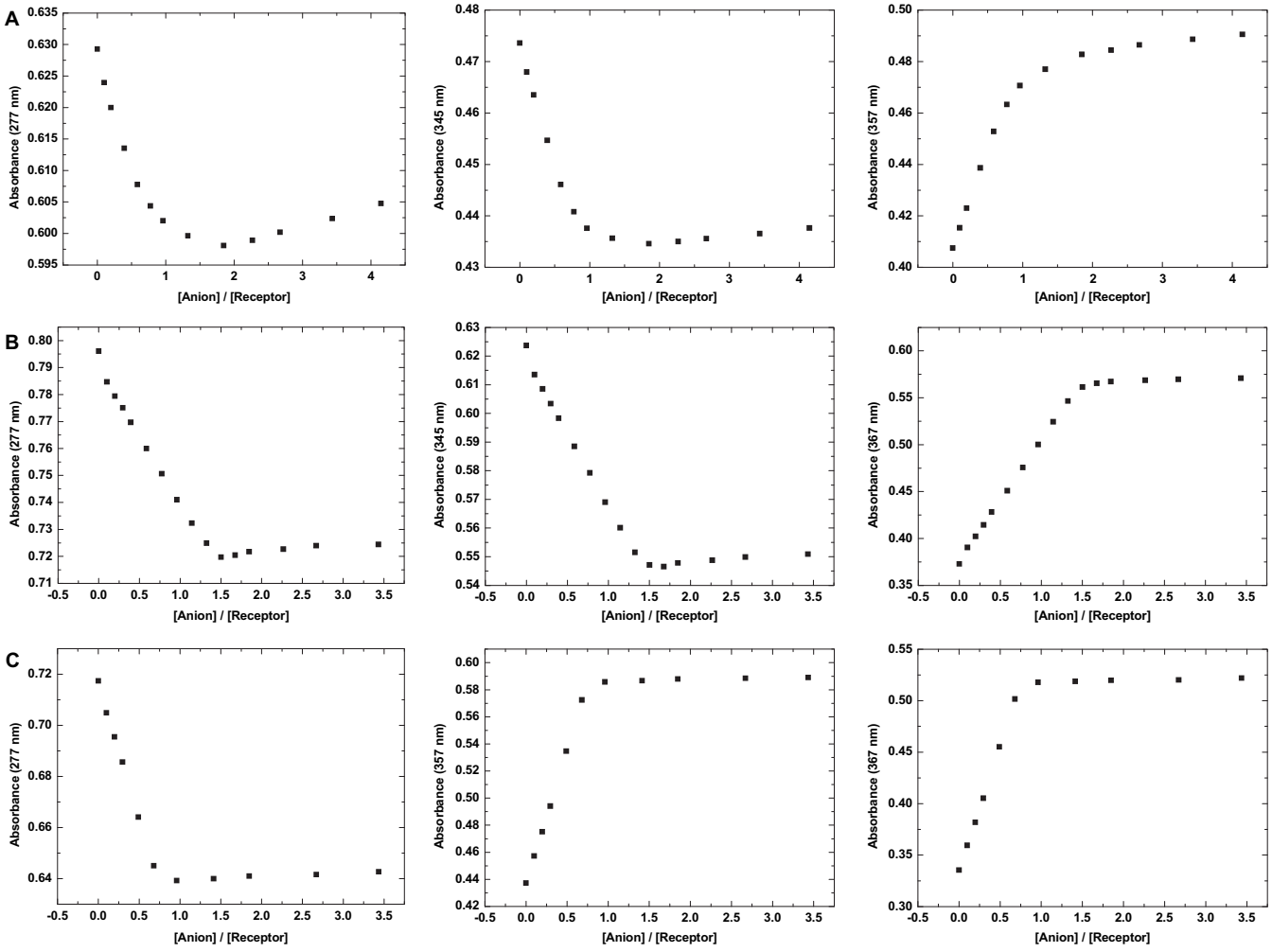


Figure 2. Absorbance vs [anion]/[**5**] molar ratio, where the anion and receptor are: (A) [maleate]/[**5a**], (B) [acetate]/[**5b**] and (C) [succinate]/[**5c**].

Table 1
Complex stoichiometries and stability constants of the anion-receptor complexes in MeCN/MeOH (1:1 v/v) solution

Entry	Receptor	Anion	Complex stoichiometry [anion]/[receptor]	Stability constant log β
1	**4**	Acetate, Succinate, Maleate	—	unresolved
2	**5a**	Acetate	1:1	8.09±0.58
			2:1	14.46±0.67
3		Succinate	1:1	7.16±0.47
			1:2	13.98±0.67
4		Maleate	1:1	6.31±0.16
			3:1	16.04±0.21
5	**5b**	Acetate	1:1	5.94±0.34
			3:2	25.35±0.27
6		Succinate	1:1	8.88±1.48
			1:2	13.70±1.50
7		Maleate	1:1	6.25±0.12
			2:1	11.00±0.27
8	**5c**	Acetate	1:1	unresolved
			3:2	22.39±0.18
9		Succinate	1:1	8.87±0.86
			1:2	14.53±0.95
10		Maleate	1:1	6.75±0.25
			2:1	10.76±0.37

the contrary, **5c** creates only one complex, viz. 3:2 one, with the mentioned anion. It is presumably due to the distance between thiouronium groups in **5c** molecule, that is, so large that the 1:1 complex cannot be formed.

Complexation of the anions (A) and the receptors (R) shows that in the case of maleate dianion it is possible to calculate more precisely the individual stability constants of their A_3R or A_2R complexes with **5** receptors (entry 4, 7 and 10 in Table 1). The presence of a small inflexion (at about 2:1 [anion]/[receptor] ratio) on the plots of absorbance vs [maleate]/[**5**] molar ratio in Figure 2A and Figure S3 (Supplementary data) confirms formation of higher order

Among the anions selected to bind with the receptors **5a–c**, only maleate creates complexes with high reliability of log β (values below 7) and relatively narrow confidence interval. Moreover, the most favourable situation for selectivity is in the case, if the stability constants of the anion-receptor complexes differ distinctly (i.e., confidence intervals do not overlap). From this point of view we turn our special attention to **5c** as a receptor, especially suitable for maleate anion.

Unfortunately, for the above-mentioned complex systems with the receptors **5a–c** it is not possible to determine reliable log β values in MeCN solutions using UV–vis method since they very often exceed 7.

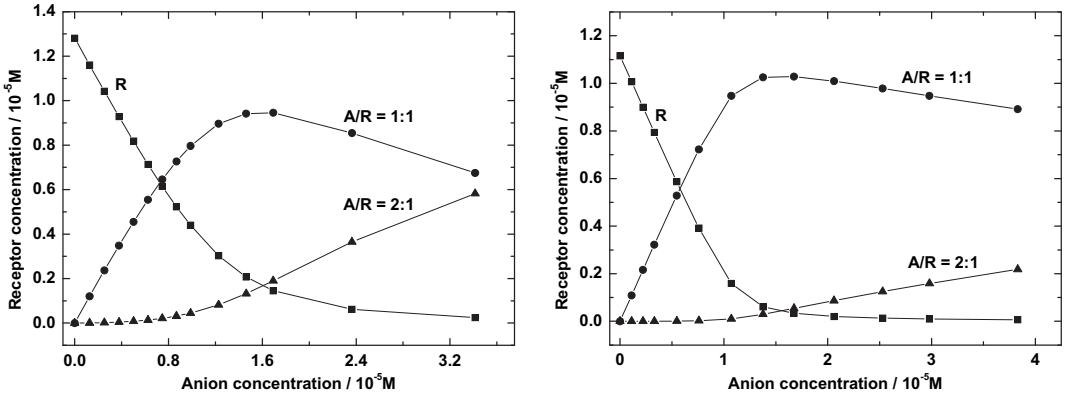


Figure 3. Concentrations of the species vs concentration of maleate anion in the complex systems with receptors: A. **5b** and B. **5c**.

complexes in the mixed solvent. Meanwhile, as shown in Figure 3 and Figure S2A (Supplementary data), the contribution of the complexes A_3R or A_2R created with **5a–c** is lower than the AR species up to ca. $4\cdot10^{-5}$ M in each case.

For the dianions (succinate and maleate) the AR complex dominates over the higher order A_mR_n complexes in the titration range. Maleate forms A_mR_n species, where $m>n$, whereas succinate complexes of higher order, vice versa, are characterized by $m<n$ (Table 1). Acetate as monoanion in the complex systems creates a more complicated situation, viz., for R=**5a** complex AR exceeds A_2R in concentration in the narrow range (0.8×10^{-5}–1.9×10^{-5} M) whereas A_3R_2 complex dominates in the whole titration range. When R is **5b** (Fig. S2B) (Supplementary data) or **5c** only complex A_3R_2 exists (entry 8 Table 1).

3. Conclusions

Isothiouronium receptors with pyrene as a chromophore were synthesized according to a new procedure based on double S-alkylation of unsymmetrical thioureas by xylylene dibromides. The obtained receptors **4** and **5** (as their tetrapropylammonium salts) were titrated with acetate, succinate and maleate anions. The observed substantial changes in their absorption spectra cause that the pyrene receptors with thiouronium fragments could be used as chromophores in the case of acetate and maleate anions. Among the solvents used only the MeCN/MeOH solvents mixture (1:1, v/v) supplies optimal conditions for formation of the complexes anion-receptor as another studied are either too weak (as MeCN) or too strong (as H_2O and MeOH) in the hydrogen bonding competition

and polarity. UV–vis absorption method enables to determine reliable log β values only for the systems of the type anion-receptor **5** in MeCN/MeOH solutions. Analysis of the stability constants provides evidence that compound **5c** is a favourable receptor for such dicarboxylic anion as maleate.

4. Experimental

NMR spectra were measured with Varian 200 GEMINI and Varian 400 GEMINI spectrometers with TMS as internal standard. TLCs were performed with silica gel 60 (230–400 mesh, Merck) and silica gel 60 PF254 (Merck). CHN analysis was performed on Perkin–Elmer 240 Elemental Analyzer whereas CHNS analysis on Heraeus Vario EL III apparatus. MS spectra were recorded on an API-365 (SCIEX) apparatus. Acetonitrile (MeCN) used in our study was HPLC grade.

4.1. Synthesis

4.1.1. Preparation of tetrapropylammonium salts

4.1.1.1. Tetrapropylammonium acetate. To a solution of tetrapropylammonium hydroxide (10 ml of 20% solution in water, 9.8 mmol) in methanol (10 ml) acetic acid was added (560 μl, 9.83 mmol). After 3 h hygroscopic crystals of tetrapropylammonium acetate were filtered off and dried under vacuum (0.450 g, 1.8 mmol, 18%): mp>360 °C.

4.1.1.2. Tetrapropylammonium maleate. To a solution of tetrapropylammonium hydroxide (20 ml of 20% solution in water, 19.7 mmol) in methanol (10 ml) maleic acid was added (1.141 g, 9.83 mmol). After 3 h hygroscopic crystals of tetrapropylammonium maleate was filtered off and dried under vacuum (1.164 g, 2.6 mmol, 24%): mp 170 °C (decomp.).

4.1.1.3. Tetrapropylammonium succinate. To a mixture of tetrapropylammonium hydroxide solution (20 ml of 20% solution in water, 19.7 mmol) and methanol (10 ml) succinic acid (1.160 g, 9.83 mmol) was added. After 3 h hygroscopic crystals of tetrapropylammonium succinate were filtered off and dried under vacuum (1.689 g, 3.44 mmol, 35%): mp 225 °C (decomp.).

4.1.2. Preparation of thiouronium salts

*4.1.2.1. 1-Nitropyrene (**1**).* To a solution of pyrene (10 g, 49.4 mmol) in ethyl acetate (140 ml) cupric nitrate trihydrate (16 g, 66.2 mmol) and acetic anhydride (12 ml, 126 mmol) were added. The reaction mixture was stirred at 60 °C for 24 h. Precipitated product was filtered off, washed with water. Crystallization from ethyl alcohol gives yellow crystals of 1-nitropyrene (6.23 g, 25.2 mmol) with 51% yield: mp 151 °C (lit. 150–152)[13]; R_f=0.70 (Hexane/AcOEt=7:3, v/v).

*4.1.2.2. 1-Aminopyrene (**2**).* To a solution of 1-nitropyrene (2.25 g, 9.1 mmol) in a mixture of ethanol and toluene (100 ml, 3:1, v/v) hydrazine monohydrate (2.5 ml, 51 mmol) was added. Then Pd/C (300 mg, 10 %) was added. The reaction mixture was refluxed for 25 min, cooled to room temperature and filtered through Celite. The filtrate was evaporated and residue was crystallized from cyclohexane to give yellow needles of 1-aminopyrene (1.108 g, 5.1 mmol) with 56% yield: mp 116–117 °C (lit. 117)[14]; R_f=0.40 (Hexane/AcOEt=7:3, v/v).

*4.1.2.3. 1-Phenyl-3-pyren-1-yl-thiourea (**3**).* To a solution of 1-aminopyrene (**2**) (300 mg, 1.38 mmol) in dry dichloromethane (5 ml) phenyl isothiocyanate (250 μl, 2.07 mmol) and *N*,*N*-dimethylaminopyridyne (10 mg) were added at room temperature. The reaction was stirred for 22 h. Precipitated product was filtered off and washed by dichloromethane to gave yellow solid of *N*-phenyl-*N*′-α-pyrenyl thiourea (361 mg, 1.02 mmol, 74%): mp 191–194 °C; R_f=0.77 (Hexane/AcOEt=4:6, v/v); IR (KBr): ν (cm^{-1})=3326 (m), 3106 (m), 2947 (m), 1587 (w), 1536 (s), 1490 (s), 1263 (m), 1244 (m), 1205 (m), 1184 (m), 845 (m), 694 (m); ^{1}H NMR (200 MHz, DMSO-d_6): δ=10.29 (s, 1H, N*H*), 9.92 (s, 1H, N*H*), 8.50–8.00 (m, 10H, Ar*H*) 7.59 (d, *J*=7.6 Hz, 2H, Ar*H*), 7.36 (t, *J*=7.6 Hz, 2H, Ar*H*), 7.15 (t, *J*=7.5 Hz, 1H, Ar*H*); ^{13}C NMR (50 MHz, DMSO-d_6): δ=181.4, 139.6, 133.0, 130.6, 130.5, 129.3, 128.4, 127.5, 127.2, 127.1, 126.7, 126.4, 125.4, 125.2, 124.9, 124.6, 124.1, 122.7. Anal. Calcd for $C_{23}H_{16}N_2S$: C, 78.38; H, 4.58; N, 7.95. Found: C, 78.39; H, 4.55; N, 7.93.%.

*4.1.2.4. Preparation of salt **4**.* To a suspension of 1-phenyl-3-pyren-1-yl-thiourea (70 mg, 0.20 mmol) in ethanol (10 ml) benzyl bromide (26 μl, 0.22 mmol) was added. The mixture was refluxed for 4 h. Then solvent was evaporated and residue was washed with diethyl ether. Yellow crystalline product was filtered off and dried (102 mg, 0.19 mmol, 95%): mp 120–123 °C; ^{1}H NMR (200 MHz, DMSO-d_6): δ=8.45–8.05 (m, 8H), 7.95–7.75 (m, 2H), 7.60–7.25 (m, 9H), 7.22 (s, 1H), 4.61 (s, 2H), 3.52 (dd, *J*=7.6 Hz, *J*=6.0 Hz, 1H). Anal. Calcd for $C_{30}H_{23}BrN_2S$+1.6H_2O: C, 65.24; H, 4.78; N, 5.07. Found: C, 65.26; H, 4.90; N, 5.10. ESI-MS: *m*/*z* 443 $[M]^+$. HRMS (ESI) calcd for $C_{30}H_{23}N_2S$ $[M-Br]^+$: requires 443.1582; found: 443.1559.

*4.1.2.5. Preparation of salt **5a**.* A suspension of *N*-phenyl-*N*′-α-pyrenyl thiourea (502 mg, 1.42 mmol) and 1,2-bis(bromomethyl)-benzene (179 mg, 0.68 mmol) in nitromethane (25 ml) was heated at 80 °C for 24 h. A green solid precipitated from the reaction mixture was filtered, washed with hexane and dried under reduced pressure (375 mg, 0.39 mmol, 58%): mp 160–170 °C; IR (KBr): ν (cm^{-1})=3037, 2850, 1599, 1569, 1493, 845; ^{1}H NMR (200 MHz, DMSO-d_6): δ=8.45–7.95 (m, 18H), 7.82 (d, *J*=9.0 Hz, 2H), 7.60–7.00 (m, 12H), 4.67 (s, 4H), 4.42 (s, 2H), 3.45 (dd, *J*=10.9 Hz, *J*=4.1 Hz, 2H). Anal. Calcd for $C_{54}H_{40}Br_2N_4S_2$+0.5 $MeNO_2$: C, 65.50; H, 4.19; N, 6.31. Found: C, 65.55; H, 3.99, N, 6.43. ESI-MS: *m*/*z* 807 $[M-HBr-Br]^+$. HRMS (ESI) calcd for $C_{54}H_{39}N_4S_2$ $[M-HBr-Br]^+$: requires 807.2616; found: 807.2602.

*4.1.2.6. Preparation of salt **5b**.* A suspension of *N*-phenyl-*N*′-α-pyrenyl thiourea (501 mg, 1.42 mmol) and 1,3-bis(bromomethyl)-benzene (179 mg, 0.68 mmol) in nitromethane (25 ml) was heated to 80 °C for 24 h. A yellow solid precipitated from the reaction mixture was filtered, washed with hexane and dried under reduced pressure (375 mg, 0.39 mmol, 58%): mp 165–175 °C; IR (KBr): ν (cm^{-1})=3041, 2850, 1600, 1568, 1493, 846; ^{1}H NMR (200 MHz, DMSO-d_6): δ=8.45–7.95 (m, 16H), 7.82 (d, *J*=9.0 Hz, 4H), 7.60–7.00 (m, 12H), 4.67 (s, 4H), 4.42 (s, 2H), 3.45 (dd, *J*=10.9 Hz, *J*=4.1 Hz, 2H). Anal. Calcd for $C_{54}H_{40}Br_2N_4S_2$+H_2O+$MeNO_2$: C, 63.04; H, 4.33; N, 6.68. Found: C, 62.75; H, 3.82; N, 6.85. ESI-MS: *m*/*z* 807 $[M-HBr-Br]^+$. HRMS (ESI) calcd for $C_{54}H_{39}N_4S_2$ $[M-HBr-Br]^+$: requires 807.2616; found: 807.2627.

*4.1.2.7. Preparation of salt **5c**.* A suspension of *N*-phenyl-*N*′-α-pyrenyl thiourea (260 mg, 0.74 mmol) and 1,4-bis(bromomethyl)benzene (92 mg, 0.35 mmol) in nitromethane (20 ml) was refluxed for 2.5 h. Yellow crystalline product was filtered off and dried reduced pressure (288 mg, 0.30 mmol, 85%): mp 170–177 °C; IR (KBr): ν (cm^{-1})=3044, 2856, 2761, 1598, 1568, 1505, 842; ^{1}H NMR (200 MHz, DMSO-d_6): δ=8.45–8.05 (m, 14H), 7.94 (d, *J*=9.2 Hz, 4H), 7.65–7.00 (m, 14H), 4.84 (s, 4H), 4.49 (s, 2H), 3.52 (dd, *J*=11.2 Hz, *J*=4.8 Hz, 2H). Anal. Calcd for $C_{54}H_{40}Br_2N_4S_2$+0.5 $MeNO_2$: C, 65.50; H, 4.19; N, 6.31. Found: C, 65.49; H, 3.89; N, 6.59. ESI-MS: *m*/*z* 807 $[M-HBr-Br]^+$. HRMS (ESI) calcd for $C_{54}H_{39}N_4S_2$ $[M-HBr-Br]^+$: requires 807.2616; found: 807.2583.

4.2. UV–vis titration experiments

Absorption spectra were recorded at room temperature on a Perkin–Elmer Lambda 40P spectrophotometer. Solutions of the pyrene derivative bromide salts (concentration 5×10^{-5} M) in acetonitrile were treated with increasing amounts of acetonitrile solutions of tetrapropylammonium acetate or maleate salts (concentration about 5×10^{-4} M) containing the same concentration of the appropriate ligand as in the cuvette. After each addition of aliquot, using a Hamilton microsyringe with micrometre screw, the UV–vis spectrum was recorded. The spectra were implemented into the SPECFIT/32 software for binding constant calculations.[15]

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Supplementary data

Supplementary data associated with this article can be found in the online version doi:10.1016/j.tet.2010.01.066.

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