

# Molecular Tweezers as Synthetic Receptors: Molecular Recognition of Cationic Substrates; An Insight into the Mechanism of Complexation

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*Dedicated to Professor Fritz Vögtle on the Occasion of his 60th Birthday*

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**Abstract.** The results of  $^1\text{H}$  NMR binding studies of molecular tweezers **1a** with various aliphatic and aromatic cations in organic solvents are described. By the use of the viologene substrates **11** and **12** bearing bulky endgroups and therefore having a dumb-bell topology it could be demonstrated that besides the obvious mechanism of complexation in which the

guest molecule enters the tweezer's cavity through the open sides of the host, a second mechanism is available in which the substrate enters the cavity through a gap emerging after a substantial spreading of the tweezer's tips by at least of about 280 pm.

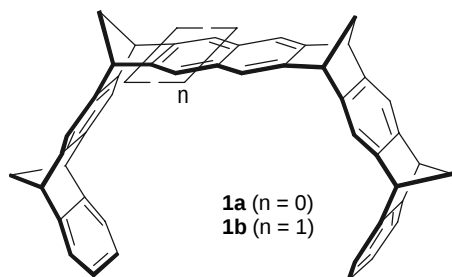
Aromatic molecules play an important role in many areas of biological and supramolecular chemistry [1] and their noncovalent interactions with other aromatic units ( $\pi$ - $\pi$ - or arene-arene interaction) [2] and positively charged ions (cation- $\pi$  interaction) [3] are of particular importance in the formation of superstructures [2-4]. The design of efficient synthetic receptors with the ability to selectively bind substrates in solution requires precise control of both their electronic and topological properties. Besides the frequently used cyclic receptors of the cyclophane-type [5] non-cyclic receptors with cavities of flexible size proved to be very effective [6]. We have recently reported on the synthesis and some supramolecular properties of the hydrocarbon compounds **1a** and **1b**, which due to their ability to selectively bind electron-deficient aromatic and aliphatic substrates as well as organic cations can be regarded as molecular tweezers [7]. Here we report on the binding properties of the benzene-spaced molecular tweezers **1a** towards various aliphatic and aromatic cations in organic solution and attempts to use this binding motive for the template synthesis of mechanically interlocked supermole-

cules of a novel clipped-rotaxane-type, as it has been already shown for the syntheses of rotaxanes and catenanes by Vögtle and Stoddart [8].

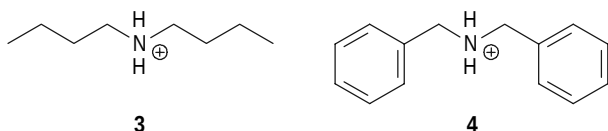
## Results and Discussion

Due to the ribbon-type concave topology the five benzene units of molecular tweezer **1a** define a cavity in which a substrate can be bound by multiple noncovalent interaction. The magnetic anisotropy of these benzene units makes the  $^1\text{H}$  NMR spectroscopy to be a very sensitive probe to detect the complexation of substrate molecules bound inside the cavity of **1a** [7]. From the results obtained in binding studies with small electron-deficient aliphatic substrates ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_2(\text{CN})_2$ ,  $\text{CH}_3\text{NO}_2$ ) [7a] and intramolecular complexation of flexible aliphatic sidechains [7b] we already know that the cavity of **1a** has an almost ideal size for the binding of methyl or methylene groups. Because of the very electron-rich character of the tweezer's concave side [9] we supposed that ammonium ions also should be suitable substrates due to multiple cation- $\pi$  interactions with the host **1a**.

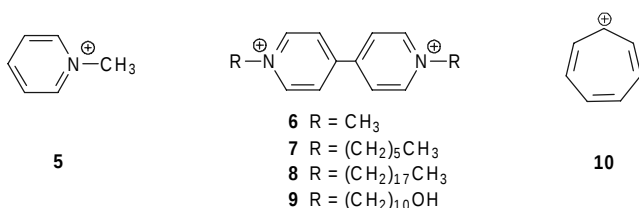
Due to the different solubility properties of the hydrocarbon **1a** and ionic substrates only  $\text{CDCl}_3$  and mixtures of  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  (v/v 1:1 or 1:2) can be used as solvents. Most of the primary ammonium ions, however, are nearly insoluble in  $\text{CDCl}_3$  or  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  mixtures even as  $\text{PF}_6^-$  salts. Therefore, we performed  $^1\text{H}$  NMR bindings studies only with the better soluble secondary ammonium salts, di-*n*-butylam-



monium tetrafluoroborate (**3**·BF<sub>4</sub><sup>−</sup>) and dibenzylammonium tetrafluoroborate (**4**·BF<sub>4</sub><sup>−</sup>), respectively, in CDCl<sub>3</sub>.



While the addition of host **1a** had no effect on the <sup>1</sup>H NMR spectrum of **4**, the <sup>1</sup>H NMR signal assigned to the α-protons in **3** shows a dramatic upfield shift after the addition of **1a** (NH-protons could not be detected under the experimental conditions). The association constant  $K_a = 30 \text{ M}^{-1}$  and the maximum chemically induced shift  $\Delta\delta_{\text{max}} = 3.2 \text{ ppm}$  (upfield) were determined at 21 °C from the dependence of the chemical shift of the α-protons in **3** ([**3**·BF<sub>4</sub><sup>−</sup>] = const.) on the concentration of **1a** by fitting the data to the binding isotherme by iterative methods [10]. The observation that the chemical shifts of the other guest protons were not significantly affected by the presence of **1a** ( $\Delta\delta_{\text{max}} < 0.1 \text{ ppm}$ ) suggests a complex geometry in which the tweezer **1a** is threaded with the chain-like substrate comparable to a pseudorotaxane [8, 11] with the positively charged nitrogen centered in the cavity [12]. The finding, that **4** is not complexed by the molecular tweezer **1a** in CDCl<sub>3</sub>, can be rationalized by the steric shielding of the ammonium center by the bulky benzyl substituents. It should be noted that neither the neutral di-*n*-butylamine nor the tertiary tri-*n*-butylammonium tetrafluoroborate is complexed by **1a**, most likely because the uncharged amine is not sufficiently electron-deficient and the tertiary ammonium salt does not fit into the cavity of **1a** due to its more spherical topology.



From earlier solid–liquid extraction experiments we already know that **1a** forms a 1:1 complex soluble in CDCl<sub>3</sub> with *N*-methylpyrazinium iodide which by itself is insoluble in chloroform [7a]. Inspired by this observation, we studied the binding properties of **1a** towards several cationic aromatic substrates, such as 5·PF<sub>6</sub><sup>−</sup> and the viologene derivatives **6**·2PF<sub>6</sub><sup>−</sup> – **9**·2PF<sub>6</sub><sup>−</sup> and the tropylium salt **10**·BF<sub>4</sub><sup>−</sup> which are soluble in mixtures of CDCl<sub>3</sub> and the more competitive solvent (CD<sub>3</sub>)<sub>2</sub>CO [11]. Table 1 summarizes the results from

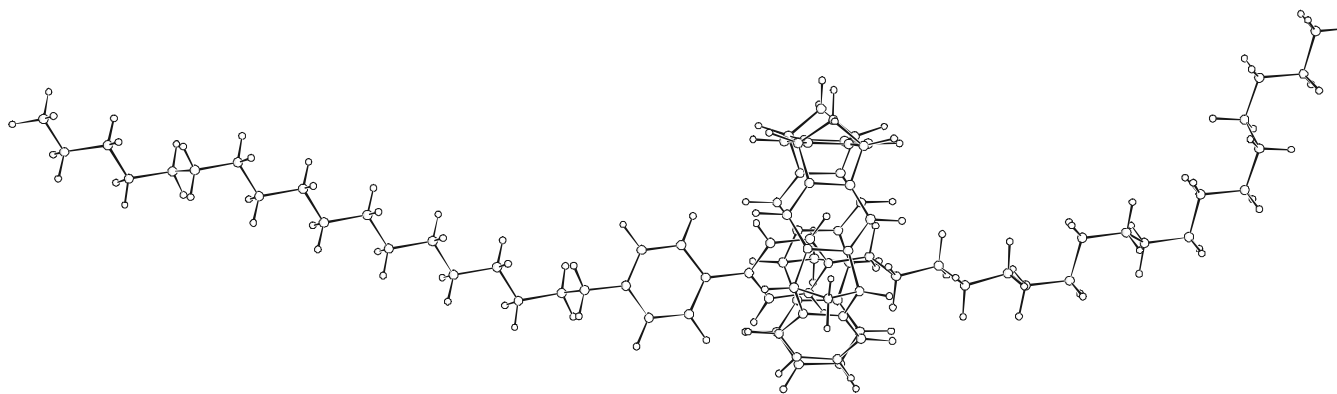
<sup>1</sup>H NMR titration experiments at room temperature. It is worth mentioning that the complex **5@1a** shows the largest upfield shift ( $\Delta\delta_{\text{max}} = 6.0 \text{ ppm}$ ) indicating that the complex geometry might be different to those of the viologene complexes ( $2 \cdot \Delta\delta_{\text{max}} = 2.8\text{--}3.2 \text{ ppm}$ ). Further insight should be gained by crystal structure analyses, but so far no suitable crystals of **5@1a** could be grown.

**Table 1** Association constants  $K_a$  (M<sup>−1</sup>), Gibbs reaction enthalpies  $\Delta G$  (kcal mol<sup>−1</sup>), and maximum chemically induced shifts  $\Delta\delta_{\text{max}}$  of complexes with **1a** as receptor at 21 °C. If no experimental error is given, the maximum error of  $K_a$  is estimated from the uncertainties in the determination of the concentration, chemical shifts etc. to be ± 10%.

| guest                                   | CDCl <sub>3</sub> /(CD <sub>3</sub> ) <sub>2</sub> CO (v/v) | $K_a$ (M <sup>−1</sup> ) | $\Delta G$ (kcal/mol) | $\Delta\delta_{\text{max}}$ (ppm) |
|-----------------------------------------|-------------------------------------------------------------|--------------------------|-----------------------|-----------------------------------|
| <b>3</b> ·BF <sub>4</sub> <sup>−</sup>  | 1 : 0                                                       | 30                       | −2.0 ± 0.1            | 3.2 ( <i>a</i> -H)                |
| <b>5</b> ·PF <sub>6</sub> <sup>−</sup>  | 1 : 1                                                       | 19 ± 3                   | −1.7 ± 0.1            | 6.0 (2-H)                         |
| <b>6</b> ·2PF <sub>6</sub> <sup>−</sup> | 1 : 2                                                       | 56                       | −2.4 ± 0.1            | 1.5 (2-H)                         |
| <b>7</b> ·2PF <sub>6</sub> <sup>−</sup> | 1 : 1                                                       | 120                      | −2.8 ± 0.1            | 1.6 (2-H)                         |
|                                         | 1 : 2                                                       | 70                       | −2.5 ± 0.1            | 1.4 (2-H)                         |
| <b>8</b> ·2PF <sub>6</sub> <sup>−</sup> | 1 : 1                                                       | 130                      | −2.9 ± 0.1            | 1.6 (2-H)                         |
| <b>9</b> ·2PF <sub>6</sub> <sup>−</sup> | 1 : 1                                                       | 130                      | −2.9 ± 0.1            | 1.6 (2-H)                         |
| <b>10</b> ·BF <sub>4</sub> <sup>−</sup> | 1 : 1                                                       | 23 ± 3                   | −1.9 ± 0.1            | 2.5                               |

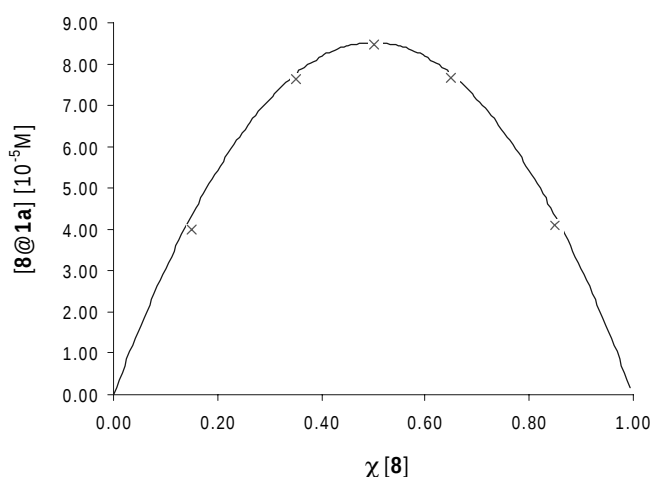
From this data it becomes evident that the monocation **5** forms a weaker complex with **1a** than the dication **6**–**9**. As expected the binding strength decreases when the amount of acetone, a competitive solvent due to its Lewis basicity and, thus, its ability to solvate the cationic substrates better than chloroform, is increased. The calculated structure (molecular mechanics, AMBER\*) of the complex **8@1a** suggests that the formation of a 1:2 complex **8@1a**<sub>2</sub> might also be possible when using the dicationic viologene substrates because the cationic nitrogen is centered in the cavity of **1a** (Figure 1). For the complexation **8** with **1a** the complex stoichiometry was determined to be 1:1, by using Job's method (Figure 2, Table 2) [17]. The calculated structure of the 1:1 complex **8@1a** is in excellent agreement with the findings that the maximum chemically induced shifts are large for the 2-H protons ( $\Delta\delta_{\text{max}} = 1.4\text{--}1.6 \text{ ppm}$ ) and the α-CH<sub>2</sub> protons ( $\Delta\alpha_{\text{max}} = 2.0\text{--}2.2 \text{ ppm}$ ) but quite small for the 3-H protons ( $\Delta\delta_{\text{max}} < 0.5 \text{ ppm}$ ).

As we have shown earlier the complexation of benzenoid aromatic substrates requires a substantial distortion of the flexible tweezer molecule **1a** from its relaxed C<sub>2v</sub> structure because of its relatively small cavity [7a]. Therefore it was surprising to us that the even bigger tropylium ion **10** is also complexed by **1a** in CDCl<sub>3</sub>/(CD<sub>3</sub>)<sub>2</sub>CO 1:1 ( $K_a = 23 \text{ M}^{-1}$ , 21 °C). We would



**Fig. 1** Side view of the structure of complex **8@1a** calculated by the use of molecular mechanics (MacroModel 5.0, AMBER\*). The molecular tweezer **1a** is threaded with the chain-like substrate with one of the positively charged nitrogen atoms centered in the cavity of **1a**.

like to emphasize that the complex **10@1a** is a charged, all hydrocarbon superstructure stabilized by about 2 kcal/mol compared to the isolated, solvated molecular moieties.

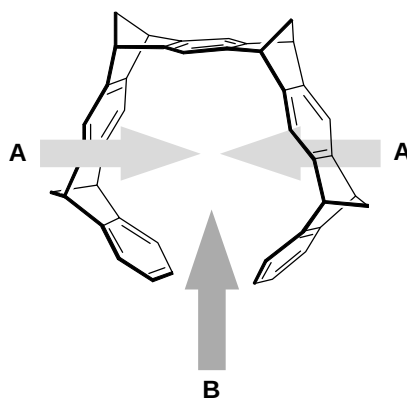


**Fig. 2** Job-Plot for the complexation of **8·2PF<sub>6</sub><sup>-</sup>** by **1a** in CDCl<sub>3</sub>/(CD<sub>3</sub>)<sub>2</sub>CO 1:1 at 21 °C. The maximum at a molar fraction *c* of substrate **8** indicates a 1:1 stoichiometry. See Table 2 for experimental details.

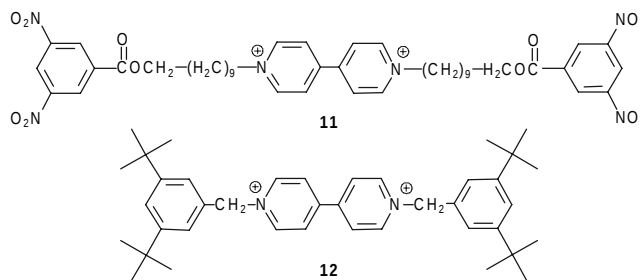
**Table 2** Determination of complex stoichiometry by the use of Job's method. Portions of the solutions of molecular tweezer (**1a**)<sub>0</sub> = 1.9×10<sup>-3</sup> M and substrate (**8·2PF<sub>6</sub><sup>-</sup>**)<sub>0</sub> = 1.9·10<sup>-3</sup> M were mixed so that the total concentration of **1a**<sub>0</sub>+**8·2PF<sub>6</sub><sup>-</sup>**<sub>0</sub> was constant in each mixture. The concentrations of the complex **8@1a** were calculated from the measured Δδ values with a Δδ<sub>max</sub> = 1.55 ppm obtained from the <sup>1</sup>H NMR titration [20].

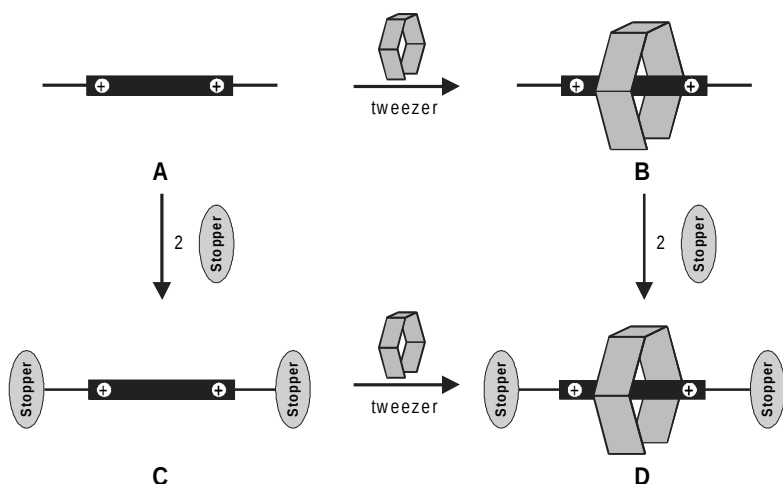
| V(mL)<br>( <b>1a</b> ) | V(mL)<br>( <b>8·2PF<sub>6</sub><sup>-</sup></b> ) | Δδ<br>(2-H) | χ<br>[ <b>8</b> ] | ( <b>8@1a</b> )<br>(10 <sup>-5</sup> M) |
|------------------------|---------------------------------------------------|-------------|-------------------|-----------------------------------------|
| 0.85                   | 0.15                                              | 0.22        | 0.15              | 4.1                                     |
| 0.65                   | 0.35                                              | 0.18        | 0.35              | 7.7                                     |
| 0.50                   | 0.50                                              | 0.14        | 0.50              | 8.6                                     |
| 0.35                   | 0.65                                              | 0.10        | 0.65              | 8.0                                     |
| 0.15                   | 0.85                                              | 0.04        | 0.85              | 4.2                                     |

The finding that the nature of the rest R of the viologene substrates **6–9** has neither a significant influence on the association constant *K<sub>a</sub>* nor on the dynamics of complexation, indicated by similar line widths in all NMR experiments [13], leads us believe that the binding event does not have to occur *via* a threading of the ribbon-type tweezer **1a** over the sidechains of the viologene substrates (mechanism A in Figure 3), but by a clipping process through the tweezer's tips over the alkane chains or the paraquat units of the substrates (mechanism B in Figure 3) [8b].

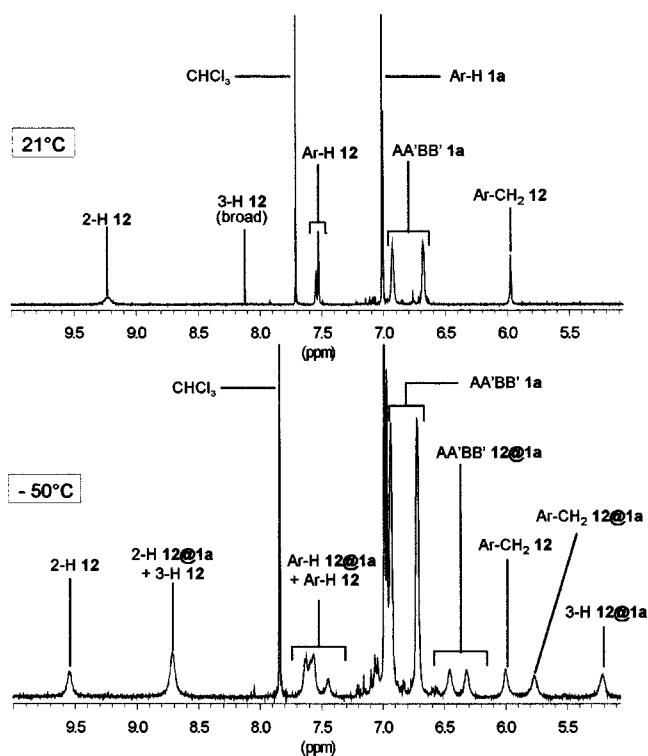


**Fig. 3** Schematic representation of the two possible mechanisms of complexation. In mechanism A the substrate enters the cavity through one of its open sides, while in mechanism B the substrate enters through the bottom after a spreading of the tweezer's tips.





**Fig. 4** Schematic representation of the possible synthetic routes to a *clipped-rotaxan*-type supermolecule **D**, which would be a stable interlocked species if the process  $C \rightarrow D$  (and *vice versa*) was not observed.



**Fig. 5** 500 MHz  $^1\text{H}$  NMR spectra of a mixture of **1a** ( $5.5 \times 10^{-3}$  M) and  $12 \cdot 2\text{PF}_6^-$  ( $2.2 \cdot 10^{-3}$  M) in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  1:1 at 21 °C (top) and -50 °C (bottom). At 21 °C the signals of the viologene protons in 2- (9.25 ppm) and 3-position (8.12 ppm) are shifted upfield with respect to their position in the absence of host **1a** (9.41 ppm [2-H], 8.67 ppm [3-H]). At -50 °C separated signals for free **12** and the complex **12@1a** can be observed.

To find out which of the supposed mechanisms is used for the complex formation of **1a** with viologene derivatives, the complexation of the potential substrates **11** and **12** was studied. Because of the bulky endgroups

(*stoppers*) of **11** and **12** a threading process (mechanism A in Figure 3) should not be possible so that if complex formation is observed, it must proceed *via* the clipping mechanism B (Figure 3).

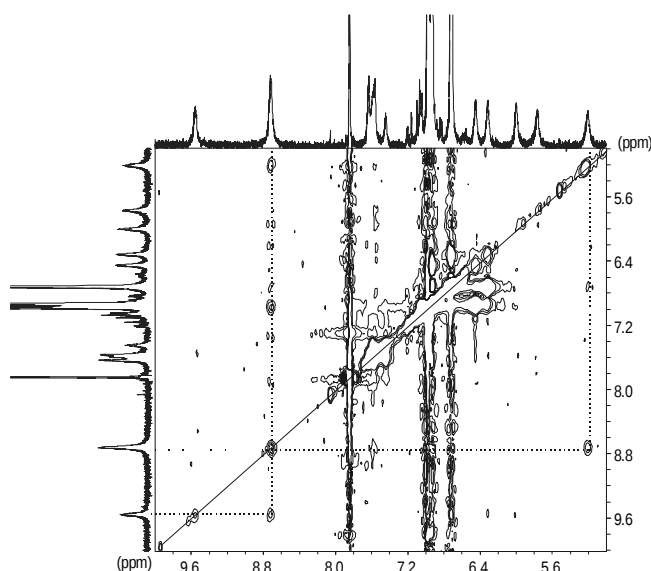
If the complex formation can only occur *via* the threading mechanism A (Figure 3) it should be possible to synthesize a thermally stable mechanically interlocked *clipped-rotaxane*-type supermolecule of type D (Figure 4).

To evaluate, if the viologene derivative **11** already equipped with 3,5-dinitrobenzoyl stopper groups forms with **1a** the complex **11@1a**, a solution of  $9 \cdot 2\text{PF}_6^-$  ( $1.5 \times 10^{-3}$  M in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$ ) was treated with 3 equivalents of 3,5-dinitrobenzoylchloride and 2 equivalents triethylamine and stirred at room temperature until full conversion leading to **11** was detected by  $^1\text{H}$  NMR [14]. Upon addition of 2 equivalents of the molecular tweezer **1a** to this solution a significant upfield shift of the  $^1\text{H}$  NMR signals of the protons of **11** in the 2- ( $\delta = 8.92$  ppm,  $\Delta\delta = 0.39$  ppm) and 3-position ( $\delta = 8.47$  ppm,  $\Delta\delta = 0.22$  ppm) as well as the  $\alpha\text{-CH}_2$ 's with respect to the nitrogen ( $\delta = 4.33$  ppm,  $\Delta\delta = 0.54$  ppm) were observed while chemical shifts of other protons were not affected. This observation demonstrates that complex formation is still possible despite the presence of the 3,5-dinitrobenzoyl stopper groups.

The complexation *via* the clipping mechanism could be demonstrated even better by the use of the dumbbell type viologene substrate **12**. Upon mixing of colorless solutions of **1a** and  $12 \cdot 2\text{PF}_6^-$  in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  1:1 an orange solid precipitates which consists of **1a** and **12** in a molar ratio of 1:1. Figure 5 shows the  $^1\text{H}$  NMR spectra of mixtures of **1a** and  $12 \cdot 2\text{PF}_6^-$  in  $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$  1:1 at room temperature and at -50 °C.

From the spectrum at 21 °C it can already be seen that **12** is complexed by **1a** and that the rate of com-

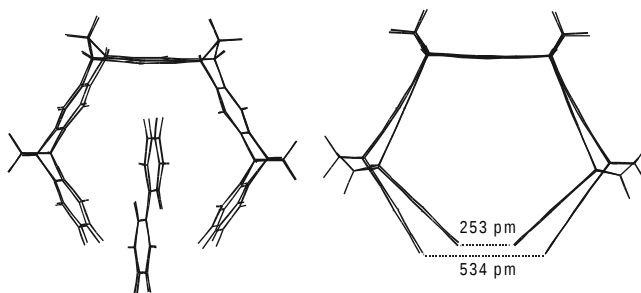
plexation is slower than that of the other viologene substrates (indicated by the line broadening of the signals assigned to **12**). At  $-50\text{ }^{\circ}\text{C}$ , however, the complexation/decomplexation equilibrium is frozen out and separated signals for free and complexed **12** can be observed. The assignment of the signals was achieved by a phase-sensitive 2D-NOESY experiment (mixing time 1.0 s) showing cross-peaks between signals involved in a dynamic exchange process (Figure 6).



**Fig. 6** 500 MHz 2D-H,H-NOESY (mixing time 1.0 s) spectrum of the same sample described in Figure 5 at  $-50\text{ }^{\circ}\text{C}$ . Dynamic exchange processes are indicated by cross peaks between corresponding peaks (see Figure 5 for assignments).

The observation that the chemically induced upfield shifts are different for **12** ( $\Delta\delta_{\text{max}}$  (3-H) = 3.50 ppm,  $\Delta\delta_{\text{max}}$  (2-H) = 0.83 ppm, and  $\Delta\delta_{\text{max}}$  ( $\alpha\text{-CH}_2$ ) = 0.19 ppm) from all other viologene substrates can be rationalized by the steric repulsion that would emerge between tweezer **1a** and the 3,5-di-*tert*-butylbenzyl substituents of **12** in a complex geometry in which the host is located at a positively charged nitrogen similar to the one depicted in Figure 1. Therefore, in the case of **12@1a** the ribbon-type tweezer **1a** seems to be located around the center of the paraquatunit to avoid this steric repulsion, thus, resulting in a large  $\Delta\delta_{\text{max}}$  for the viologene protons in the 3-position. From the coalescence of the signals at  $\delta = 5.2\text{ ppm}$  and  $8.7\text{ ppm}$  ( $\Delta\delta = 3.5\text{ ppm}$ ,  $\Delta\nu = 1750\text{ Hz}$ ) assigned to 3-H of **12** in the complex **12@1a** and free **12**, respectively, at  $(283 \pm 5)\text{ K}$  the rate constant  $k$  of the complexation/decomplexation process can be estimated to be  $k \approx 2.22 \cdot \Delta\nu = 3890\text{ s}^{-1}$  and, hence, the Gibbs activation enthalpy  $\Delta G^\ddagger$  to be ca. 12 kcal/mol. To answer the question, by how much the tweezer's tips have to spread apart from each other to allow a viologene substrate to enter the cavity through the bottom of **1a**

(mechanism B), we have performed model calculations (molecular mechanics, AMBER\* and MM3\*) with **1a** and biphenyl as a substrate. In these calculations we positioned one aromatic ring of the biphenyl substrate between the tweezer's tips, which may correspond to the transition state of the complex formation between **1a** and biphenyl, and optimized the structure. Then we measured the H–H distances between the terminal H-atoms (2-H...14-H and 3-H...13-H, respectively) and compared it to the corresponding distances calculated for the empty tweezer **1a** (Figure 7).



**Fig. 7** a) Superimposition of the energetic minima of structures calculated with the two force-fields AMBER\* and MM3\*. The model substrate biphenyl is forced to be planar, and the position of one of its rings is constrained between the tweezer's tips. b) Front view of the superimposed calculated structures (AMBER\*) of the empty tweezer (H–H distance 253 pm) and the tweezer in its spreaded geometry (534 pm). According to these calculations this spreading requires only 4.2 kcal/mol of extra strain energy.

By the use of the AMBER\* force field we calculated a spreading from 253 pm in the empty **1a** to 534 pm in the "transition state" (MM3\*: 291 to 568 pm). We also calculated that the dramatic distortion of the geometry of **1a** requires only 4.2 kcal/mol (AMBER\*) and 1.0 kcal/mol (MM3\*), respectively, of extra strain energy which demonstrates the surprising flexibility of the tweezer. In order to gain some information on the activation barrier of mechanism B, we compared the steric energies of the geometrically optimized complex biphenyl@**1a** (AMBER\*: H H distance: 410 pm,  $E = 229.2\text{ kcal/mol}$ ) with the "transition state" of the complex formation (AMBER\*: H H distance: 534 pm,  $E = 242.5\text{ kcal/mol}$ ). The difference  $\Delta E = 13.3\text{ kcal/mol}$  can be considered to be a rough estimate of the expected activation barrier. These calculations are in good agreement with the experimental findings and the results from crystal structure analyses and earlier molecular mechanics and semiempirical calculations [7, 15].

Consequently, in solution [16] none of the *clipped-rotaxane*-type supermolecule investigated here is stable at room temperature because due to the unexpected flexibility of **1a** a spreading of the tweezer's tips allows the axle to escape from the tweezer.

The experiments presented here prove that the hydrocarbon tweezer **1a** due to its electronic and topological properties [9] has the ability to selectively bind not only neutral electron-deficient aromatic and aliphatic substrates [7] but also cationic substrates in organic media by the use of multiple cation- $\pi$  interactions. We are currently investigating the binding properties of a water-soluble derivative of **1a** to transfer this novel binding motive to aqueous solutions [16].

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## Experimental

IR: Bio-Rad FTS 135. — UV: J+M Tidas FG Cosytec RS 422. —  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT H,H-COSY, C,H-COSY, NOESY, HMQC, HMBC: Bruker AMX 300, Bruker Avance DRX 500;  $^1\text{H}$  NMR titration experiments: Varian Gemini XL 200; the undeuterated amount of the solvent was used as an internal standard. When mixtures of  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  were used, the  $d_5$ -acetone peak was referenced to 2.05 ppm. — All melting points are uncorrected. — All solvents were distilled prior to use.

### Determination of $K_a$ . $^1\text{H}$ NMR titration method

In the titration experiments the total substrate concentration  $[\text{S}]_0$  is kept constant, whereas the total receptor concentration  $[\text{R}]_0$  is varied. This was done in the way, that a defined amount of the receptor R was dissolved in 0.5 ml of a solution containing the substrate concentration  $[\text{S}]_0$ .  $\Delta\delta$  is determined from the chemical shift of the pure substrate and the chemical shift of the substrate measured in the  $^1\text{H}$ -NMR spectrum (200 MHz, 21 °C) of this mixture. Successive addition of further solution containing  $[\text{S}]_0$  leads to a dilution of the concentration  $[\text{R}]_0$  in the mixture while  $[\text{S}]_0$  is kept constant. The measurement of the chemical shift of the substrate dependent from the concentration  $[\text{R}]_0$  affords the data pairs ( $\Delta\delta$  and  $[\text{R}]_0$ ). The fitting of the data to the (1:1) binding isotherme by iterative methods [10, 17], gives the parameters  $K_a$  and  $\Delta\delta_{\text{max}}$ .

### Molecular Mechanics Calculations

All calculations were performed on a SGI Indy 4400 with the program MacroModel 5.0 [20]. Optimized complex geometries were calculated from a minimum of 500 different starting geometries by the use of the MonteCarlo (MC) algorithm.

### *N,N*-Bis-(10-hydroxydecyl)-4,4'-bipyridinium hexafluorophosphate (**9**·2PF $_6^-$ )

A solution of 4,4'-bipyridine (1.6 g, 10.2 mmol) and 10-bromo-1-decanol [18] (8.0 g, 33.7 mmol) in DMF (30 mL) was heated at 140 °C under an argon atmosphere for 16 h. After cooling to room temperature the precipitated yellow dibromide **9**·2Br $^-$  (6.2 g, 96%) was filtered off, washed with dichlo-

romethane and dried *in vacuo*. For the anion exchange the crude **9**·2Br $^-$  (0.5 g, 0.8 mmol) was dissolved in methanol (30 mL), saturated aqueous ammonium hexafluorophosphate solution (ca. 5 mL) and water (20 mL) were slowly added. The precipitated colorless solid was filtered off and dried *in vacuo*. The crude product was recrystallized from acetone/water to yield **9**·2PF $_6^-$  (450 mg, 74%) as a colorless solid. — *m.p.* 265–270 °C (dec.). — IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 3602 (OH), 3139 (CH), 3073 (CH), 2923 (CH), 2851 (CH), 1644 (C=C), 833 (PF), 557 (PF). — FAB-MS (glycerine),  $m/z$  (%) = 615 (1.5) [ $\text{M}^+ - \text{PF}_6^-$ ], 470 (100) [ $\text{M}^+ - 2\text{PF}_6^-$ ], 313 (27) [ $\text{M}^+ - 2\text{PF}_6^- - \text{C}_{10}\text{H}_{20}\text{OH}$ ]. —  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta/\text{ppm}$  = 8.91 (d, 4H,  $^3J(2\text{-H}, 3\text{-H})$  = 8.0 Hz, 2-H), 8.38 (d, 4H, 3-H), 4.62 (t, 4H,  $^3J(5\text{-H}, 6\text{-H})$  = 7.4 Hz, 5-H), 3.47 (m, 4H,  $^3J(13\text{-H}, 14\text{-H})$  = 7.4 Hz, 14-H), 2.45 (t, 2H,  $^3J(\text{O-H}, 14\text{-H})$  = 6.5 Hz, O-H), 1.99 (m, 4H, 6-H), 1.25–1.55 (m, 28 H). —  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta/\text{ppm}$  = 26.43 (t), 26.53 (t), 29.48 (t), 29.87 (t), 30.06 (t), 30.08 (t), 31.84 (t), 33.50 (t), 62.50 (t), 63.05 (t), 128.09 (d, C-3), 146.46 (d, C-2), 150.82 (s, C-4).  $\text{C}_{30}\text{H}_{50}\text{F}_{12}\text{N}_2\text{O}_2\text{P}_2$  Calcd.: C 47.37 H 6.63 N 3.68 (760.67) Found: C 47.59 H 6.64 N 3.45.

### *N,N*-Bis-(3,5-di-*tert*-butylbenzyl)-4,4'-bipyridinium hexafluorophosphate (**12**·2PF $_6^-$ )

A solution of 4,4'-bipyridine (1.7 g, 11.0 mmol) and 1-bromomethyl-3,5-di-*tert*-butylbenzene [19] in acetonitrile (20 mL) was heated under reflux for 3 h. After cooling to room temperature the solidified reaction mixture is diluted with dichloromethane (50 mL), and the yellow dibromide **12**·2Br $^-$  (7.5 g, 95%) is filtered off and dried *in vacuo*. For the anion exchange the crude **12**·2Br $^-$  (0.50 g, 0.78 mmol) was suspended in water (20 mL), and methanol was added slowly until all of the dibromide is dissolved. Saturated aqueous ammonium hexafluorophosphate solution (ca. 0.5 mL) was added slowly, the precipitated crude product filtered off, washed thoroughly with water and dried *in vacuo* to yield **12**·2PF $_6^-$  (0.55 g, 93%) as a colorless solid. — *m.p.* 235–238 °C. — IR (KBr):  $\tilde{\nu}/\text{cm}^{-1}$  = 3137 (CH), 3072 (CH), 2960 (CH), 2905 (CH), 2867 (CH), 1638 (C=C), 833 (PF), 557 (PF). —  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/d_6\text{-Aceton}$  1:2):  $\delta/\text{ppm}$  = 1.28 (s, 36H, *t*-Butyl-H), 6.06 (s, 4H, benzyl-H), 7.54 (s, 6H, 2-toluy-H, 4-toluy-H), 8.71 (d, 4H,  $^3J(2\text{-H}, 3\text{-H})$  = 9.0 Hz, 3-bipy-H), 9.45 (d, 4H, 2-H). —  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3/d_6\text{-Aceton}$  1:2):  $\delta/\text{ppm}$  = 30.87 (q), 34.78 (s), 65.65 (t), 123.82 (d, toluy-C-2), 124.14 (s, toluy-C-3), 127.44 (d, toluy-C-4), 131.20 (s, toluy-C-1), 145.65 (d, bipy-C-3), 150.04 (s, bipy-C-4), 152.44 (d, bipy-C-2).  $\text{C}_{40}\text{H}_{54}\text{F}_{12}\text{N}_2\text{P}_2$  Calcd.: C 56.34 H 6.38 N 3.28 (852.19) Found: C 56.12 H 6.40 N 3.33.

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