Molecular Tweezers as Synthetic Receptors: Molecular Recognition of Electron-Deficient Aromatic and Aliphatic Substrates

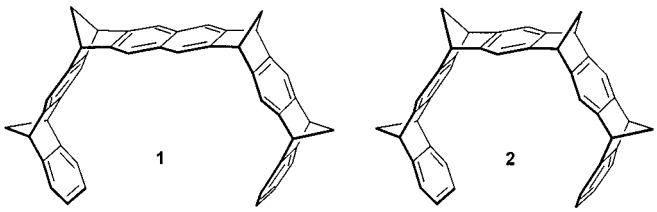
Frank-Gerrit Klärner,*[a] Ulrich Burkert,[a] Markus Kamieth,[a] Roland Boese,[b] and Jordi Benet-Buchholz[b]

Abstract: Syntheses and supramolecular properties of the molecular tweezers **1** and **2**, containing naphthalene and benzene spacer units, respectively, are described. They selectively bind electron-deficient aromatic and aliphatic substrates, for example di- and tetracyanobenzenes **11**–**14**, 1,4-dinitrobenzene (**15**), *p*-benzoquinone (**16**), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (**17**), 1,2,4,5-tetrafluorobenzene (**20**), acetonitrile, and malononitrile. They form stable complexes with the cationic substrate *N*-methylpyrazinium iodide (**19**) that are soluble in chloroform. A quantitative investigation using NMR titration and solid–liquid extraction shows that the naphthalene-spaced tweezer **1** forms stronger complexes with aromatic and quinoid substrates than the benzene-spaced tweezer **2** ($\Delta\Delta G = 1.5 \pm 1$ kcal mol^{-1}), whereas the aliphatic substrates are only complexed by receptor **2**. Force-field calculations (AMBER*) and single-crystal structure analyses reveal that **1** has an almost ideal geometrical topology for the complexation of aromatic substrates, while complexation of these substrates by the smaller receptor **2** requires expansion of the tweezer tips by about 2 Å. This causes an extra strain energy in **2** of 1–2 kcal mol^{-1}. According to semiempirical AM1 calculations, the electrostatic potential surfaces (EPSs) of molecular tweezers **1** and **2** are surprisingly negative on the concave sides of the molecules and, hence, complementary to those of the electron-deficient substrates.

Keywords: arene–arene interaction · host–guest chemistry · molecular recognition · molecular tweezers · supramolecular chemistry

Introduction

Simple synthetic receptors with molecular pockets or cavities can act as models for far more complicated biological systems, which are important, for example, for protein folding, molecular recognition of substrates by enzymes, or the formation of membranes.[1] The study of such receptors should provide information about structure and stability of receptor–substrate complexes and noncovalent interactions responsible for their formation. Besides the relatively strong and therefore often dominant hydrogen bonding,[2] ion pairing,[3] and the hydrophobic effect in aqueous media,[4] the arene–arene interactions[5] are of particular importance for the formation of superstructures. As a result of many experimental and theoretical investigations, the attractive character of both CH–π and π–π interactions is commonly accepted. Here we report on the syntheses and some supramolecular properties of the hydrocarbons **1** and **2**, which, owing to their ability to selectively bind electron-deficient aromatic and aliphatic compounds as well as organic cations, can be regarded as molecular tweezers.



Results and Discussion

The tweezer molecule **1**, containing a naphthalene spacer unit, can be synthesized in four steps starting with reduction of the previously reported diketone **3**[6] by $NaBH_4$. The resulting diol **4** is treated with *p*-toluenesulfonylchloride and triethylamine to produce **5** with an overall yield of 48%. Repetitive Diels–Alder reactions of bisdienophile **5** with diene **6**[7] proceed stereospecifically to yield the bisadduct **7**, which can be converted to molecular tweezer **1** by oxidative dehydrogen-

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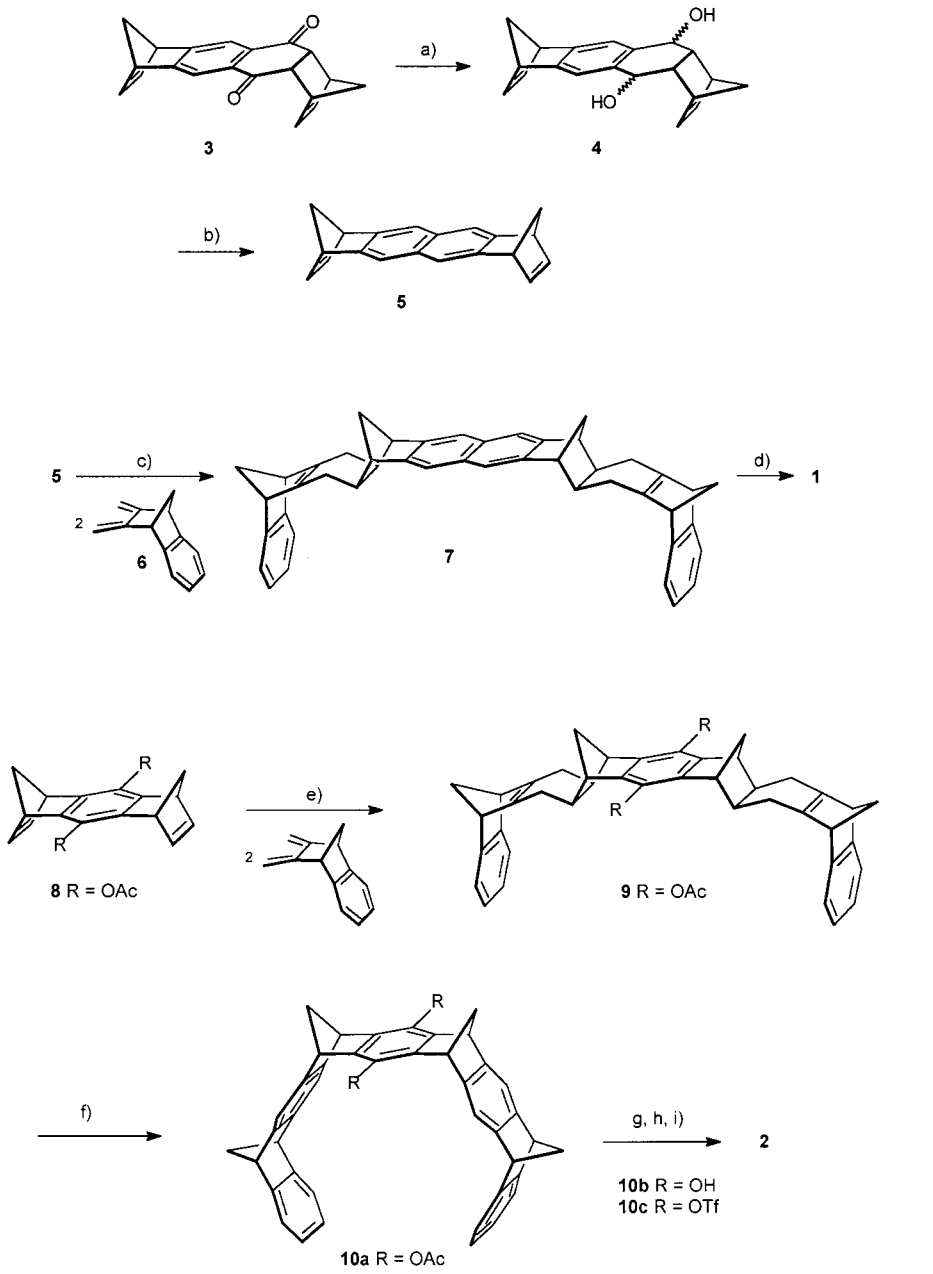
ation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone(DDQ) in an overall yield of 30% (Scheme 1).[8] The tweezer **2**, containing only benzene spacer units, can be synthesized following an analogous route. Repetitive Diels–Alder reactions of the known bisdienophile **8**[6] with diene **6** and subsequent DDQ dehydrogenation of bisadduct **9** produce the substituted tweezer **10a** with an overall yield of 60%.[9] Removal of the acetate groups can be accomplished in three steps, which lead to **2** as shown in Scheme 1.



Scheme 1. Synthesis of the molecular tweezers **1** and **2**. Reaction conditions and yields: a) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, methanol, 0°C, 4 h, 95%; b) *p*-CH_3–C_6H_4–SO_2Cl, pyridine, 20°C, 20 h, 50%; c) $(C_2H_5)_3N$ (catalytic amount), toluene, 160°C, 5 d, 70%; d) DDQ, toluene, 100°C, 2 h, 43%; e) $(C_2H_5)_3N$ (catalytic amount), toluene, 160°C, 5 d, 71%; f) DDQ, toluene, 110°C, 2 h, 83%; g) $LiAlH_4$, tetrahydrofuran, 60°C, 5h, 98%; h) $(CF_3–SO_2)_2O$ (Tf_2O), pyridine, 20°C, 20 h, 98%; i) $PdCl_2(PPh_3)_2$, 1,3-bis(diphenylphosphino)propane, dimethylformamide/NBu_3/HCO_2H, 100°C, 90 h, 82%.

Because of their ribbon-type concave topology, the five arene units of the molecular tweezers **1** and **2** define a cavity in which a substrate molecule can be bound by multiple noncovalent interactions. The magnetic anisotropy of these arene units makes ^1H NMR spectroscopy a very sensitive probe for uncovering the complexation of substrate molecules inside the cavities of **1** and **2**. In the ^1H NMR spectrum of a 1:2.5 mixture of 1,4-dicyanobenzene **11** and tweezer **1** in $CDCl_3$, formation of the complex **11@1** can be easily detected by the

Abstract in German: *Es werden Synthesen und supramolekulare Eigenschaften der molekularen Pinzetten **1** und **2** mit Naphthalin- bzw. Benzolspacereinheiten beschrieben. **1** und **2** binden selektiv elektronenarme aromatische oder aliphatische Substrate, beispielsweise die Di- und Tetracyanbenzole **11**–**14**, 1,4-Dinitrobenzol **15**, p-Benzochinon **16**, TCNQ **17**, Tetrafluorbenzol **20**, Acetonitril und Malodinitril. Mit dem kationischen Substrat N-Methylpyraziniumiodid **19** bilden **1** und **2** stabile, in Chloroform lösliche Komplexe. Eine mit Hilfe der NMR-Titrationsmethode oder der Fest-Flüssig-Extraktionstechnik durchgeführte quantitative Untersuchung zeigt, daß die Naphthalinpinzette **1** stärkere Komplexe mit aromatischen oder chinoiden Substraten bildet als die kleinere Benzolpinzette **2**. Dagegen werden aliphatische Substrate nur von **2** als Rezeptor gebunden. Nach Kraftfeldrechnungen (AMBER*) und Kristallstrukturanalysen besitzt **1** eine nahezu ideale Topologie für die Komplexierung von aromatischen Substraten, während bei dem kleineren Rezeptor **2** eine entsprechende Komplexbildung eine erhebliche Aufweitung (von ca. 2 Å) des Abstandes zwischen den terminalen C-Atomen erfordert, die in **2** eine zusätzliche Spannungsenergie von ca. 1–2 kcal mol^{-1} verursacht. Die mit Hilfe der semiempirischen AM1-Methode berechneten elektrostatischen Potentialoberflächen der Pinzetten **1** und **2** sind jeweils auf der konkaven Molekülseite überraschend negativ und damit komplementär zu den positiven Potentialen der elektronenarmen Substrate. Damit läßt sich die Bindungspräferenz dieser Substrate zu den Rezeptoren **1** und **2** erklären.*

upfield shift of the signal of **11**. This shift is chemically induced by the presence of **1** ($\Delta\delta = \delta_0 - \delta_{obs} = 3.0$) (Figure 1a). Over a relatively large temperature range (from $+40\,^{\circ}C$ to $-60\,^{\circ}C$), the complex formation and dissociation processes **11**+**1** $\rightleftharpoons$ **11@1** are fast with respect to the NMR time scale. Thus, only

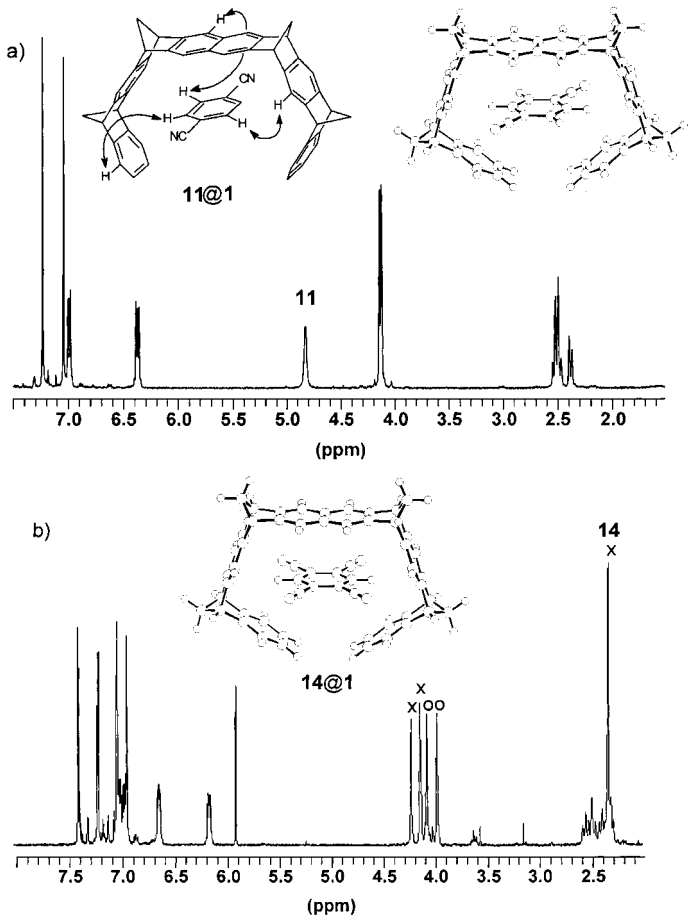


Figure 1. a) Complex **11@1**, colorless crystals, m.p. 230 °C, ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): [**1**] = 0.05 M, [**11**] = 0.02 M; cross peaks in the 2D NOESY spectra between hydrogen atoms are marked with curved arrows. b) Complex **14@1**, bright yellow crystals, m.p. 230 °C, UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 287$ (18830), 294 (18750), 318 (5490), 332 (5100), 422 nm (930); ^{1}H NMR (300 MHz, $(CDCl_2)_2$, 21 °C): [**1**] = 0.02 M, [**14**] = 0.01 M, $\Delta\delta$ (**14**) = 5.9; peaks of complexed **1** and **14** are marked with × and peaks of free **1** with o.

the signal averaged between those of free and complexed **11** is observed. A NOE (nuclear Overhauser effect) experiment using the 2D NOESY technique gives an insight into the close spatial proximity of the host and guest protons indicated by crosspeaks between signals of protons connected by double-headed arrows in Figure 1a. The association constant K_a = [**11@1**]/[**11**] [**1**] = 110 M^{-1} and the maximum chemically induced shift in the complex **11@1** ($\Delta\delta_{max} = 4.35$) were determined at 21 °C from the dependence of $\Delta\delta_{obs}$ ([**11**]$_0$ is constant) on the concentration of **1** by an iterative nonlinear regression analysis.[10] A ^{1}H NMR titration experiment of **11** with **1** at $-10\,^{\circ}C$ ($K_a = 190$ M^{-1}, $\Delta\delta_{max} = 4.38$) showed that $\Delta\delta_{max}$ is not significantly temperature-dependent. Therefore, the enthalpy ΔH and entropy ΔS of complexation could be determined by variable-temperature single-point analyses (Table 1).[11]

In $(CDCl_2)_2$, 1,2,4,5-tetracyanobenzene (**14**) forms a very stable bright yellow complex with **1** (CT absorption λ = 420 nm). In this case, the mutual reaction between **1** and **14** is slow with respect to the NMR time scale so that at room temperature, if [**1**]$_0$ > [**14**]$_0$ separate ^{1}H NMR signals of free and complexed **1** are observed (Figure 1b) which show a coalescence at 81 °C. From the analysis of the temperature-dependent lineshapes of these signals, the Gibbs enthalpy of activation for the complex formation was calculated to be $\Delta G^{\ddagger} = 16.7 \pm 0.2$ kcal mol^{-1}.

The naphthalene tweezer **1** and the benzene tweezer **2** are both able to form host–guest complexes with a variety of electron-deficient substrates (Scheme 2). The maximum chemically induced shifts $\Delta\delta_{max}$, the association constant K_a and, hence, the Gibbs energies ΔG of complexation were determined at 21 °C by ^{1}H NMR titration. The enthalpies ΔH and entropies ΔS of complexation were calculated from the temperature dependance of K_a obtained by *single-point* analyses as already described for the formation of **11@1**. The pure hydrocarbons **1** and **2** form complexes soluble in chloroform with the cationic substrate *N*-methylpyrazinium iodide (**19**), which by itself is insoluble in chloroform. Thus, K_a and, hence, ΔG for these complexes could only be determined by solid–liquid extraction experiments.[12] The results are summarized in Table 1. Electron-rich aromatic compounds such as benzene, toluene, anisol, phenol, or aniline do not form complexes with **1** or **2**. The finding that benzene and toluene can be used as solvents in binding studies demonstrates the selectivity of the receptors **1** and **2** towards electron-deficient substrates.

The thermodynamic parameters (Table 1) indicate that complexation is largely the result of an enthalpic receptor–substrate interaction (ΔH). In accordance with other molecular recognition studies,[13] we have also observed a solvent dependence of the thermodynamic parameters. The modest solubility of the hydrocarbons **1** and **2**, however, allows only a small variation in solvent polarity. The following trend of decreasing binding strengths (K_a) was observed: benzene > toluene > chloroform > THF (Table 1). Comparison of the naphthalene-spaced receptor **1** with its smaller benzene-spaced analogue **2** demonstrates that **1** is the better receptor for aromatic substrates ($\Delta\Delta G = 1.5 \pm 1$ kcal mol^{-1}) whereas the aliphatic substrates such as acetonitrile or malononitrile are only complexed inside the smaller cavity of **2**.

The structures of the complexes **11@1**, **14@1**, **17@1**, and **17@2** (the latter two shown in Figure 2) determined by single-crystal structure analyses are in very good agreement with structures obtained with molecular modeling calculations (molecular mechanics and semiempirical methods).[14] These results suggest that the naphthalene-spaced tweezer **1** has an almost ideal geometrical topology for the complexation of benzene derivatives, while complexation of these substrates by the benzene-spaced tweezer **2** requires an expansion of the tweezer's tips (by about 2 Å from 3.8 Å in empty **2** to 5.8 Å in **17@2**).[15] Also, in order to maximize the interaction between host and guest, **2** loses its C_{2v} symmetry in the complex. This expansion of the tweezer's tips, which is mainly caused by bond angle distortions and therefore should not require much extra strain energy, explains the different selectivities of **1** and

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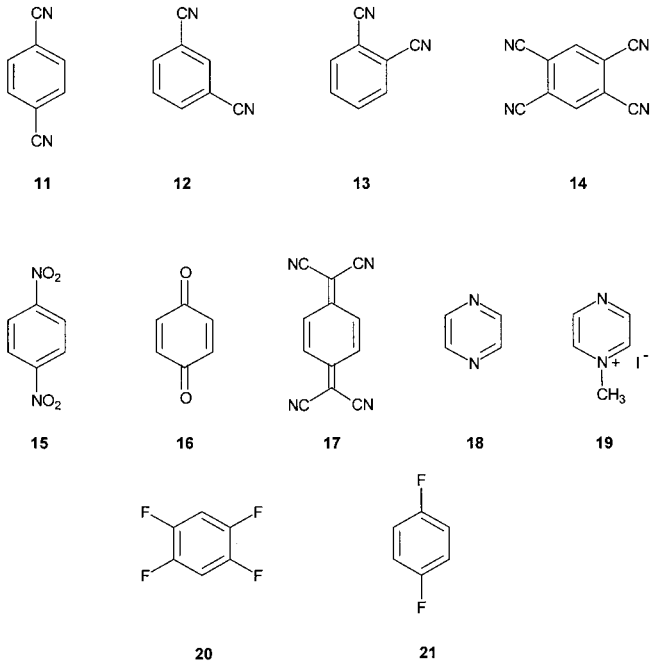
Table 1. Association constants K_a [M^{-1}], Gibbs reaction enthalpies ΔG [kcal mol^{-1}], reaction enthalpies ΔH [kcal mol^{-1}], reaction entropies ΔS [cal mol^{-1} K^{-1}], and maximum chemically induced shifts $\Delta\delta_{max}$ of complexes with **1** and **2** as receptors at 21 °C. The maximum error of K_a is estimated from the uncertainties in the determination of the concentration, chemical shifts, and so on to be ±10%. The standard deviation of the regression is $\Delta H \leq$ 0.2 kcal mol^{-1} and $\Delta S \leq 0.5$ cal mol^{-1} K^{-1} with $R^2 \geq 0.995$.

Substrate	Receptor **1**					Receptor **2**					Solvent
	K_a	ΔG	ΔH	ΔS	$\Delta\delta_{max}$	K_a	ΔG	ΔH	ΔS	$\Delta\delta_{max}$	
11	110	−2.8	−2.8	0.6	4.3	10	−1.3	−1.9[a]	−1.7[a]	3.5	$CDCl_3$
11	145	−2.9	−4.2	−4.5	2.7						[D_6]benzene
11	60	−2.4	−2.0	1.1	2.8						[D_8]THF
12	85	−2.6	−3.5	−3.1	5.3	< 1					$CDCl_3$
13	40	−2.1	−3.4	−4.4	5.2	< 1					$CDCl_3$
15	45	−2.2	−1.4	2.8	5.5	17	−1.7	−2.1	−1.4	3.5	$CDCl_3$
15						80	−2.6	−4.3	−6.0	1.7	[D_6]benzene
15						30	−2.0	−1.6	1.6	2.0	[D_8]toluene
15						15	−1.7	−2.2	−1.8	3.8	$(CDCl_2)_2$
16	20	−1.8	−4.6	−9.7	2.8	< 1					$CDCl_3$
17	[b]				3.6	1100	−4.1			2.9	$CDCl_3$
18	8	−1.2	−2.4	−4.1	1.3	< 1					$CDCl_3$
19	35000[c]	−6.1				3500[c]	−4.8				$CDCl_3$
20	26	−1.6	−9.1	−25	1.2	< 1					$CDCl_3$
CH_3CN	< 1					15	−1.6	−2.6	−3.6	5.3	$CDCl_3$
CH_3CN	< 1					82	−2.6	−5.1	−8.7	3.0	[D_6]benzene
$CH_2(CN)_2$	< 1					36	−2.1	−3.4	−4.6	4.5	$CDCl_3$
$CH_2(CN)_2$	< 1					60	−2.4	−7.0	−15.4	2.2	[D_6]benzene

[a] The reaction isotherm ($\ln K_a$ vs $1/T$) is not linear in the investigated temperature range from −50 °C to 20 °C and therefore ΔH is temperature-dependent. The stated values are valid for 21 °C with $\Delta C_p = -17$ cal mol^{-1} K^{-1}. [b] Because of the high stability of complex **17@1**, it is impossible to determine the concentration dependence of the substrate signal with the ^{1}H NMR titration method. [c] The values of K_a were determined from the (receptor:substrate) ratio in the ^{1}H NMR spectra after extraction of the chloroform-insoluble substrate **19** with a solution of receptors **1** or **2** in $CDCl_3$.



Scheme 2. Substrates for the complexes with **1** and **2** as receptors.

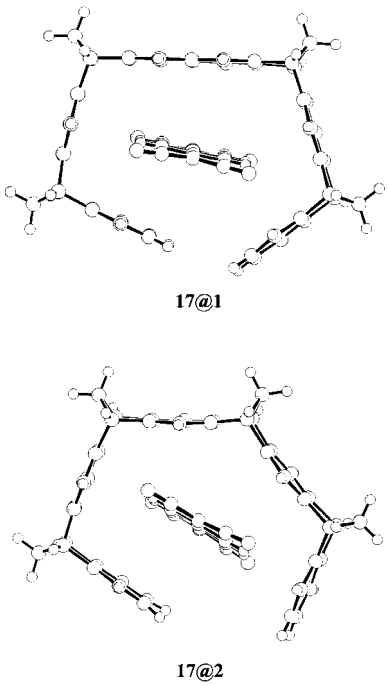


Figure 2. Diagrams from crystal structure determinations of the complexes **17@1** (dark violet crystals, m.p. 230 °C, UV/Vis (solid, reflexion): λ_{max} = 650 nm; ^{1}H NMR (300 MHz, $CDCl_3$, 21 °C): $\Delta\delta_{max} = 3.6$) and **17@2** (dark violet crystals, m.p. 225 °C).

2 towards benzene derivatives. The extra strain energy required for the 2 Å expansion for the formation of **17@2** is calculated by molecular mechanics (AMBER*) to be 1–2 kcal mol^{-1}.[14] This calculation is in good agreement with the experimental observations and explains why **1** forms stronger complexes with aromatic substrates than **2**. However, molecular modeling calculations indicate that the cavity of **2** is the ideal size for complexation of small aliphatic substrates (CH_3CN, $CH_2(CN)_2$) because of attractive CH–π interactions, which have also been observed in self-assembly processes of aliphatic side chains connected to the central benzene moiety in derivatives of **2**.[8]

The experimental results presented here are in excellent agreement with the electrostatic model of π–π interactions. The electrostatic potential surfaces (EPSs) of molecular

tweezers **1** and **2** calculated with the semiempirical AM1 method (Figure 3) show surprisingly negative potentials on the concave sides. According to quantum chemical calculations, this seems to be a general phenomenon of nonconjugated π systems with convex – concave topologies. In contrast, when analogous calculations were performed for the aromatic and aliphatic substrates (Figure 3), the complementary nature

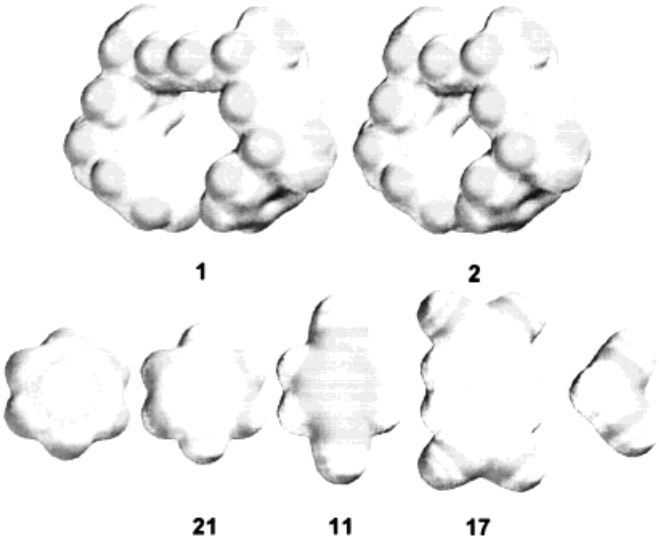


Figure 3. Semiempirically calculated (AM1) electrostatic potential surfaces (EPSs) of the molecular tweezers **1** and **2** (top) and the potential substrate molecules benzene, 1,4-difluorobenzene (**21**), 1,4-dicyanobenzene (**11**), TCNQ (**17**), and malononitrile (bottom, left to right).

of their EPSs becomes evident.[16] Calculations show that hexafluorobenzene, despite its electrostatically very positive π surface,[17] is not bound by **1** or **2** because of repulsive interactions with the fluorine atoms which make up the negative part of the molecule. This is consistent with the experimental observation that the ^{19}F NMR chemical shift of hexafluorobenzene does not change upon addition of **1** or **2** to the NMR sample. The observation that 1,4-dicyanobenzene (**11**) is complexed by **1** while 1,4-difluorobenzene (**21**) is not ($K_a < 1$) can also be visualized by comparison of their EPSs, because the potential at the hydrogen atoms of **11** is more positive than the corresponding potential in **21**. With relatively simple semiempirical calculations, supramolecular properties of molecules based on electrostatic interactions can be visualized. The investigation of the molecular tweezers **1** and **2** described here shows that the geometric topology as well as electronic structure is important for the binding properties of the receptor molecules.

Experimental Section

IR: Bio-Rad FTS 135. UV: J + M Tidas FG Cosytec RS 422. ^1H NMR, ^{13}C NMR, DEPT H,H-COSY, C,H-COSY, NOESY, HMQC, HMBC: Bruker AMX 300; ^1H NMR titration experiments: Varian Gemini XL 200; the undeuterated amount of the solvent was used as an internal standard. Positions of the protons of the methano bridges are indicated by the letters i (*innen*, towards the center of the molecule) and a (*außen*, away from the center of the molecule). MS: Fisons Instruments VG ProSpec 3000 (70 eV). All melting points are uncorrected. Column chromatography: Silicagel 0.063 – 0.2 mm. All solvents were distilled prior to use. Ampoules were sealed in vacuo after three freeze (2-propanol/dry ice) and thaw cycles with argon as an inert gas.

1,4,4a,5,7,10,12,12a-Octahydro-1,4:7,10-dimethanonaphthacene-5,12-diol (**4**): Sodium borohydride (0.76 g, 20.1 mmol) was added to a cooled (0 °C) solution of diketone **3**[6] (2.86 g, 9.9 mmol) and cerium(III) chloride heptahydrate (7.5 g, 20 mmol) in methanol (50 mL) at such a rate that the temperature of the reaction mixture did not rise significantly above 0 °C. After complete addition, the reaction mixture was allowed to warm to room temperature and then quenched by addition of water (100 mL). The resulting mixture was extracted three times with diethyl ether and the combined ether layers were washed successively with water and brine. The organic layers were dried over anhydrous magnesium sulfate and filtered, and the filtrate concentrated in vacuo to afford **4** as a colorless solid (2.74 g, 95 %). M.p. 195 °C; MS (70 eV) *m/z* (%): 292 (83) [M^+], 274 (77) [$M^+ - H_2O$], 208 (100) [$M^+ - H_2O - C_5H_6$]; IR (KBr): = 3355 cm^{-1} (OH), 2963 (CH); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.43$ (d, 1H, ^2J(13-H^i, 13-H^a) = 8 Hz, 13-H^i), 1.49 (dm, 1H, 13-H^a), 2.19 (d, 1H, ^2J(14-H^i, 14-H^a) = 7 Hz, 14-H^i), 2.30 (dm, 1H, 14-H^a), 2.62 (m, 2H, 4a-H, 12a-H), 2.94 (t, 2H, ^3J(1-H, 2-H) = 2 Hz, 1-H, 4-H), 3.46 (s, 2H, -OH), 3.86 (t, 2H, ^3J(7-H, 8-H) = 2 Hz, 7-H, 10-H), 4.72 (s, 2H, 5-H, 12-H), 6.02 (m, 2H, 2-H, 3-H), 6.75 (m, 2H, 8-H, 9-H), 7.14 (s, 2H, 6-H, 11-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 45.31$ (d, C-1, C-4), 46.33 (d, C-4a, C-12a), 50.14 (d, C-7, C-10), 52.82 (t, C-13), 70.45 (t, C-14), 71.25 (d, C-5, C-12), 120.91 (d, C-6, C-11), 133.86 (d, C-2, C-3), 137.28 (s, C-5a, C-11a), 142.88 (d, C-8, C-9), 152.00 (s, C-6a, C-10a); $C_{20}H_{20}O_2$ (292.37): calcd C 82.16, H 6.89; found C 82.24, H 6.85.

1,4,7,10-Tetrahydro-1,4:7,10-dimethanonaphthacene (5): *p*-Toluenesulfonylchloride (5.5 g, 29 mmol) was added to a stirred solution of **4** (0.75 g, 2.6 mmol) in anhydrous pyridine (10 mL). After addition of anhydrous triethylamine (5 mL), the mixture was stirred for 20 h at room temperature. The reaction mixture was filtered and the filtrate, after being concentrated in vacuo to half of its volume, was eluted with hexane through a silica gel column. Recrystallization of the product fraction evaporated in vacuo from ethanol yielded **5** as colorless crystals (330 mg, 50 %). M.p. 172 °C; MS (70 eV) *m/z* (%): 256 (100) [M^+]; IR (KBr): = 3061 cm^{-1} (CH), 2983 (CH); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.21$ (d, 2H, ^2J(13-H^i, 13-H^a) = ^2J(14-H^i, 14-H^a) = 6 Hz, 13-H^i, 14-H^i), 2.33 (dm, 2H, 13-H^a, 14-H^a), 3.92 (m, 4H, 1-H, 4-H, 7-H, 10-H), 6.69 (m, 4H, 2-H, 3-H, 8-H, 9-H), 7.44 (s, 4H, 5-H, 6-H, 11-H, 12-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 49.61$ (d, C-1, C-4, C-7, C-10), 67.06 (t, C-13, C-14), 119.53 (d, C-5, C-6, C-11, C-12), 129.88 (s, C-5a, C-11a), 142.17 (d, C-2, C-3, C-8, C-9), 148.06 (s, C-4a, C-6a, C-10a, C-12a); $C_{20}H_{16}$ (256.34): calcd C 93.71, H 6.29; found C 93.90, H 6.42.

2,2a,3,4,9,10,10a,11,14,14a,15,16,21,22,22a,23-Hexadecahydro-2,11:4,9:14,23:16,21-tetramethanodecacene (7): A solution of diene **6** (315 mg, 1.87 mmol), bisdienophile **5** (120 mg, 0.47 mmol), and anhydrous triethylamine (0.1 mL) in anhydrous toluene (10 mL) was heated to 160 °C for 5 d in a sealed ampoule. The reaction mixture was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate 40:1) leading to **7** as colorless solid (195 mg, 70 %). M.p. 225 – 230 °C (decomp); MS (70 eV) *m/z* (%): 576 (100) [M^+]; HR-MS (70 eV), calcd ($C_{46}H_{40}$) 592.3130; found 592.3133; IR (KBr): = 3080 cm^{-1} (CH), 2958 (CH); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.56$ (m, 4H, 6a-H, 10a-H, 18a-H, 22a-H), 1.69 (d, 2H, ^2J(26-H^a, 26-H^i) = ^2J(27-H^a, 27-H^i) = 6 Hz, 26-H^a, 27-H^a), 2.09 (d, 2H, 26-H^i, 27-H^i), 2.20 (dm, 2H, ^2J(25-H^a, 25-H^i) = 8 Hz, 25-H^a, 28-H^a), 2.28 (dm, 2H, 25-H^i, 28-H^i), 2.42 (m, 8H, 6-H, 11-H, 18-H, 23-H), 3.05 (s, 4H, 7-H, 22-H, 10-H, 19-H), 3.60 (s, 4H, 5-H, 12-H, 17-H, 24-H), 6.81 (m, 4H, 2-H, 3-H, 14-H, 15-H), 7.11 (m, 4H, 1-H, 4-H, 13-H, 16-H), 7.35 (s, 4H, 8-H, 9-H, 20-H, 21-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 29.63 (t, C-6, C-11, C-18, C-23), 40.85 (d, C-6a, C-10a, C-18a, C-22a), 44.07 (t, C-26, C-27), 52.34 (d, C-7, C-10, C-19, C-22), 53.52 (d, C-5, C-12, C-17, C-24), 66.39 (t, C-25, C-28), 117.87 (d, C-8, C-9, C-20, C-21), 120.55 (d, C-1, C-4, C-13, C-16), 123.86 (d, C-2, C-3, C-14, C-15), 131.39 (s, C-8a, C-20a), 146.66 (s, C-5a, C-11a, C-17a, C-23a), 147.47 (s, C-7a, C-9a, C-19a, C-21a), 151.98 (s, C-4a, C-12a, C-16a, C-24a).

2,4,9,11,14,16,21,23-Octahydro-2,11:4,9:14,23:16,21-tetramethanodecacene (1): DDQ (428 mg, 1.89 mmol) was added to a solution of **7** (140 mg, 0.24 mmol) in toluene (20 mL). The intensively stirred mixture was immediately placed in an oil bath preheated to 120 °C and kept at 120 °C for two hours. The reaction mixture was allowed to cool down to room temperature. The excess of DDQ was converted to $DDQH_2$ by reaction with added 1,4-cyclohexadiene (0.3 mL). After filtration, the filtrate was

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concentrated in vacuo. Purification of the crude product by column chromatography (silica gel, hexane/ethyl acetate 30:1) yielded **1** as a colorless solid (86 mg, 43 %). M.p. > 300 °C; MS (70 eV) *m/z* (%): 584 (100) [M^+]; IR (KBr): = 3095 cm^{-1} (CH), 3046 (CH), 2962 (CH); UV/Vis ($CHCl_3$): λ_{max} ($\lg\varepsilon$) = 256 (4.68), 289 (4.38), 319 (3.65), 334 (3.74); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (m, 4H, 25-H^i, 25-H^a, 28-H^i, 28-H^a), 2.47 (dm, 2H, ^2J(26-H^a, 26-H^i) = ^2J(27-H^a, 27-H^i) = 8 Hz, 26-H^a, 27-H^a), 2.52 (dm, 2H, 26-H^i, 27-H^i), 4.06 (s, 4H, 5-H, 12-H, 17-H, 24-H), 4.16 (s, 4H, 7-H, 10-H, 19-H, 22-H), 6.76 (m, 4H, 2-H, 3-H, 14-H, 15-H), 7.05 (m, 4H, 1-H, 4-H, 13-H, 16-H), 7.07 (s, 4H, 6-H, 11-H, 18-H, 23-H), 7.29 (s, 4H, 8-H, 9-H, 20-H, 21-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.49 (d, C-7, C-10, C-19, C-22), 51.02 (d, C-5, C-12, C-17, C-24), 64.83 (t, C-26, C-27), 67.63 (t, C-25, C-28), 116.15 (d, C-6, C-11, C-18, C-23), 119.40 (d, C-8, C-9, C-20, C-21), 121.53 (d, C-1, C-4, C-13, C-16), 124.14 (d, C-2, C-3, C-14, C-15), 130.21 (s, C-8a, C-20a), 146.96 (s, C-6a, C-10a, C-18a, C-22a), 147.12 (s, C-5a, C-11a, C-17a, C-23a), 147.58 (s, C-7a, C-9a, C-19a, C-21a), 150.58 (s, C-4a, C-12a, C-16a, C-24a); $C_{46}H_{32}$ (584.76): calcd C 94.48, H 5.52; found C 94.35, H 5.55.

8,19-Diacetoxy-5,6,6a,7,9,9a,10,11,16,17,17a,18,20,20a,21,22-hexadecahydro-5,22:7,20:9,18:11,16-tetramethanononacene (**9**): A solution of diene **6** (2.0 g, 12 mmol), bisdienophile **8**[6] (1.0 g, 3 mmol), and anhydrous triethylamine (0.3 mL) in a 2:1 mixture of anhydrous toluene and acetonitrile (30 mL) was heated to 160 °C for 5 d in a sealed ampoule. Upon concentration of the reaction mixture in vacuo to a volume of about 5 mL, the product precipitated. It was then filtered off, washed thoroughly with cyclohexane, and dried in vacuo. The colorless product **9** (1.45 g, 71 %) was used without further purification. M.p. 260–265 °C; MS (70 eV) *m/z* (%): 658 (55) [M^+], 490 (50) [$M^+ - C_{13}H_{12}$]; HR-MS (70 eV), calcd ($C_{46}H_{42}O_4$) 658.3083; found 658.3082; IR (KBr): = 3062 cm^{-1} (CH), 2965 (CH), 2932 (CH), 1762 (C=O), 1185 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (m, 4H, 24-H, 25-H), 1.9–2.35 (m, 16H, 6-H, 6a-H, 9a-H, 10-H, 12a-H, 17-H, 20a-H, 21-H, 26-H), 2.28 (s, 6H, $COCH_3$), 2.83 (s, 4H, 7-H, 9-H, 18-H, 20-H), 3.53 (s, 4H, 5-H, 11-H, 16-H, 22-H), 6.81 (m, 4H, 2-H, 3-H, 13-H, 14-H), 7.08 (m, 4H, 1-H, 4-H, 12-H, 15-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.75 (q, CH_3), 29.53 (t, C-6, C-10, C-17, C-21), 38.72 (d, C-6a, C-9a, C-17a, C-20a), 45.60 (t, C-24, C-25), 53.40 (d, C-5, C-11, C-16, C-22), 67.12 (t, C-23, C-26), 120.59 (d, C-1, C-4, C-12, C-15), 123.87 (d, C-2, C-3, C-13, C-14), 135.00 (s, C-7a, C-8a, C-18a, C-19a), 139.10 (s, C-8, C-19), 146.96 (s, C-5a, C-10a, C-16a, C-21a), 151.90 (s, C-4a, C-11a, C-15a, C-22a), 168.95 (s, C=O).

8,19-Diacetoxy-5,7,9,11,16,18,20,22-octahydro-5,22:7,20:9,18:11,16-tetramethanononacene (10a): DDQ (1.0 g, 4.4 mmol) was added to a solution of **9** (400 mg, 0.60 mmol) in toluene (15 mL). The intensively stirred mixture was placed immediately into an oil bath preheated to 120 °C and kept at 120 °C for two hours. The reaction mixture was allowed to cool down to room temperature. The excess DDQ was converted to $DDQH_2$ by reaction with added 1,4-cyclohexadiene (0.3 mL). After filtration, the filtrate was concentrated in vacuo. Purification of the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate 3:1) yielded **10a** as a colorless solid (320 mg, 83 %). M.p. > 300 °C; MS (70 eV) *m/z* (%): 650 (100) [M^+], 607 (19) [$M^+ - COCH_3$], 565 (14) [$M^+ - 2\,COCH_3$]; HR-MS (70 eV), calcd ($C_{46}H_{34}O_4$) 650.2457; found 650.2457; IR (KBr): = 3060 cm^{-1} (CH), 2975 (CH), 2938 (CH), 2860 (CH), 1765 (C=O), 1202 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (d, 2H, ^2J(24-H^a, 24-H^i) = 9.2 Hz, 24-H^a, 25-H^a), 2.34 (s, 6H, $COCH_3$), 2.40 (m, 4H, 23-H, 26-H), 2.49 (d, 2H, 24-H^i, 25-H^i), 3.97 (s, 4H, 5-H, 11-H, 16-H, 22-H), 4.04 (s, 4H, 7-H, 9-H, 18-H, 20-H), 6.73 (m, 4H, 2-H, 3-H, 13-H, 14-H), 7.05 (m, 4H, 1-H, 4-H, 12-H, 15-H), 7.12 (s, 4H, 6-H, 10-H, 17-H, 21-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.85 (q, CH_3), 48.73 (d, C-7, C-9, C-18, C-20), 52.00 (d, C-5, C-11, C-16, C-22), 68.90 (t, C-24, C-25), 70.15 (t, C-23, C-26), 116.55 (d, C-6, C-10, C-17, C-21), 121.46 (d, C-1, C-4, C-12, C-15), 124.66 (d, C-2, C-3, C-13, C-14), 137.05 (s, C-8, C-19), 141.27 (s, C-7a, C-8a, C-18a, C-19a), 146.22 (s, C-6a, C-9a, C-17a, C-20a), 147.60 (s, C-5a, C-10a, C-16a, C-21a), 150.20 (s, C-4a, C-11a, C-15a, C-22a), 161.80 (s, C=O).

8,19-Dihydroxy-5,7,9,11,16,18,20,22-octahydro-5,22:7,20:9,18:11,16-tetramethanononacene (10b): A suspension of the diacetate **10a** (210 mg, 0.32 mmol) in tetrahydrofuran (15 mL) was slowly added to a suspension of lithium aluminum hydride (100 mg, 2.64 mmol) kept at 0 °C. After warming to room temperature, the reaction mixture was heated under reflux for 5 h, then quenched under argon at 0 °C with a saturated aqueous solution of ammonium chloride (15 mL) and acidified with 1M aqueous HCl. This mixture was extracted three times with chloroform. The combined organic layers were washed successively with water and brine, dried over sodium sulfate, and concentrated in vacuo. Recrystallization from ethanol yielded **10b** as a colorless crystalline solid (180 mg, 98 %). M.p. 280 °C (decomp); MS (70 eV) *m/z* (%): 566 (100) [M^+]; HR-MS (70 eV): calcd ($C_{42}H_{30}O_2$) 566.2245; found 566.2247; IR (KBr): = 3390 cm^{-1} (OH), 2970 (CH), 2932 (CH), 1456 (C=C); ^{1}H NMR (300 MHz, [D_6]acetone): δ = 2.18 (dm, 2H, ^2J(24-H^i, 24-H^a) = ^2J(25-H^i, 25-H^a) = 7.8 Hz, 24-H^a, 25-H^a), 2.23 (d, 2H, 24-H^a, 25-H^a), 2.30 (m, 4H, 23-H, 26-H), 4.05 (s, 4H, 5-H, 11-H, 16-H, 22-H), 4.22 (s, 4H, 7-H, 9-H, 18-H, 20-H), 6.80 (m, 4H, 2-H, 3-H, 13-H, 14-H), 7.03 (s, 4H, 6-H, 10-H, 17-H, 21-H), 7.05 (m, 4H, 1-H, 4-H, 12-H, 15-H); ^{13}C NMR (75 MHz, [D_6]acetone): δ = 47.40 (d, C-7, C-9, C-18, C-20), 51.10 (d, C-5, C-11, C-16, C-22), 68.10 (t, C-23, C-24, C-25, C-26), 116.22 (d, C-6, C-10, C-17, C-21), 121.42 (d, C-1, C-2, C-12, C-15), 124.78 (d, C-2, C-3, C-13, C-14), 136.41 (s, C-7a, C-8a, C-18a, C-19a), 147.23 (s, C-6a, C-9a, C-17a, C-20a), 148.14 (s, C-5a, C-10a, C-16a, C-21a, C-8, C-19), 150.90 (s, C-4a, C-11a, C-15a, C-22a).

8,19-Bis-trifluoromethansulfonoxy-5,7,9,11,16,18,20,22-octahydro-5,22:7,20:9,18:11,16-tetramethanononacene (10c): Trifluoromethanesulfonic anhydride (690 mg, 2.44 mmol) was slowly added to a solution of **10b** (275 mg, 0.49 mmol) in pyridine (30 mL) kept at 0 °C. After being stirred for 24 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted three times with diethyl ether. The combined organic layers were washed thoroughly with 1.5 M aqueous HCl and dried over sodium sulfate. After concentration in vacuo, the yellow residue was purified by column chromatography (silica gel, chloroform) to yield **10c** as a colorless solid (400 mg, 98 %). M.p. > 300 °C; MS (70 eV) *m/z* (%): 830 (100) [M^+], 564 (55) [$M^+ - 2\,CF_3SO_2$]; IR (KBr): = 3050 cm^{-1} (CH), 2970 (CH), 2936 (CH), 2863 (CH), 1425 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (m, 4H, 23-H, 26-H), 2.44 (d, 2H, ^2J(24-H^i, 24-H^a) = ^2J(25-H^i, 25-H^a) = 7.2 Hz, 24-H^i, 25-H^i), 2.58 (d, 2H, 24-H^a, 25-H^a), 4.09 (s, 4H, 5-H, 11-H, 16-H, 22-H), 4.35 (s, 4H, 7-H, 9-H, 18-H, 20-H), 6.78 (m, 4H, ^3J(1-H, 2-H) = 3.0 Hz, 2-H, 3-H, 13-H, 14-H), 7.10 (m, 4H, 1-H, 4-H, 12-H, 15-H), 7.20 (s, 4H, 6-H, 10-H, 17-H, 21-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.46 (d, C-7, C-9, C-18, C-20), 51.24 (d, C-5, C-11, C-16, C-22), 69.05 (t, C-23, C-26), 70.75 (t, C-24, C-25), 117.14 (d, C-6, C-10, C-17, C-21), 118.62 (q, C-F_3, ^1J (C-F) = 318 Hz), 121.55 (d, C-1, C-4, C-12, C-15), 124.79 (d, C-2, C-3, C-13, C-14), 136.66 (s, C-8, C-19), 144.13 (s, C-7a, C-8a, C-18a, C-19a), 144.74 (s, C-6a, C-9a, C-17a, C-20a), 148.47 (s, C-5a, C-10a, C-16a, C-21a), 150.03 (s, C-4a, C-11a, C-15a, C-22a); $C_{44}H_{28}F_6O_6S_2$ (830.81): calcd C 63.61, H 3.40; found C 63.44, H 3.43.

5,7,9,11,16,18,20,22-octahydro-5,22:7,20:9,18:11,16-tetramethanononacene (2): A suspension of **10c** (350 mg, 0.42 mmol), 1,3-bis(diphenylphosphino)propane (66 mg, 0.16 mmol), bis(triphenylphosphino)palladium(II) chloride (39 mg, 0.06 mmol), and formic acid (0.4 mL) in dimethyl formamide (5 mL) and tri-*n*-butylamine (1 mL) was stirred under argon at 100 °C for 72 h. After addition of 1.5 M HCl (30 mL), the mixture was extracted three times with methyl *tert*-butyl ether, the combined organic layers were washed three times with 1.5 M aqueous HCl and dried over sodium sulfate, and the solvent was evaporated in vacuo. Purification of the yellow residue by column chromatography (silica gel, chloroform/*n*-hexane 1:1) yielded **2** as colorless crystals (190 mg, 82 %). M.p. > 300 °C; MS (70 eV) *m/z* (%): 534 (100) [M^+]; IR (KBr): = 3072 cm^{-1} (CH), 2971 (CH), 2933 (CH), 2858 (CH), 1448 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (m, 8H, 23-H, 24-H, 25-H, 26-H), 3.95 (s, 4H, 5-H, 11-H, 16-H, 22-H), 4.03 (s, 4H, 7-H, 9-H, 18-H, 20-H), 6.71 (m, 4H, 2-H, 3-H, 13-H, 14-H), 7.03 (m, 4H, 1-H, 4-H, 12-H, 15-H), 7.08 (s, 2H, 8-H, 19-H), 7.09 (s, 4H, 6-H, 10-H, 17-H, 21-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.20 (t), 51.33 (t), 68.81 (d), 70.79 (d), 116.00 (d), 116.07 (d), 121.38 (d), 124.53 (d), 147.20 (s), 147.38 (s), 147.52 (s), 150.36 (s); $C_{42}H_{30} \cdot CHCl_3$ (654.08): calcd C 78.96, H 4.78; found C 79.11, H 4.95.

Determination of K_a by ^{1}H NMR titration: In the titration experiments, the total substrate concentration $[S]_o$ was kept constant whereas the total receptor concentration $[R]_o$ was varied. This was achieved by dissolving a defined amount of the receptor R in 0.5 mL of a solution containing the substrate concentration $[S]_0$. $\Delta\delta$ was determined from the chemical shift of the pure substrate and the chemical shift of the substrate measured in the ^{1}H NMR spectrum (200 MHz, 21 °C) of this mixture. Successive addition of further solution containing $[S]_0$ led to a dilution of the concentration $[R]_0$ in the mixture while $[S]_0$ is kept constant. Measurement of the chemical shift of the substrate dependent on the concentration $[R]_0$ afforded the data

pairs $\Delta\delta$ and $[R]_0$. Fitting of the data to the (1:1) binding isotherm by iterative methods[10] delivered the parameters K_a and $\Delta\delta_{max}$.

Determination of K_a using the solid–liquid-extraction method: In all solid–liquid extraction experiments, the concentration of free substrate [S] was considered to remain constant and be equal to the maximum concentration of the substrate, $[S]_{max}$, soluble in the applied solvent (here, chloroform). By subtracting this value from the observed concentration of the substrate in the solution of the complex, $[S]_o$, the concentration of complexed substrate, $[S]_{compl} = [S]_{obs} - [S]_{max}$, was obtained. In the case of exclusive formation of a 1:1 complex, $[S]_{compl}$ is equal to the concentration of complex, [RS], and the concentration of complexed receptor. The concentration of free receptor was obtained by subtracting this value from the total concentration of the receptor $[R]_o$.

For the determination of the maximum solubility of substrate **19** in chloroform, $[S]_{max}$, a suspension of solid **19** in chloroform was exposed to ultrasound for 10 min. After centrifugation for 10 min, the solvent of 3 mL of the decanted solution was evaporated in vacuo. The residue was dissolved in 10 mL water and a UV-VIS spectrum was recorded. The amount of **19** in this sample was determined by recording a calibration curve by the use of UV-VIS spectra for four aqueous solutions of **19** in the concentration range from 10^{-5} to 10^{-4} M^{-1}. From the linear plot of the absorption at $\lambda = 275$ nm against the concentration of **19** in the calibration curve, the maximum solubility of the **19** in chloroform, $[S]_{max}$, was determined to be 3.073×10^{-4} M^{-1}. The concentration of substrate **19** in solution with **1** or **2**, $[S]_{obs}$, was obtained by exposing a suspension of solid **19** in $CDCl_3$ containing **1** or **2** in the concentration $[R]_0$ to ultrasonication. After centrifugation, the ^{1}H NMR spectrum of the decanted solution delivered the ratio between $[R]_0$ as receptors and $[S]_{obs}$. K_a was obtained by means of Equation (1).

$$K_a = \frac{[RS]}{[R]\,[S]} = \frac{([S]_{obs} - [S]_{max})}{([R]_0 - [S]_{obs} + [S]_{max})[S]_{max}} \quad (1)$$

Determination of ΔH and ΔS by variable-temperature (VT) single-point analyses: When the maximum chemically induced shift $\Delta\delta_{max}$ is known, K_a can easily be calculated from the observed $\Delta\delta$ in a single mixture of receptor R and substrate S using Equation (2).

$$K_a = ([R]_0 - P[S]_0)^{-1}\frac{P}{1-P}; \qquad P = \frac{\Delta\delta}{\Delta\delta_{max}} \quad (2)$$

With the assumption that the value of $\Delta\delta_{max}$ determined by ^{1}H NMR titration at 21 °C was not significantly temperature-dependent, this single-point analysis allowed easy determination of K_a values at variable temperatures. The ΔH and ΔS values were determined with the van't Hoff equation [Eq. (3)] from the linear plot of $(\ln K_a)$ vs. $1/T$.

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

In the case of the VT single-point analyses of complex **11@2** in $CDCl_3$, we observed a significant curvature of the van't Hoff plot ($R^2 = 0.9723$ for linear regression). We believe that the reason for this curvature is the temperature dependence of ΔH, that is, a significant difference in the heat capacities C_p of free receptor and substrate on the one hand and their 1:1 complex on the other. If ΔC_p is not negligibly small, determination of ΔH and ΔS requires a nonlinear regression analysis following Equation (4),[11]

$$R\ln K_a = -\left(\frac{\Delta H_0}{T}\right) + \Delta C_p \ln T + (\Delta S_0 - \Delta C_p) \quad (4)$$

where $\Delta H = \Delta H_0 + T\Delta C_p$; $\Delta S = \Delta S_0 + \Delta C_p \ln T$. For complex **11@2** in $CDCl_3$ (van't Hoff plot shown in Figure 4 **11@2**) we determined the K_a values listed in Table 2. By fitting the $(\ln K_a)$ vs. $1/T$ data to Equation (4), we calculated $\Delta H_0 = 3.118$ kcal mol^{-1}, $\Delta S_0 = 93.26$ cal mol^{-1} K^{-1}, and $\Delta C_p = -17$ cal mol^{-1} K^{-1}.

Table 2. K_a values for complex **11@2** in $CDCl_3$.

T [K]	294	278	263	248	233	218
K_a [M^{-1}]	10	12	13	15	18	19

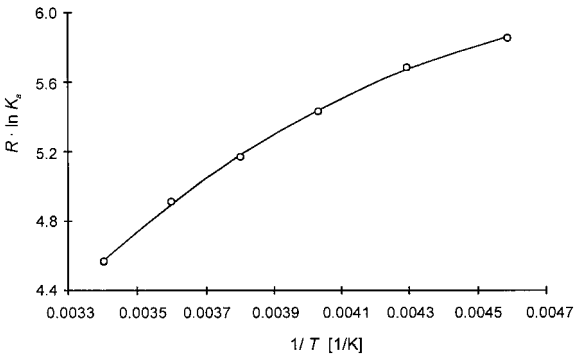

Figure 4. Van't Hoff plot for the complexation of 1,4-dicyanobenzene (**11**) by **2**, in $CDCl_3$. Iterative fitting affords $\Delta C_p = -17$ cal mol^{-1} K^{-1}.

Crystal structure determination: Measurements were recorded with a Siemens SMART-CCD diffractometer with $Mo_{K\alpha}$ radiation; absorption correction was carried out with the Siemens SADABS program. The structure was solved by direct methods (SHELXS). Hydrogen atoms were calculated and refined as riding groups with the 1.2-fold isotropic U value of the corresponding carbon atom.

Crystal data of 11@1: $C_{46}H_{32} \cdot C_6H_4(CN)_2$, $M_r = 688.88$, $T = 298$ K, cell dimensions: $a = 7.6346(2)$, $b = 10.8366(4)$, $c = 24.1494(9)$ Å, $\beta = 93.195(2)°$, $V = 1994.85(12)$ Å^3; monoclinic crystal system, $Z = 2$, $\rho_{calcd} = 1.187$ g cm^{-3}, $\mu = 0.068$ mm^{-1}, space group: $P2/n$, data collection of 8255 intensities, 3399 independent ($R_{merg} = 0.0303$, $1.69° \le \Theta \le 25.62°$), 1859 observed [$F_o \ge 4\sigma(F)$], correction of absorption: R_{merg} before/after: 0.0270/0.0226, max/min transmission: 1.00/0.55, structure refinement on F^2 (SHELXTL 5.03) (253 parameters), $R1 = 0.0535$, $wR2$ (all data) $= 0.1465$, $w^{-1} = \sigma^2(F_o^2) + (0.080P)^2$, $P = [\max(F_o^2) + (2F_c^2)]/3$, maximum residual electron density: 0.223 e Å^{-3}.

Crystal data of 14@1: $C_{46}H_{32} \cdot C_6H_2(CN)_4 \cdot CH_2Cl_2$, $M_r = 823.81$, $T = 298$ K, crystal dimensions: $0.32 \times 0.24 \times 0.15$ mm^3, cell dimensions: $a = 10.7215(2)$, $b = 27.6104(2)$, $c = 15.9754(3)$ Å, $\beta = 94.727(1)°$, $V = 4715.2(2)$ Å^3, monoclinic crystal system, $Z = 4$, $\rho_{calcd} = 1.215$ Mgm^{-3}, $\mu = 0.18$ mm^{-1}, space group: $P2_1/n$, data collection of 52751 intensities, 4399 independent ($R_{merg} = 0.0066$, $1.5° \le \Theta \le 20.0°$), 3494 observed [$F_o \ge 4\sigma(F)$], correction of absorption: R_{merg} before/after: 0.0928/0.040, max/min transmission 1.00/0.61, structure refinement on F^2 (SHELXTL 5.03) (613 parameters). Because of the total disorder of the solvent molecule, the structure could not be refined satisfactorily and the value for $R1$ remained greater than 12%. Therefore, no further data was given. Nevertheless, the receptor **1** with the substrate **14** could be located and the sketches in the manuscript are based upon this model.

Crystal data of 17@1: $C_{46}H_{32} \cdot C_8H_4(CN)_4$, $M_r = 788.95$, $T = 178$ K, crystal dimensions: $0.22 \times 0.15 \times 0.11$ mm^3, cell dimensions: $a = 17.4523(3)$, $b = 9.35240(10)$, $c = 27.7794(4)$ Å, $\beta = 107.0250(10)°$, $V = 4335.48(11)$ Å^3, monoclinic crystal system, $Z = 4$, $\rho_{calcd} = 1.209$ g cm^{-3}, $\mu = 0.071$ mm^{-1}, space group: $P2_1/c$, data collection of 24421 intensities, 5472 independent ($R_{merg} = 0.0447$, $2.31° \le \Theta \le 22.5°$), 3977 observed [$F_o \ge 4\sigma(F)$], correction of absorption: R_{merg} before/after: 0.0411/0.0373, max/min transmission 1.00/0.68, structure refinement on F^2 (SHELXTL 5.03) (559 parameters), $R1 = 0.0434$, $wR2$ (all data) $= 0.1159$, $w^{-1} = \sigma^2(F_o^2) + (0.0575P)^2 + (0.582P)$, $P = [\max(F_o^2) + (2F_c^2)]/3$, maximum residual electron density: 0.167 e Å^{-3}.

Crystal data of 17@2: $C_{42}H_{30} \cdot C_8H_4(CN)_4 \cdot CHCl_3$, $M_r = 858.27$, $T = 293$ K, crystal dimensions: $0.41 \times 0.16 \times 0.08$ mm^3, cell dimensions: $a = 9.8501(2)$, $b = 17.4528(2)$, $c = 23.52540(10)$ Å, $V = 4044.29(10)$ Å^3, orthorhombic crystal system, $Z = 4$, $\rho_{calcd} = 1.410$ g cm^{-3}, $\mu = 0.274$ mm^{-1}, space group: $P2_12_12_1$, data collection of 13300 intensities, 4988 independent ($R_{merg} = 0.1315$, $2.53° \le \Theta \le 22.5°$), 3511 observed [$F_o \ge 4\sigma(F)$], correction of absorption: R_{merg} before/after: 0.0894/0.0812, max/min transmission 1.00/0.35, structure refinement on F^2 (SHELXTL 5.03) (559 parameters), $R1 = 0.0711$, $wR2$ (all data) $= 0.1934$, $w^{-1} = \sigma^2(F_o^2) + (0.1151P)^2$, $P = [\max(F_o^2) + (2F_c^2)]/3$, absolute structure parameter 0.04(14), maximum residual electron density: 0.638 e Å^{-3}.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopolds-

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hafen (Germany) (fax: (+ 49) 7247-808-606; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 408724 (**17@1**), 408726 (**11@1**), 408725 (**17@2**).

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