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Synthesis and characterization of new aromatic tweezers and complex formation with tropylium ion in 1,2-dichloroethane

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ABSTRACT: A series of benzene and pyridine tweezers bearing phenyl, naphthyl and anthryl receptor units was prepared and characterized. The x-ray crystal structure of the 1,3-bis(9-methanolanthracene)methylbenzene ligand (**5**) is reported. UV–visible and NMR spectroscopy were used to investigate the host–guest chemistry of the new ligands in complexation with tropylium tetrafluoroborate as a model aromatic cationic guest in 1,2-dichloroethane. The appearance of coloured charge-transfer absorption bands demonstrates the complex formation with a tropylium ion. The enlargement of aryl receptor size from phenyl and naphthyl to anthryl increases the stability of complexes. Electron donor–acceptor interactions are an important driving force for complexation by molecular tweezers. The results are discussed and compared with those of previously studied systems containing crown ethers and podands. The bisanthracenes **5** and 1,3-bis(9-methanolanthracene)methylpyridine (**6**) are especially interesting in displaying both complexation ability and intramolecular cycloaddition via charge-transfer excitation. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: charge-transfer; cleft; cycloaddition; recognition; stacking; tropylium

INTRODUCTION

Exploring the potentials of π–π stacking and cation–π interactions[1] in molecular recognition has been an intensively studied area in supramolecular chemistry. In particular, attention has been focused on the role of non-covalent interactions in the formation of novel supramolecular assemblies.[2] The formation of a supramolecular entireness demands the existence of several cooperative non-covalent interactions, such as interactions with participation of hydrogen (H-bonds), electrostatic, charge-transfer, dispersion, ion-mediated and hydrophobic interactions.[3] The incorporation of a substrate into a host cavity forming inclusion complexes is another way to attain supramolecular structures.[4]

Various host molecules capable of binding neutral or ionic aromatic guests between aromatic surfaces have been synthesized. Macrocyclic hosts bearing electron-rich aromatic atoms such as cyclophanes, calixarenes and homocalixcarenes have dominated. However, molecular clefts offer an interesting approach to study molecular recognition based on π–π and cation–π interactions.[5] Usually molecular clefts or tweezers have been constructed of one spacer unit and two complexing receptors forming hosts with varying degrees of rigidity depending on design. Rebek's baseball assemblies of two or more cleft-like structures represent an example of the highlights of the development.[6] Podands with central benzene and pyridine units and rigid donor end groups (e.g. 8-hydroxyquinoline) were studied in the late 1970s by Vögtle and Weber.[7]

We have observed that π–π stacking interaction plays an important role in the complexation between benzene-substituted crown ethers and various electron-deficient ions such as tropylium,[8] pyridinium,[9] imidazolium and pyrazolium.[10] It also has an important role in the complex formation between podands bearing aromatic end groups and a tropylium cation.[11] We describe here a class of

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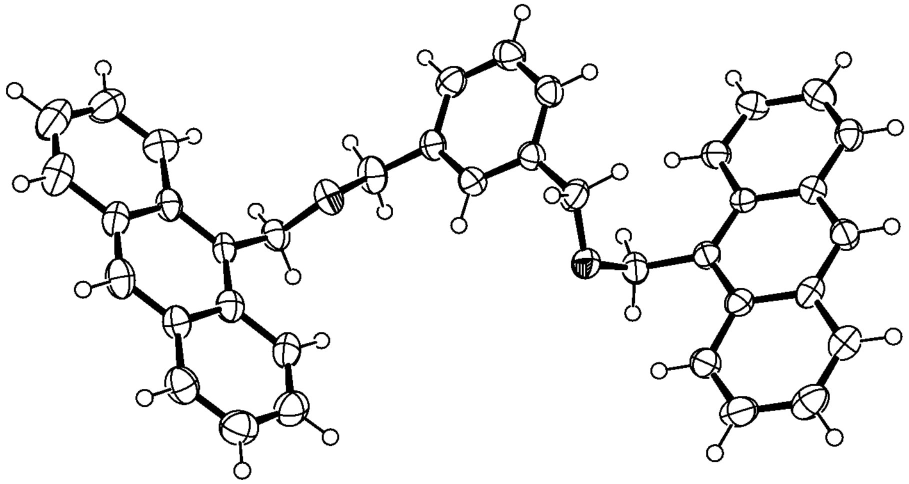


Figure 1. Ball-and-stick representation of the solid-state structure of the **5**

molecular receptors that are able to bind aromatic cations by means of charge-transfer, π–π and cation–π interactions. We studied the capability of the hosts for complexation towards aromatic molecules using a tropylium tetrafluoroborate guest in 1,2-dichloroethane (DCE) by UV–visible absorption spectrophotometry. In addition, a comparison between crown ethers and podands host structures was undertaken as it was expected to be informative for the development of new host molecules.

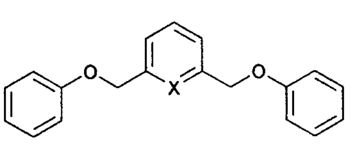
RESULTS AND DISCUSSION

Synthesis

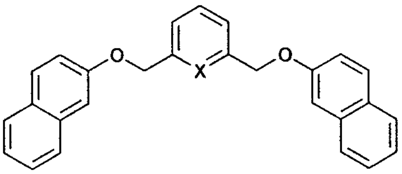
A starting point for the design of tweezer structures was our earlier complexation studies of crown ethers and podands with organic cations.[8–11] It has been shown that the preorganization of ligand structure has great importance in the complexation and it has been argued to be the central determinant of complex stability.[12] However, if the ideal binding conformation with a rigid host is not achieved or desired, then a flexible host that can adopt a more favourable conformation will often better bind the guest even though there may be a loss of degrees of freedoms.[13]

The basic structure of our hosts contains three building blocks: a spacer unit, connecting arms or bridge units and receptor units. This simple construction concept gives us possibilities to build up different hosts by varying only some of the building blocks. We introduced different aromatic ring systems for receptor unit by the Williamson ether synthesis.

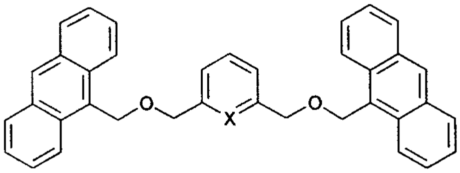
Syntheses of the phenoxy and naphthoxy derivatives **1**–**4** were executed in a straightforward way by refluxing reactants and potassium carbonate as a base and acetone or acetonitrile as a solvent. A similar procedure was attempted in the synthesis of the tweezers **5** and **6**. 9-Hydroxymethylanthracene reacted inadequately with 1,3-bisbromomethylbenzene without forming **5** and only a poor yield of the monosubstituted compounds was obtained in the reaction with 1,3-bisbromomethylpyridine. The tweezers **5** and **6** were prepared by using sodium hydride in dry DMF with 39 and 78% yield, respectively.



1 X = C
2 X = N



3 X = C
4 X = N



5 X = C
6 X = N

It has been debated that the spacer unit should be rigid in order to prevent self-association of the complexing chromophores and increase the complexation efficiency over a flexible analogue.[14] Zimmerman *et al.* prepared rigid molecular tweezers providing a ca 7 Å interchro-

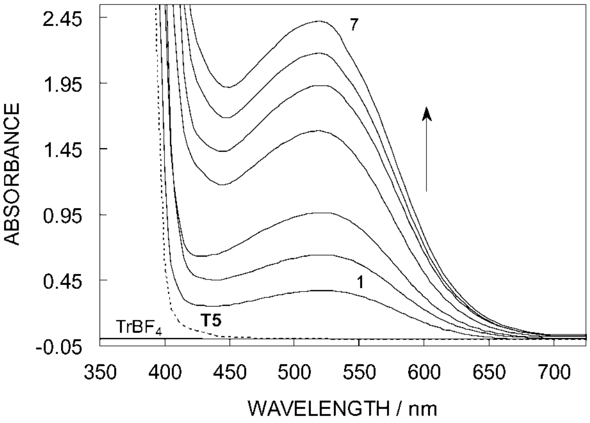


Figure 2. Absorption spectra of tropylium tetrafluoroborate (2.0 mM) in DCE solution at 25 °C in the presence of increasing amounts of **5**: (1) 3.1; (2) 5.3; (3) 9.8; (4) 20.8; (5) 30.3; (6) 41.7; and (7) 55.0 mM. The dashed line represents the spectrum of **5**

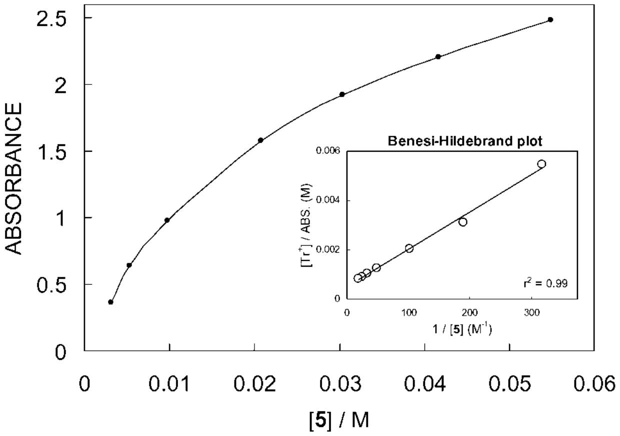


Figure 3. Plots obtained in experiments carried out for the evaluation of the stability constants in the complexation of tweezer **5** with tropylium tetrafluoroborate (2.0 mM) in DCE solution at 25.0 °C. Inset: Benesi–Hildebrand plot

mophore distance, preventing self-association.[5a] However, rigid molecules with a highly preorganized structure can still form intermolecular associations of two clefts via chromophores which can be observed in the crystal packing of molecular tweezers.[15] The cleft receptors prepared in this study have an inflexible central spacer and bendable arms attached to planar aryl receptors. The aromatic receptor units should be adequate to undergo π–π stacking interactions with aromatic molecules. Likewise, the enlargement of the aromatic surface in the tweezer could improve and strengthen the complexation with an aromatic guest. In addition, the relatively flexible arms between the spacer unit and aromatic receptors were expected to allow the formation of a tweezer-like structure in the complexation event. The x-ray structure of 1,3-bis(9-methanolanthracene)methylbenzene (**5**) in Fig. 1 is representative of the ligands synthesized in this work.

Complexation of tropylium tetrafluoroborate in 1,2-dichloroethane

Because the tropylium ion has been shown to be a useful guest for the investigation of π–π interactions,[11] we studied the complexation capability of the ligands towards an organic guest with tropylium tetrafluoroborate in DCE by UV–visible absorption spectrophotometry. Rathore *et al.*[16] have shown that UV–visible spectral analyses provide quantitative information on the intermolecular associations of different aromatic donor–acceptor complexes, and such measurements also established charge-transfer absorption to be a sensitive analytical tool for evaluating the steric inhibition of the donor–acceptor association that is important in molecular recognition. Tropylium itself is a monocharged organic cation containing even numbers of electrons. It is an aromatic, cationic and relatively stable carbenium ion.[17] It forms intensely coloured charge-transfer complexes in diverse solvents, which is a great advantage when the stability of the complexes is measured by spectrophotometry.[18,19]

The complexation of the tweezers in DCE with tropylium tetrafluoroborate was followed by absorption changes in the UV–visible spectra. Tropylium tetrafluoroborate in DCE exhibits a maximum absorption at 279 nm and the pure tweezers have no absorptions at wavelengths over 400 nm in the visible region. A characteristic colour, from yellow to red depending on the ligand used, developed spontaneously on addition of tweezer to a solution of tropylium tetrafluoroborate in a dry solvent. The electronic spectrum of the tweezers in the presence of tropylium ion exhibited a broad wavelength absorption at ca 300–600 nm. For example, the addition of **5** to DCE solutions containing tropylium salt led to the appearance of a new absorption band with maximum at about 524 nm, not found in the spectrum of either tropylium tetrafluoroborate or **5**. The intensity of the new band increased with incremental additions of tweezer. The band is indicative of a charge-transfer interaction and the formation of a molecular complex between tropylium ion and the tweezer (Fig. 2). Typical double-reciprocal or Benesi–Hildebrand plots for the tweezer–tropylium ion complexes gave a linear relationship for the entire range of concentrations tested, indicating the existence of 1:1 stoichiometry of the complexes (Fig. 3). Values for the stability constants K and molar absorptivities of the complexes ε_C in DCE for the tweezer–tropylium ion complexes were calculated by the Rose and Drago method.[8,20] The results are presented in Table 1.

The hosts **1** and **2** form weak charge-transfer complexes with the tropylium cation and the stability constants are comparable to those for benzene–tropylium interactions in similar systems. The **3** and **4** complexes with tropylium have K values of 6.6 and 28 dm^3 mol^{-1},

Table 1. Stability constants, molar absorptivities of complexes and free energies of binding for the interaction of tweezers [(0.5–10) × 10^{-2} M] with tropylium ion (2.0 × 10^{-3} M) in 1,2-dichloroethane solution at 25 °C

Tweezer[a]	λ_{obs} (nm)	K ($dm^3\ mol^{-1}$)	ε_C($dm^3\ mol^{-1}\ cm^{-1}$)	$-\Delta G°$(kJ mol^{-1})	r^2
1	600	3.0 ± 0.2	2249 ± 187	2.7	0.9999
2	405	2.3 ± 0.3	453 ± 65	2.1[b]	0.9999
3	430	6.6 ± 0.4	284 ± 16	4.7	0.9999
4	516	27.6 ± 2.8	227 ± 10	8.2	0.9972
5	520	41.2 ± 0.7	1853 ± 17	9.2	0.9999
6	510	57.3 ± 4.9	1348 ± 78	10.0	0.9989
2B24C8[c]	425	273.5 ± 13.8	1060 ± 13	13.91	—
POD1[d]	410	7.6 ± 1.0	662 ± 43	5.01	0.9966
POD2[d]	470	7.1 ± 0.4	1408 ± 69	4.85	0.9999
POD3[d]	502	86.2 ± 4.6	1765 ± 31	11.05	0.9995

[a] Crown ethers and podands are included for comparison: dibenzo-24-crown-8 (**2B24C8**), 1,10-diphenyl-1,4,7,10-tetraoxaundecane (**POD1**), 1,10-dinaphthalene-1,4,7,10-tetraoxaundecane (**POD2**), 1,12-bis(anthryl-9)-2,5,8,11-tetraoxadodecane (**POD3**).
[b] 35 °C.
[c] Ref. 8.
[d] Ref. 11.

respectively. Similarly, **6** (57 dm^3mol^{-1}) has a higher stability constant than **5** (41 dm^3mol^{-1}). The difference could be caused by the nitrogen atom, known as a strong electron donor, in the pyridine tweezer. We have shown earlier that the number of oxygen atoms involved in the complexation with tropylium has an impact on the stability of the complexes formed between crown ethers with different ring sizes and tropylium ion.[8] Pyridine nitrogen and oxygen atoms in connecting arms can accept hydrogen bonds connecting tropylium closer to the host molecule.

It is now well documented that benzene-substituted crown ethers are able to form stable complexes with tropylium and other electron-deficient organic cations.[8–10] The x-ray structures of solid complexes have revealed that organic cations are inserted into the cavity of the macrocycle between two adjacent benzene rings.[10] A similar wrap-around phenomenon was not encountered in the complexation of the non-cyclic counterpart of benzene-substituted crown ethers, podands, with a tropylium ion.[11] Recently, Klärner's group studied a rigid tweezer host in complexation experiments with tropylium tetrafluoroborate.[21] The ribbon-type concave topology of the five benzene units shapes the molecular tweezer that is able to bind substrate inside the preorganized cleft cavity. The tweezer–tropylium system

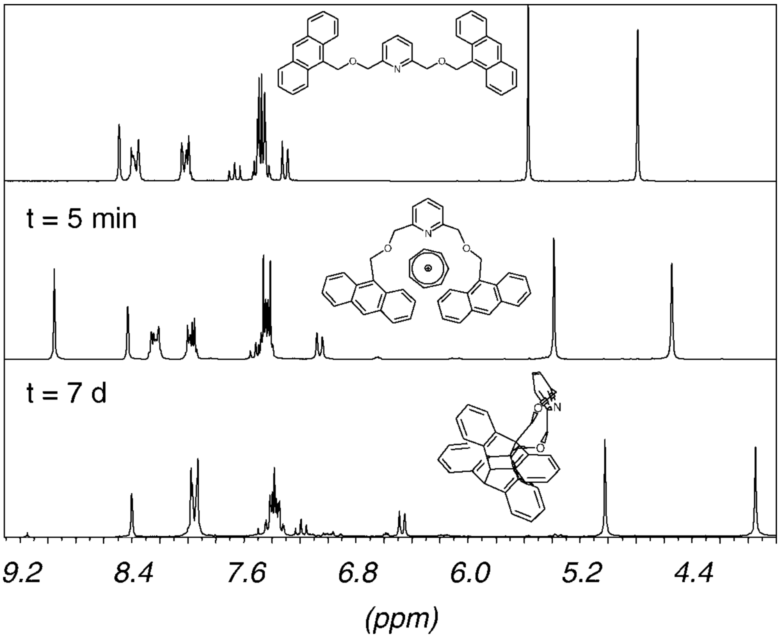


Figure 4. ^1H NMR spectrum of **6** (40 mM) and the spectra of a mixture of **6** (40 mM) and tropylium tetrafluoroborate (1 mM) after 5 min and 7 days of mixing of solutions recorded at 200 MHz in acetonitrile-d_3–chloroform-*d* (1:1) at 25 °C. A free tropylium ion has a singlet at 9.26 ppm

has a *K* value of 23 $dm^3 mol^{-1}$, determined by ^1H NMR titration in 1:1 solution of $CDCl_3$–$(CD_3)_2CO$ at 21 °C. The results indicate that a preorganized rigid structure of ligands is not the only requirement to produce stable complexes with aromatic organic cations such as tropylium ion. The number and type of donor atoms that are a capable of hydrogen bonding and the area of the aromatic surface that has an ability to undergo a π–π stacking interaction evidently have considerable importance in tweezer–tropylium ion complexation.[22]

The time stability of the complexes formed between tweezers and a tropylium ion was investigated by measuring the stability constants for **1**, **3**, **5** and **6** with different time intervals. Only insignificant changes were observed for **1** and **3** and they were within the determination accuracy. However, it is worth emphasizing that the absorption measurements should be carried out immediately after mixing the donor and the acceptor solutions together. This seems to be particularly important in the case of the bisanthracene ligands **5** and **6** that behaved differently. A well-known phenomenon of dimerization of anthracene in solution[23] was also observed in our study. The disappearance of the original colour of **5**–tropylium and **6**–tropylium systems was monitored by UV–visible spectrophotometry at maximum charge-transfer absorbance wavelength. The deep red colour that formed directly after mixing **5** and tropylium DCE solutions slowly turned green. A similar phenomenon occurred for **6**. The reaction of **6** was followed also by 200 MHz proton NMR spectroscopy. The kinetic investigations showed that absorbance vs time curves were single exponential measured at 524 nm for **5** and at 502 nm for **6**. The rate of cycloaddition was calculated to be first order with respect to the concentration of ligands. The values of the observed rate constant, k_{obs}, were 2.5×10^{-5} s^1 ($t_{1/2} = 7$ h 45 min) for **5** and 3.7×10^{-5} s^{-1} ($t_{1/2} = 5$ h 18 min) in DCE and 3.0×10^{-5} s^{-1} ($t_{1/2} = 6$ h 30 min) in acetonitrile-d_3–chloroform-*d* (1:1) for **6** at 25 °C. The concentration of tropylium tetrafluoroborate was held constant (2×10^{-3} M) in all measurements. The rate constants observed were found to be independent of the initial concentration of tweezer. The NMR spectra in Fig. 4 indicate the formation of the cycloaddition product of **6**. After 7 days the intramolecular $[4\pi + 4\pi]$ cycloadduct was formed almost completely. The rate constant results and spectroscopic evidence indicate that charge-transfer transitions play an important role in bringing about chemical changes in bisanthracene–tropylium systems. Masnovi and Kochi have shown that substituted anthracenes with electron acceptors [e.g. tetracyanoethylene (TCNE)] in solution afforded slowly Diels–Alder adducts on standing in the dark.[24]

It is worth adding that the small amount of solid lepidopterene could be isolated when equimolar amounts of **5** and tropylium tetrafluoroborate were dissolved in acetonitrile–dichloromethane (1:1) and the solvent mixture was left to evaporate slowly (the crystal structure of lepidopterene is available as supplementary data at the epoc website at http://www.wiley.com/epoc). The prime intent was to prepare a single crystal of the complex. The bisanthracene ligand **5** partially reacted to give lepidopterene[25] in the solution exposed to daylight. The influence of the tropylium ion or light on the formation of lepidopterene was not investigated in detail in this work. Lepidopterene is a tetracyclic benzenoid hydrocarbon whose crystal structure has been previously determined.[26] The long central C—C bonds in the dimers of anthracene have been cited as extreme examples of bond lengthening as a result of through-bond coupling. The central carbon–carbon bond length in lepidopterene is 1.651 Å in the re-determined x-ray structure (pdb file as a supplementary data at the epoc website at http://www.wiley.com/epoc). The published structures have central bond lengths 1.642 and 1.645 Å, respectively[26] (for visualization see the files tweezer 5 and lepidopterene at the epoc website at http://www.wiley.com/epoc).

In conclusion, new non-macrocyclic receptors have been synthesized and shown to complex with tropylium cation in organic solvents. Electron donor–acceptor interactions are an important driving force for complexation by molecular tweezers. The appearance of charge-transfer absorption bands demonstrates the complex formation with tropylium ion. Comparison of the stability constants in Table 1 shows that varying the aryl receptor unit from phenyl and naphthyl to anthryl can increase the stability of the complex. Additionally, the addition of a nitrogen donor atom into the spacer unit increases the stability constants of the complex formed. Among these systems, bisanthracenes are especially interesting in displaying both complexation with a tropylium ion and intramolecular $[4\pi + 4\pi]$ cycloaddition via charge-transfer excitation. It seems appropriate to assume that the cycloaddition of anthracene ligands observed can been employed to modulate the binding ability and also to prepare new molecules. Our current efforts are directed to take advantage of the phenomena observed and we shall report further new results in the near future.

EXPERIMENTAL

Materials and methods

The starting materials were purchased from commercial sources and used without further purification, unless mentioned otherwise. Acetonitrile (Fluka) and 1,2-dichloroethane (Lab-Scan) were dried and distilled according to literature procedures.[27] Thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel. Compounds were detected by UV spectrophotometry. Flash column chromatography was performed on the silica gel with the solvents specified. ^1H and ^{13}C NMR spectra were recorded on a Bruker

Advance DPX200 spectrometer. NMR chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS). The coupling constants are expressed in hertz (Hz). Electron ionization (EI) mass spectra were obtained using a Kratos MS 80 mass spectrometer operating with the DART data system. Electronspray ionization (ESI) mass spectra were recorded on an LCT time-of-flight mass spectrometer (Micromass) with an OpenLynx 3 data system. The desolvation temperature was 120 °C and N_2 was used as nebulizer and desolvation gases. UV–visible spectra were recorded with a Phillips PU 8740 or Shimadzu UV-1601 spectrophotometer with matched glass or quartz cells of 10 mm pathlength. The cell containing the solution was maintained within ±0.05 °C (±0.1 °C in the kinetic measurements) of a set temperature by circulating water from a thermostated bath through a double-walled cell insert. The temperature inside the cell was monitored with a digital thermometer. Elemental analyses were carried out with a Perkin-Elmer 2400 apparatus. Melting-points were determined with a Thermopan microscope (Reichert, Vienna, Austria) melting-point apparatus and are uncorrected.

Syntheses

General procedure for the synthesis of substituted tweezers. A mixture of 1,3-bisbromomethylbenzene or 1,3-bisbromomethylpyridine (5 mmol), aromatic alcohol (10 mmol) and K_2CO_3 (1.282 g, 10 mmol) was stirred and heated at reflux in 30 ml of acetone or acetonitrile for 16–24 h under a nitrogen atmosphere, after which the reaction mixture was allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The organic layer was separated and washed with 5% NaOH solution, water and brine and dried over $MgSO_4$. Evaporation gave the crude product, which was subjected to further purification.

1,3-Bisphenoxymethylbenzene (1). The product was recrystallized from MeOH, affording a white crystalline solid in 75.4% yield, m.p. 75 °C (lit.[28] 71–76 °C); (found C, 82.73; H, 5.88. $C_{20}H_{18}O_2$ requires C, 82.73; H, 6.25%); ^1H NMR ($CDCl_3$, 25 °C), δ 7.519 (1H, phenyl), 7.402 (3H, phenyl, d, $J = 1.34$ Hz), 7.24–7.33 (5H, aryl, m), 6.93–7.01 (6H, aryl, m), 5.081 (4H, OCH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 70.5, 115.5, 121.7, 127.1, 127.7, 129.5, 130.2, 138.2, 159.4; EIMS (70 eV), *m/z* 290 [M^+].

2,6-Bisphenoxymethylpyridine (2). The crude product was recrystallized from acetone, affording a 65% yield of white crystals, m.p. 73 °C (lit.[29] 72–74 °C); (found C, 78.33; H, 5.88; N, 4.81. $C_{19}H_{17}NO_2$ requires C, 78.08; H, 5.87; N, 4.79%); ^1H NMR ($CDCl_3$, 25 °C), δ 7.76 (1H, pyridine, t, $J = 7.75$ Hz), 7.49 (2H, pyridine, d, $J = 7.72$ Hz), 6.96–7.04 (6H, aryl, m), 5.25 (4H, OCH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 70.8, 115.2, 120.5, 121.6, 130.0, 138.1, 157.3, 158.8; EIMS (70 eV), *m/z* 291 [M^+].

1,3-Bisnaphthoxymethylbenzene (3). Recrystallization from acetone afforded a crystalline solid in 54% yield, m.p. 133 °C (found C, 82.73; H, 5.88. $C_{20}H_{18}O_2$ requires C, 82.73; H 6.25%); ^1H NMR (acetone-d_6, 25 °C), δ 7.73–7.85 (4H, aryl, m), 7.21–7.54 (28H, aryl, m), 5.292 (4H, OCH_2, s); ^{13}C NMR (acetone-d_6, 25 °C), δ 69.5, 107.2, 118.8, 123.5, 126.2, 126.7, 126.8, 127.0, 127.4, 128.5, 129.1, 129.3, 134.7, 137.7, 156.7; EIMS (70 eV), *m/z* 390 [M^+].

2,6-Bisnaphthoxymethylpyridine (4). The crude product was recrystallized from acetone, yield 71%, m.p. 142–143 °C (found C, 82.54; H, 5.36; N, 3.56. $C_{19}H_{17}NO_2$ requires C, 82.84; H, 5.41; N, 3.58%); ^1H NMR ($CDCl_3$, 25 °C), δ 7.67–7.85 (7H, aryl, m), 7.21–7.55 (10H, aryl, t), 5.37 (4H, OCH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 71.0, 107.8, 119.2, 120.7, 124.3, 126.8, 127.3, 128.0, 129.6, 130.0, 134.8, 138.1, 156.7, 157.1; EIMS (70 eV), *m/z* 391 [M^+].

1,3-Bis(9-methanolanthracene)methylbenzene (5). At room temperature, to a solution of NaH (0.53 g, 11 mmol) (50% in mineral oil, washed previously with *n*-pentane) in dry DMF (20 ml), 9-hydroxymethylanthracene 2.08 g (10 mmol) was added dropwise with stirring in dry DMF (10 ml). Stirring was continued for 30 min after the end of the addition. A dry DMF solution (10 ml) of α,α-dibromo-*m*-xylene, 1.32 g (5 mmol), was then introduced drop wise. The reaction mixture was heated for 20 h at 80 °C before cooling to room temperature. The excess of NaH was quenched by adding a few drops of water, then the solvent was removed *in vacuo* and the residue was partioned between water (30 ml) and dichloromethane (40 ml). The organic layer was washed twice with 1 M HCl, water and brine and dried over $MgSO_4$. Evaporation gave the crude product, which was recrystallized from acetone, affording a light-yellow solid in 39% yield, m.p. 163 °C (found C, 87.89; H, 5.81. $C_{38}H_{30}O_2$ requires C, 88.00; H, 5.38%); ^1H NMR ($CDCl_3$, 25 °C), δ 8.45 [1H, Ant(5), s], 8.2–8.4 (4H, aryl, m), 7.9–8.5 (4H, aryl, m), 7.3–7.5 (12H, aryl, m), 5.48 (4H, Ant-OCH_2, s), 4.71 (4H, Ph-OCH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 64.8, 73.0, 125.0, 125.6, 126.8, 128.1, 128.3, 129.1, 129.2, 129.3, 129.6, 131.8, 132.1, 139.3; EIMS (70 eV), *m/z* 518 [M^+].

1,3-Bis(9-methanolanthracene)methylpyridine (6). By the procedure described for **5** but starting with 1,3-bisbromomethylpyridine, a yellow residue was obtained and purified with flash chromatography (150:1 CH_2Cl_2–MeOH) to afford a light-yellow solid in 78% yield, m.p. 163 °C (found C, 85.18; H, 55.63; N, 2.70. $C_{37}H_{29}NO_2$ requires C, 85.52; H, 5.52; N, 2.75%); ^1H NMR ($CDCl_3$, 25 °C), δ 8.35–8.50 (6H, aryl, m), 7.92–8.30 (4H, aryl, m), 7.25–7.65 (11H, aryl, m), 5.63 (4H, Ant-OCH_2, s), 4.84 (4H, Py-OCH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 65.3, 73.6, 120.7, 124.8, 125.4, 126.6, 128.8, 129.0, 129.4, 131.5, 131.8, 137.6, 158.4; ESIMS exact mass (Micromass LCT, ESI+), *m/z* 520.2277 ($[M + H]^+$); required, 520.2295.

1,3,5-Cycloheptatrienylium tetrafluoroborate. The tropylium salt was prepared according to literature procedures,[30] m.p. 203 °C (decomp.); ^{1}H NMR (CD_3CN, 30 °C), δ 9.24 (7H, s).

Complexation studies. Stability constant determination by UV–visible spectroscopy. The stability constant for 1:1 complexation was defined by a method described in detail elsewhere.[8] The absorption measurements were made immediately after the mixing of tweezer and tropylium solutions. The Rose–Drago equation is

$$\frac{1}{K} = \frac{A - A_0}{\varepsilon_C - \varepsilon_A} - C_A - C_D + \frac{C_D \cdot C_A \cdot (\varepsilon_C - \varepsilon_A)}{A - A_0} \tag{1}$$

where A_0 is the absorbance of pure acceptor solution, A is the absorbance of the acceptor–donor solution, C_A and C_D are the initial concentrations of acceptor and donor, respectively and ε_C and ε_A are the molar absorptivities of complex and acceptor in solution, respectively. The equation contains two unknown constants, K and ε_C, which were evaluated by an iteration method with a PC implementing a SigmaPlot Scientific Graphing System Version 4.0 program (Jandell Scientific). The errors in K and ε_C were evaluated numerically by standard deviations of single K and ε_C values usually obtained from 6–10 measurements.

X-ray crystallographic data

1,3-Bis(9-methanolanthracene)methylbenzene (5). Single crystals suitable for x-ray crystallography were grown by slow evaporation of dichloromethane solution.

Crystal data. $C_{38}H_{30}O_2$, $M = 518.62$, orthorhombic space group $P2_{1ab}$ (No. 29), $a = 8.0706(4)$, $b = 17.513(1)$, $c = 19.050(1)$ Å, $V = 2692.6(3)$ Å^3, $Z = 4$, $D_x = 1.279$ mg m^{-3}, μ(Mo Kα) = 0.077 mm^{-1}. The data were recorded from colourless, plate-like crystals of size 0.05 × 0.15 × 0.30 mm on a Nonius Kappa CCD diffractometer using graphite monochromatized Mo Kα radiation [λ(Mo Kα) = 0.71073 Å] and $T = 173.0(2)$ K. 159 frames were collected using the φ scan data collection method with an oscillation angle of 1.0° and the exposure time of 2 × 25 s. The data were processed by Denzo-SMN.[31] There were 10 448 reflections in the range $2.98 \leq \theta \leq 27.88°$, with 5450 independent ($R_{int} = 0.104$) and 2637 observed [$I > 2\sigma(I)$]. The reflections were collected for Lorentz polarization effects and no absorption correction was used.

The structure was solved by direct methods (SHELXS-97)[32] and refined on F^2 (SHELXL-97)[33] The hydrogen atoms were calculated to their idealized positions with isotropic thermal factors (1.2 times the C thermal parameter) and refined as riding atoms. The weighting scheme was $w = 1/[\sigma^2(F_o^{\,2}) + (0.0191P)^2]$, where $P = [\mathrm{Max}(F_o^{\,2}, 0) + 2F_c^{\,2}]/3$. The final residuals were $R = 0.068$ and $wR = 0.100$ for 2637 unique data with $I > 2\sigma(I)$ and $R = 0.175$, $wR = 0.129$ for all data and for 362 parameters.

The crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 153263.

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