closing metathesis. The RCM reactions can be greatly accelerated by the addition of HCl which is believed to generate the highly reactive complex **2** in solution.

Experimental Section

3: Complex **1** (0.91 mmol) and KO*t*Bu (3.2 mmol) were combined in C_6H_6 (30 mL). The reaction mixture was stirred for 24 h during which time it changed color from purple to brownish red. The solvent was frozen and removed by sublimation under vacuum. The resulting solids were suspended in a mixture of C_6H_6 (0.5 mL) and pentane (50 mL). CuCl (9.1 mmol) was added, and the suspension was stirred for 20 min, and then cooled at $-30\,^{\circ}C$ for 24 h. The supernatant solution was decanted and the solvent removed under vacuum to give **3** as a dark brown foamy solid (52 % yield). This solid is typically about 95 % pure (by ^{31}P NMR), and contains traces of $CuCl(PCy_3)$ polymer. ^1H NMR (400 MHz, C_6D_6): $\delta = 15.5$ (d, $^3J_{P,H} = 4.4$ Hz, 1H, Ru=CH), 7.88 (d, $^2J_{H,H} = 7.3$ Hz, 2H, *ortho*-H), 7.27 (t, $^2J_{H,H} = 7.3$ Hz, 1H, *meta*-H), 7.17 (s, 2H, *para*-H), 2.4 – 1.1 (m, 33H, PCy_3), 1.29 (s, 9H, *t*Bu); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): $\delta = 83.5$ (s); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 230.5$ (d, $^2J_{P,C} = 15.2$ Hz, Ru=C), 152.1, 129.9, 125.3, 124.6, 74.50, 36.69, 34.57, 34.48, 34.14, 33.68, 33.44, 31.52, 29.61, 28.84, 28.70, 28.51, 28.37, 27.48, 27.24.

4: Hexafluoro-*tert*-butanol (0.5 mL) was added to a solution of complex **3** (0.41 mmol) in pentane (25 mL). The reaction was stirred for 30 min then cooled to $-30\,^{\circ}C$ for 24 h. The supernatent solution was decanted and the solvents were removed under vacuum to give an oily dark brown solid. The product was recrystallized from a minimum volume of pentane to afford reddish crystals of **4** (40 % yield). ^1H NMR (400 MHz, C_6D_6): $\delta = 17.5$ (s, 1H, Ru=CH), 7.88 (d, $^2J_{H,H} = 5.9$ Hz, 2H, *ortho*-H), 7.14 (m, 3H, *meta*-H and *para*-H), 2.4 – 1.1 (m, 33H, PCy_3); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): $\delta =$ 80.1 (s);. ^{19}F NMR (283 MHz, C_6D_6): $\delta = -77.93$ (s), -79.27 (s); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 262.6$ (d, $^2J_{P,C} = 18$ Hz, Ru=C), 150.6, 131.0, 130.4, 126.1 (q, $^1J_{F,C} = 288$ Hz), 125.4 (q, $^1J_{F,C} = 288$ Hz), 124.5, 34.33, 34.00, 29.49, 28.40, 28.26, 27.02, 20.46; elemental analysis calcd (%) for $C_{33}H_{45}F_{12}O_2PRu$: C 47.54, H 5.44; found: C 47.19, H 5.41.

5: The same procedure as for complex **4**, but using perfluoro-*tert*-butanol, afforded **5** as a reddish microcrystalline solid (37 % yield). ^1H NMR (400 MHz, C_6D_6): 19.2 (s, 1H, Ru=CH), 7.72 (d, $^2J_{H,H} = 7.34$ Hz, 2H, *ortho*-H), 7.14 (m, 3H, *meta*-H and *para*-H), 2.1 – 0.8 (m, 33H, PCy_3); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): $\delta = 75.1$ (s); ^{19}F NMR (283 MHz, C_6D_6): $\delta =$ -73.55 (s); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 286.5$ (d, $^2J_{P,C} = 15.2$ Hz, Ru=C), 151.4, 130.0, 129.6, 125.6, 123.0 (q, $^1J_{F,C} = 292$ Hz), 35.20, 34.90, 32.23, 31.91, 31.66, 31.63, 29.91, 28.34, 28.21, 27.95, 27.80, 26.94, 26.75; elemental analysis calcd (%) for $C_{33}H_{39}F_{18}O_2PRu$: C 42.09, H 4.17; found: C 41.60, H 4.18.

Crystal Structure of **3**: Dark red-brown blades were grown from pentane: $C_{33}H_{57}O_2PRu$ (617.83), crystal dimensions: $0.21 \times 0.16 \times 0.03$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.0120(7)$, $b = 20.5338(14)$, $c =$ 15.7802(11) Å, $\beta = 92.1300(10)^{\circ}$, $Z = 4$, $V = 3241.9(4)$ Å^3, $\rho_{calc} =$ 1.266 mg m^{-3}, $T = 93$ K, $2\Theta = 57.5^{\circ}$, 29820 reflections were measured, 7759 independent reflections were obtained ($R_{int} = 0.0683$) on a Bruker SMART diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods,[13a] with refinement by full-matrix least squares of F^2 [13b]: $R_1 = 0.0328$, $wR_2 = 0.0527$ (for $I > 2\sigma(I)$), $R_1 = 0.0611$, $wR_2 = 0.0569$ (for all data), residual electron density : $+0.632/-0.510$ e Å^{-3}. 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-140726. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk), and structure factors are available on request from xray@caltech.edu.

Received: May 16 2000 [Z15131]

[1] K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, New York, **1997**.

[2] a) E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887 – 3897; b) M. Ulman, R. H. Grubbs, *J. Org. Chem.* **1999**, *64*, 7202 – 7207.

[3] O. M. Aagaard, R. J. Meier, F. Buda, *J. Am. Chem. Soc.* **1998**, *120*, 7174 – 7182.

[4] a) R. R. Schrock, *Polyhedron* **1995**, *14*, 3177 – 3195; b) R. R. Schrock, *Tetrahedron* **1999**, *55*, 8141 – 8153.

[5] D. M. Lynn, B. Mohr, R. H. Grubbs, *J. Am. Chem. Soc.* **1998**, *120*, 1627 – 1628.

[6] For a comprehensive review see: K. G. Caulton, *New J. Chem.* **1994**, *18*, 25 – 41.

[7] P. Schwab, J. Ziller, R. H. Grubbs, *J. Am. Chem. Soc.* **1996**, *118*, 100 – 110.

[8] For example, see: S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974 – 3975.

[9] Representative examples of Ru···CH agostic interactions include: a) S. Takahashi, S. Hikichi, M. Akita, Y. Moro-oka, *Organometallics* **1999**, *18*, 2571 – 2573; b) M. A. Bennett, S. Pelling, G. B. Robertson, W. A. Wickramaginghe, *Organometallics* **1991**, *10*, 2166 – 2172.

[10] a) D. J. Huang, K. Folting, K. G. Caulton, *J. Am. Chem. Soc.* **1999**, *121*, 10318 – 10322; b) D. J. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter, T. Scheiring, *J. Am. Chem. Soc.* **1999**, *121*, 8087 – 8097; c) W. Baratta, E. Herdtweck, P. Rigo, *Angew. Chem.* **1999**, *111*, 1733 – 1735; *Angew. Chem. Int. Ed.* **1999**, *38*, 1629 – 1631.

[11] Complexes **4** and **5** have also been characterized by X-ray crystallography, and their structures are qualitatively similar to that of **3**. However, reliable bond lengths and angles could not be determined because of the extreme disorder of the CF_3 groups in both molecules.

[12] We have attempted to study the binding of other ligands (including THF, PMe_3, and CH_3CN) to these complexes. Complexes **2** – **4** do not appear to bind THF, while the other ligands lead to decomposition or to a mixture of products.

[13] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1968**, *46*, 467 – 473; b) G. M. Sheldrick, SHELXL-97: Program for Structures Refinement, University of Gottingen, Germany, **1997**.

Calix[6]arene as a Wheel for Rotaxane Synthesis**

Arturo Arduini, Riccardo Ferdani, Andrea Pochini,* Andrea Secchi, and Franco Ugozzoli

Rotaxanes and catenanes[1] are interesting supermolecules that have been extensively studied for their use in the preparation of molecular switches. A possible approach to their synthesis is based on the formation of an axial complex between a molecular wheel that is used as the host and a specific guest that is employed as the axle.

[*] Prof. A. Pochini, Prof. A. Arduini, Dr. R. Ferdani, Dr. A. Secchi
Dip.to di Chimica Organica e Industriale dell'Università
Parco Area delle Scienze
17/A, 43100, Parma, (Italy)
Fax: (+39) 0521-905472
E-mail: pochini@unipr.it

Prof. F. Ugozzoli
Dip.to di Chimica Generale e Inorganica Chimica Analitica Chimica Fisica
Università di Parma and Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.
Parco Area delle Scienze, 17/A, 43100 Parma (Italy)

[**] We thank MURST for financial support within the "Supramolecular Devices" project and C.I.M. of the University of Parma for mass and NMR measurements.

In this context calixarenes, which are versatile and potent receptors, have never been used as molecular wheels and, in spite of their similarity to cyclodextrins,[2] no examples of axial complexation where all their inner binding sites are simultaneously involved in the binding of the guest have been reported. In fact the two rims in these macrocycles have usually been considered as distinct and separate domains.[3] Examples exist in which the two calixarene rims have been shown to act in a combined manner, for example, in the recognition of both cations and anions[4] or to exchange information between them.[5] A rational approach to the synthesis of a calixarene-based rotaxane was thus undertaken to explore the possibility of utilizing a calixarene receptor as a molecular wheel.

The calix[6]arene platform was chosen on the basis of its ring size and because it posseses an annulus large enough to allow a sufficiently bulky and elongated guest to cross the two rims. On the basis of our previous studies on the binding ability of calix[6]arene derivatives[6] compound **1**,[7] which is "preorganized" by the presence of 1,3,5-trimethoxy-2,4,6-trioctyloxy groups on the lower rim[8] and bears three phenylureido groups which extend the apolar cavity, was chosen as the wheel and the dioctylviologen dication was selected as the axle (Scheme 1).

Direct experimental evidence of complex formation and consequently of the passage of the guest through the macrocycle annulus was obtained by extraction experiments and ^{1}H NMR studies on the complex formed. The triphenylureidocalix[6]arene derivative **1** is able to dissolve the colorless crystals of dioctylviologen ditosylate (**2a**) in chloroform to afford a deep purple solution. Similar results were obtained by using the dioctylviologen diiodide.[9] The ^{1}H NMR spectrum of the solution obtained by equilibrating a suspension of dioctylviologen diiodide (**2b**) in $CDCl_3$ with a solution of **1** showed the formation of a 1:1 adduct. The main features of the NMR spectrum (Figure 1) are the extensive upfield shift (1 to 3 ppm) of the signals corresponding to the aromatic CH and NCH_2 hydrogen atoms of the guest, which indicates that it is included inside the calix[6]arene cavity. The six protons of the host ureido groups suffer a downfield shift from $\delta = 6.7$ and 7.1 to $\delta = 8.00$ and 8.33, respectively, which suggests their participation in hydrogen-bonding interactions with the two iodine anions. Particularly informative was the observation that the protons of the methoxy groups present at the lower rim of **1**, which resonate at $\delta = 2.82$ in the free calixarene because they are oriented into the calixarene cavity, are shifted downfield ($\Delta\delta = 1.12$) in the complex. This observation indicates that their orientation has changed to a situation where they are no longer affected by the shielding effect of the aromatic cavity.

These data, together with 2D NMR experiments, could be rationalized with the hypothesis that a pseudorotaxane[1] **3** was formed (Scheme 1). Evidence for the stability of this complex came from

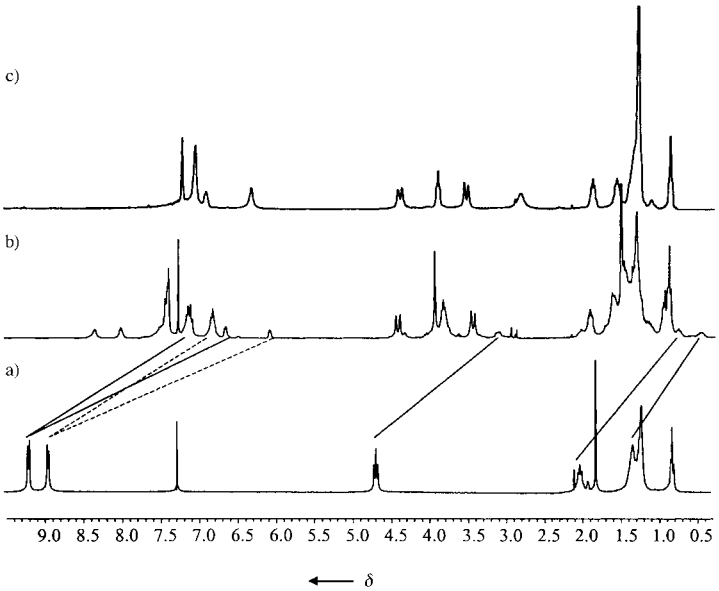
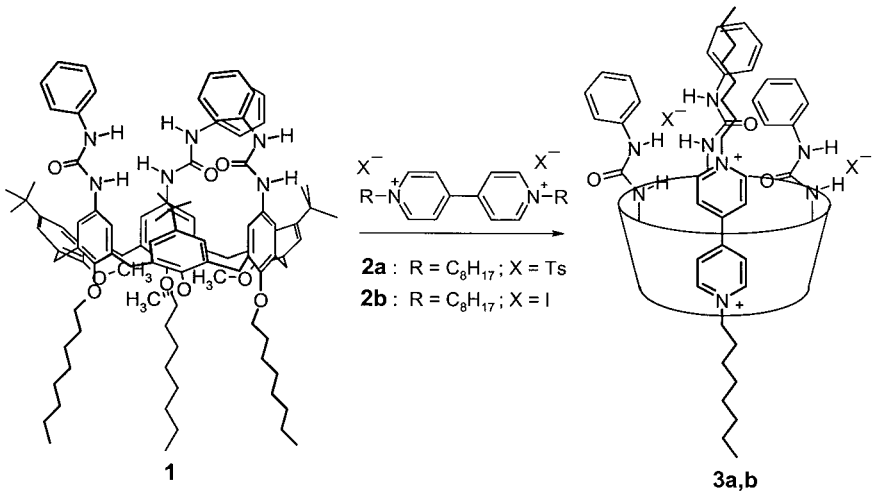


Figure 1. ^{1}H NMR spectra (300 MHz, 300 K) of: a) dioctylviologen diiodide (**2b**) in 10% $CD_3CN/CDCl_3$; b) pseudorotaxane **3b** in $CDCl_3$; c) triphenylureidocalix[6]arene (**1**) in $CDCl_3$.

thin layer chromatography which showed that it was possible to separate the complex in aprotic solvents without competitive decomplexation processes occurring. The slow evaporation of the solution containing host **1** and **2b** gave red crystals of **3b** that were suitable for X-ray analysis (Figure 2).[10] Analysis of the structure shows that all the binding sites present in the host are involved in the stabilization of the supramolecular structure (Figure 3). The N1 atom is located 0.399(6) Å above the least-squares plane through the bridging methylene groups of the calixarene and points its attached octyl chain across the lower annulus of the macrocycle, thus expelling the three methoxy groups from the aromatic cavity. The lower pyridinium ring of the guest is sandwiched and stacked by rings F and B of the host (the distance between the centroids of these rings is 6.810(8) Å) and is almost perpendicular to rings A and D of the host. The two hydrogen atoms on C1 and C5 of the guest and the two hydrogen atoms of the octyl chain (C11) are involved in hydrogen-bonding inter-



Scheme 1. Synthesis of pseudorotaxanes **3a**,**b**.

  0044-8249/00/11219-3596 $ 17.50+.50/0

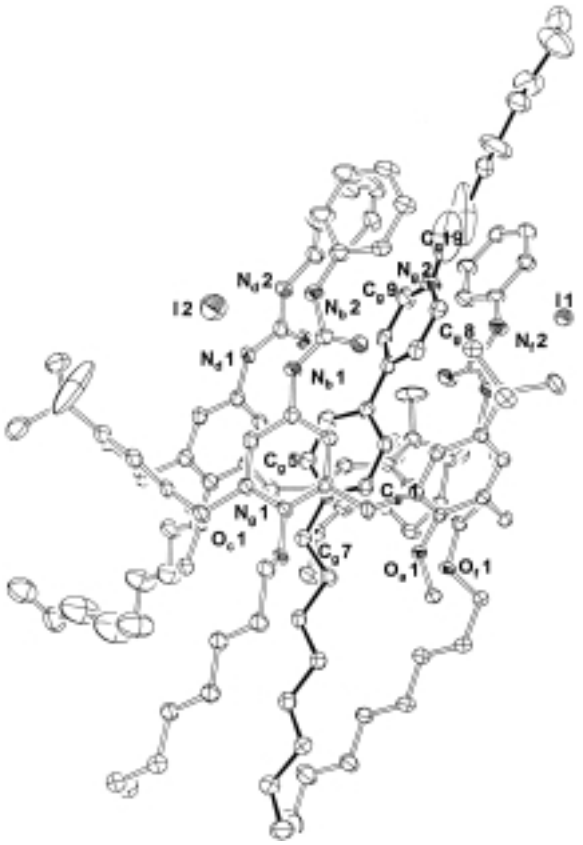


Figure 2. X-ray crystal structure of pseudorotaxane **3b** at 173 K. The hydrogen atoms are omitted for clarity, and the bonds of the guest are darkened for clarity.

actions with the three oxygen atoms of the host methoxy groups. The hydrogen atoms on C8 of the upper ring of the guest as well as one of those belonging to C19 form CH–π interactions with the phenyl groups D′ (2.639(8) Å) and B′ (2.641(8) Å), respectively. The two iodide ions also participate in the assembly process through hydrogen-bonding interactions with the NH ureido groups of the host.

The formation of the pseudorotaxane was then exploited to synthesize a rotaxane.[11] Refluxing the diol axle **4** and wheel **1** in toluene gave an homogeneous deep red solution. This solution was then treated with diphenylacetyl chloride, which acted as the stopper (Scheme 2). Purification of the reaction mixture gave the rotaxane **5** in 25% yield. The ^{1}H NMR spectrum of **5** was very similar to that of the pseudorotaxane. The presence of a singlet at $\delta = 5.05$, a multiplet at $\delta = 7.29$, and a triplet at $\delta = 4.17$ for the ω CH_2 protons are indicative of the introduction of the two stoppers

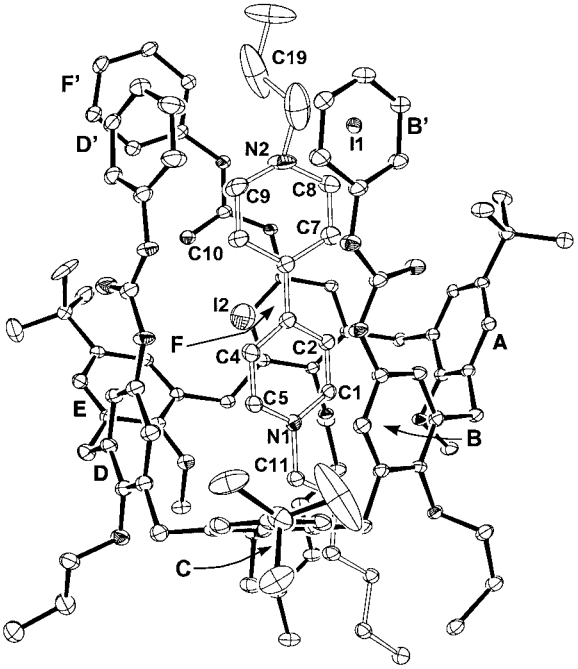
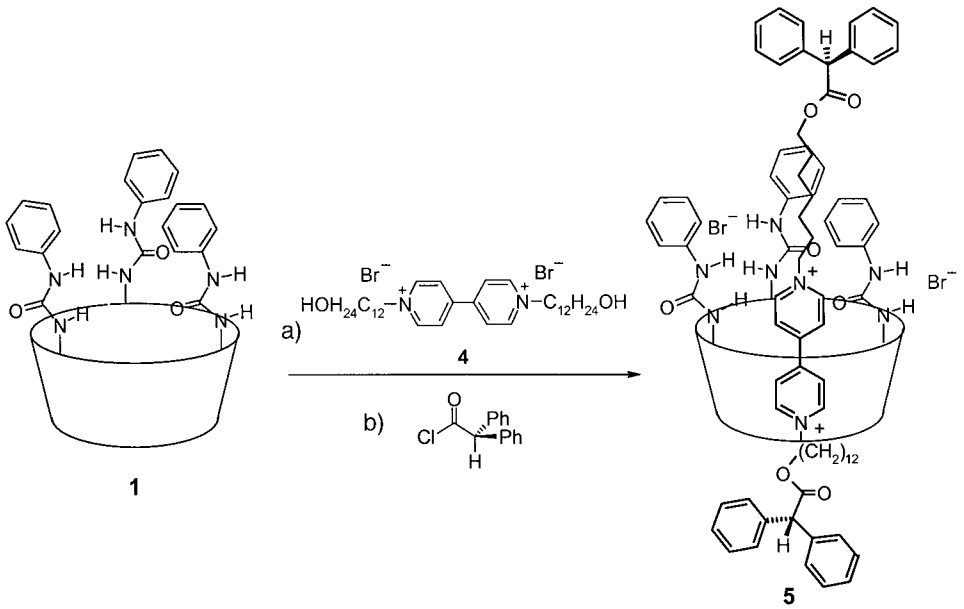


Figure 3. Structure of **3b** showing the numbering of the atoms and groups; part of the host strucure is omitted for clarity.

at the ends of the axle. The ESI-MS spectrum and the elemental analysis of **5** are in agreement with the proposed structure.

Further studies to understand the role of the single interactions which stabilize and drive the formation of these unprecedented calixarene complexes and to extend the field of application to other calixarenes and ammonium salts to the preparation of molecular switching systems are in progress in our laboratories.

Received: April 25, 2000 [Z15026]



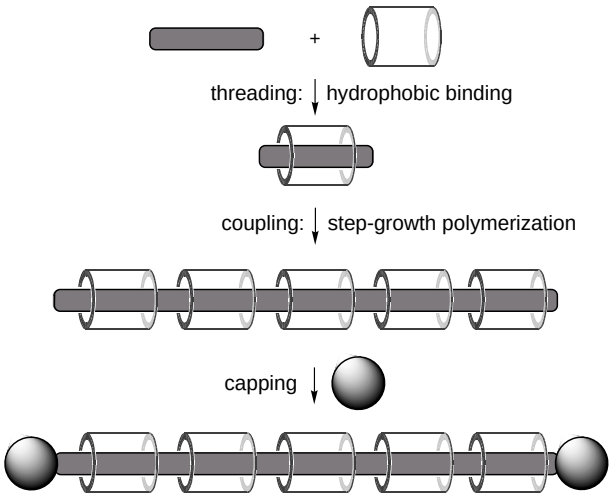
Scheme 2. Synthesis of rotaxane **5**. a) toluene, reflux, 24 h; b) toluene, reflux, 72 h.

[1] See, for example, a) F. M. Raymo, J. F. Stoddart, *Chem. Rev.* **1999**, *99*, 1643; b) C. Seel, F. Vögtle, *Chem. Eur. J.* **2000**, *6*, 21, and references therein.
[2] a) *Comprehensive Supramolecular Chemistry*, *Vol. 3* (Eds.: J. Szejtli, T. Osa), Pergamon, Oxford, **1996**; b) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959.
[3] C. D. Gutsche *Calixarenes Revisited—Monograph in Supramolecular Chemistry* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1998**.
[4] See, for example, a) J. Scheerder, J. P. M. van Duynhoven, J. F. J. Egbersen, D. N. Reinhoudt, *Angew. Chem.* **1996**, *108*, 1172; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1090; b) N. Pelizzi, A. Casnati, A. Friggeri, R. Ungaro, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1307.
[5] See, for example, a) R. Castro, L. A. Godìnez, M. C. Criss, A. E. Kaifer, *J. Org. Chem.* **1997**, *62*, 4928; b) A. Mirzoian, A. E. Kaifer, *Chem. Eur. J.* **1997**, *3*, 1052; c) A. Ikeda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 3102; d) K. N. Koh, K. Araki, S. Shinkai, Z. Asfari, J. Vicens, *Tetrahedron Lett.* **1995**, *36*, 6095; e) A. Ikeda, T. Tsudera, S. Shinkai, *J. Org. Chem.* **1997**, *62*, 3568.
[6] See, for example, A. Arduini, L. Domiano, L. Ogliosi, A. Pochini, A. Secchi, R. Ungaro, *J. Org. Chem.* **1997**, *62*, 7866.
[7] Triureidocalix[6]arene (**1**) was synthesized as described in J. J. Gonzàlez, R. Ferdani, E. Albertini, J. M. Blasco, A. Arduini, A. Pochini, P. Prados, J. de Mendoza, *Chem. Eur. J.* **2000**, *6*, 73.
[8] J. P. M. van Duynhoven, R. G. Janssen, W. Verboom, S. M. Franken, A. Casnati, A. Pochini, R. Ungaro, J. de Mendoza, P. M. Nieto, P. Prados, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1994**, *116*, 5814.
[9] The ditosylate of dioctylviologen is a colorless solid which is very insoluble in $CDCl_3$. As a result its diodide, which is a deep purple solid, was used because of its better solubility and sharper NMR spectra.
[10] X-ray structural analysis was performed on an Enraf Nonius CAD4 diffractometer with graphite monochromated $Cu_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data collection and refinement for $C_{128}H_{174}I_2N_8O_9$ at 173 K: transparent plate $0.20 \times 0.40 \times 0.5$ mm^3, triclinic, space group $P\bar{1}$ no. 2, $a = 15.407(5)$, $b = 27.122(5)$, $c = 14.688(5)$ Å, $\alpha = 94.65(2)$, $\beta = 90.83(2)$, $\gamma = 75.88(2)^\circ$, $V = 5933(3)$ Å^3, $Z = 2$, $M_r = 2222.64$, $\rho_{calcd} = 1.244$ g cm^{-3}, $\mu = 5.9$ cm^{-1}, $\theta_{max} = 65$, 21 077 reflections were collected ($\pm h, \pm k, +l$), of which 20 151 were unique ($R_{int} = 0.06$) and 11 677 observed ($F_o > 4\sigma(F_o)$). The structure was solved by direct methods using SIR92 (A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined on F using SHELXL-96 software (G. M. Sheldrick, *SHELXL-96*, University of Göttingen, Germany, **1996**). Data were corrected for Lorentz and polarization effects. Absorption correction was applied by Ψ scan measurements (min/max transmission factor = 0.75). The terminal aliphatic chains on the phenol oxygen atoms were affected by severe static disorder arising from several slightly different orientations. It proved impossible to rationalize the disorder in terms of different orientations with different site occupancy factors and the refinement was carried out with geometrical constraints on the chains. All non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogen atoms were taken in their calculated positions "riding" on their parent atoms (1346 parameters, 30 constraints). Final $R_1 = 0.092$ and $wR_2 = 0.294$ with GOF = 0.984. Largest difference peak and hole 1.77 and -2.92 e Å^{-3}, respectively. Geometrical calculations were obtained by PARST95 (M. Nardelli, *J. Appl. Crystallogr.* **1995**, *28*, 659). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141315. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[11] Calix[4]arene has been used as a stopper for rotaxane synthesis: C. Fischer, M. Nieger, O. Mogck, V. Böhmer, R. Ungaro, F. Vögtle, *Eur. J. Org. Chem.* **1998**, 155.

Insulated Molecular Wires: Synthesis of Conjugated Polyrotaxanes by Suzuki Coupling in Water**

Peter N. Taylor, Michael J. O'Connell, Luke A. McNeill, Michael J. Hall, Robin T. Aplin, and Harry L. Anderson*

The semiconductivity and fluorescence of conjugated polymers result in potential applications, particularly in the area of electroluminescent display devices.[1] We are interested in enhancing the luminescence, stability, and processability of these polymers by threading them through macrocycles to form conjugated polyrotaxanes, as a type of "insulated molecular wire".[2, 3] Recently we proposed the general route to conjugated polyrotaxanes outlined in Scheme 1. Hydrophobic binding fixes the monomer inside



Scheme 1. Hydrophobic binding directs the synthesis of an insulated molecular wire.

the cavity of a macrocycle, this 1:1 pseudorotaxane complex is then polymerized to form a conjugated polypseudorotaxane, which is coupled to bulky end groups to give the polyrotaxane. Our initial attempts at realizing this scheme used a cationic cyclophane as the macrocycle and Glaser coupling as the polymerization reaction. This failed to give polyrotaxanes higher than the [3]rotaxanes, due to problems of unthreading, aggregation, and precipitation of the growing polymer

[*] Dr. H. L. Anderson, Dr. P. N. Taylor, M. J. O'Connell, Dr. L. A. McNeill, M. J. Hall, Dr. R. T. Aplin
University of Oxford
Department of Chemistry, Dyson Perrins Laboratory
South Parks Road, Oxford OX1 3QY (UK)
Fax: (+44) 1865-275674
E-mail: harry.anderson@chem.ox.ac.uk

[**] We are grateful to Carol A. Stanier for valuable discussion and to Professor Christopher J. Schofield for providing facilities for gel electrophoresis. Disodium 1-aminonaphthalene-3,6-disulfonate was generously provided by Dr. M. G. Hutchings of BASF plc (Cheadle Hulme, UK). This project is funded by the Engineering and Physical Sciences Research Council (UK).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

  0044-8249/00/11219-3598 $ 17.50+.50/0