Computational Details

We have used Unix versions of the Gaussian 94[17] and Gamess USA[18] programs installed on an Alphaserver 1200 Compaq machine. The geometry optimizations and frequency calculations performed at the second-order Møller–Plesset[19] level of theory (including the inner shell electrons for the correlation) were based on analytical gradients and second derivatives, whereas the geometry optimizations performed at the coupled cluster[20] level of theory (including the contribution of single and double excitations, and an estimate of connected triples) were based on the algorithm by Fletcher and Powell.[21] The optimization of $FBeHe^+$ performed at the MCQDPT level of theory[22] was based on a numerical grid of 0.05 Å size. The reference wavefunction, expanded on RHF orbitals within the C_{2v} Abelian subgroup, was derived from an active space of 12 electrons in 10 orbitals. The MP2(FULL)/6-31G(d) geometries were used to calculate the G3 total energies following the procedure described in the literature.[10] With respect to the previous G2 theory,[23] G3 significantly improves the calculation of the thermochemical properties of molecules such as CF_4, SiF_4, and NF_3. Therefore, the G3 thermochemical properties of the $FBeNg^+$ adducts should be accurate to within less than 2 kcal mol^{-1}.

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Self-Assembly of Rotaxane-Like Complexes with Macrocycles Containing Reversible Coordinate Bonds**

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Remarkable advances in noncovalent and covalent chemistry have led to the efficient synthesis of various interlocked and intertwined supramolecular species with new functions.[1] Rotaxanes are supermolecules composed of two distinct molecular components—a beadlike molecule and a dumbbell-shaped molecule—which possess mutual recognition motifs that exert weak intermolecular forces when they are assembled in a threading mode. The beadlike components used for the synthesis of rotaxanes to date are all covalently bonded macrocycles such as cyclodextrins, crown ethers, cucurbituril, and cationic or neutral cyclophanes.[1] Although a variety of transition metal bridged macrocycles were reported over the last decade,[2] none has been employed yet for the construction of rotaxanes.[3] This is possibly due to the lack of driving forces for the formation of rotaxane-like assemblies, or because of self-aggregation into other supramolecular species such as catenanes.[4] When macrocycles that are bridged by coordinate bonds are employed as bead molecules instead of conventional covalent macrocycles, an additional feature of the resulting rotaxanes is that the formation and dissociation might be reversibly controlled under certain conditions. In addition, the kinetic stability of rotaxanes could also be controlled by modifying the coordination sites of the ligands or by selecting an appropriate combination of transition metal and ligand. Here we report for the first time the reversible formation of rotaxane-like complexes from macrocycles that contain weak coordinate bonds.

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

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The mononuclear macrocycle **1a** (Figure 1), the bead component of the rotaxane, was self-assembled from osmium tetraoxide, 2,3-dimethyl-2-butene, and the precursor bis-pyridyl ligand.[5,6] Upon mixing **1a** (2 mM) with approximately

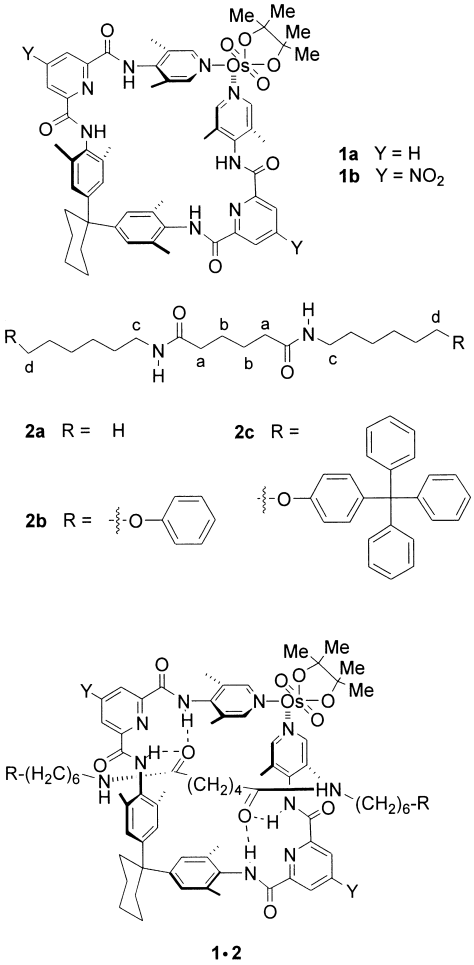

Figure 1. Macrocycles **1a**–**b**, threads **2a**–**c**, and schematic depiction of complexes **1**·**2**.

one equivalent of **2a** in $CDCl_3$ at $23 \pm 1\,^{\circ}C$, two NH signals of **1a** were shifted downfield ($\Delta\delta = 0.75$ and 0.88) as a result of hydrogen-bond formation. More importantly, the upfield shift of the H_a and H_b signals of **2a** ($\Delta\delta > 0.5$) strongly suggested that the adipic amide moiety of **2a** is inserted into the cavity of **1a**. These observations are consistent with the X-ray crystal structure (Figure 2),[7] which clearly shows a pseudo-rotaxane complex, stabilized by four N–H···O=C hydrogen bonds in which the N–H protons of **1a** are located near the π electrons rather than near the lone-pair electrons of the carbonyl groups.[8]

We then prepared two dumbbell-shaped threads **2b** and **2c**, which possess phenoxy and 4-tritylphenoxy stoppers at the ends, respectively. The former stopper is small enough to penetrate into the cavity of **1a**, but the latter is too bulky to pass through the cavity. The changes in the ^1H NMR spectrum of **2b** in $CDCl_3$ on addition of the macrocycle **1a** were similar to those observed for **2a**; time-averaged ^1H NMR signals for the free and complexed species were obtained (Figure 3b).

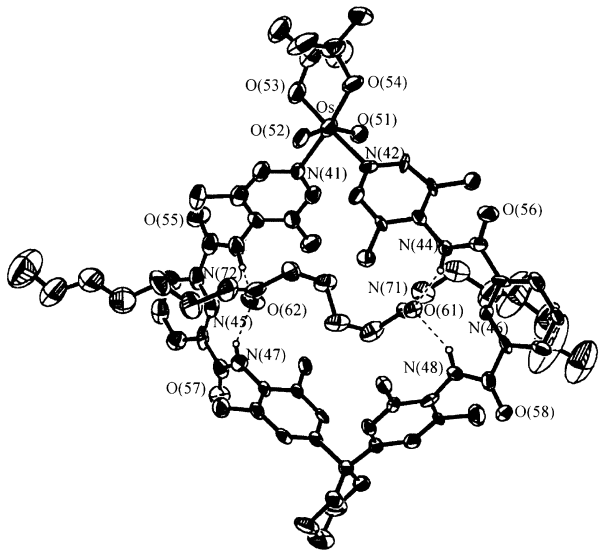

Figure 2. X-ray crystal structure of pseudo-rotaxane complex **1a**·**2a**. The dotted lines indicate hydrogen bonds, of which the N···O distances are 2.81–2.93 Å. All CH hydrogen atoms are omitted for clarity.

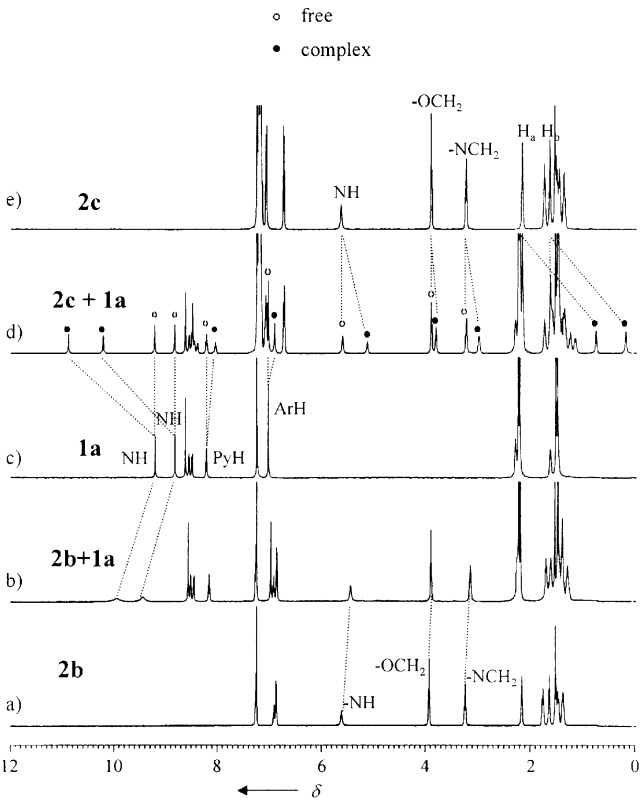

Figure 3. ^1H NMR spectra (500 MHz, $CDCl_3$, 23 °C) of a) **2b** (2 mM), b) **2b** (2 mM) + **1a** (2 mM), c) **1a** (2 mM), d) **1a** (2 mM) + **2c** (2 mM), and e) **2c** (2 mM).

The thread **2c**, with its much bulkier stopper, however, showed completely different behavior from **2a** and **2b** in the ^1H NMR spectrum (Figure 3d). The sharp and widely separated signals observed with thread **2c** indicate that the formation and dissociation of the complex **1a**·**2c** are slow on the NMR timescale. Two NH signals of complexed **1a** are shifted downfield relative to free **1** ($\Delta\delta = 1.40$ and 1.68) as a result of hydrogen-bond formation. Furthermore, the H_a and

H_b signals of complexed **2c** appear in the far upfield region ($\delta\delta = 0.77$ and 0.20, respectively), and this indicates that these hydrogen atoms are located inside the cavity and surrounded by the aryl walls of **1a**, as a result of the formation of a rotaxane-like assembly. The binding constants between the macrocycle **1a** and the threads **2a–c**, measured in $CDCl_3$ at $23 \pm 1\,^{\circ}C$ by ^1H NMR titration (**2a** and **2b**)[9] or ^1H NMR integration (**2c**),[10] were $(1.3 \pm 0.1) \times 10^3\,M^{-1}$ for **2a**, $(9.0 \pm 0.5) \times 10^2\,M^{-1}$ for **2b**, and $(5.6 \pm 0.6) \times 10^2\,M^{-1}$ for **2c**. The values depend only slightly on the size of the stoppers at the remote ends of the threads ($\Delta\Delta G^0 < 0.5$ kcal mol^{-1}).

Since the macrocycle **1a** contains weak, reversible Os^{VI}–N coordinate bonds, two pathways are possible for formation of complexes with threads (Figure 4). One is a slipping process in

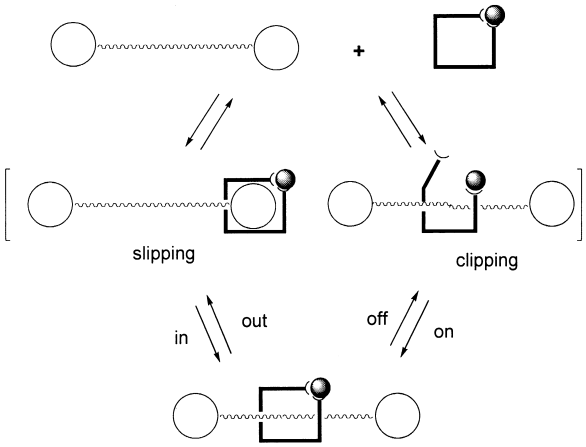

Figure 4. Schematic representation of two possible pathways for the formation and dissociation of complexes **1**·**2**.

which the threads are squeezed in and out the cavity of the macrocycle. The other is a clipping process that involves the dissociation of the Os^{VI}–N coordinate bond, followed by the formation of intermediate complexes, and finally the reconstruction of the coordinate bond. Both processes are possible for **2a** (no stopper) and **2b** (small stopper). However, only the clipping process is possible when the stopper is too bulky to pass through the cavity of **1a**, as in **2c**. The ^1H NMR spectra (Figure 3) clearly indicate that the rate of interconversion between the free species and the complex of **1a** and **2a** (or **2b**) is faster than that with **2c**, and this implies that the slipping process is faster than the clipping process. For quantitative comparison, an EXSY experiment[11] was performed on the complex **1a**·**2c**, and the activation barrier $\Delta G^{\ddagger}$ for the exchange process between the free species and the complex was calculated to be 15.5 ± 0.1 kcal mol^{-1} at 296 K, which corresponds to a rate constant k of $24 \pm 4\,s^{-1}$. The energy barrier $\Delta G^{\ddagger}$ for the binding process of **1a** and **2b** was 12.3 ± 0.1 kcal mol^{-1}, based on the coalescence temperatures of the NH (261 K) and NCH_2 (253 K) signals of thread **2b**.[12]

Due to the reversible nature of the Os^{VI}–N bonds, the relative population of the rotaxane-like complex **1a**·**2c** could be precisely controlled by varying the concentrations. The amount of the complex in $CDCl_3$ solution gradually increased with increasing concentrations of the individual components, from about 30% (1 mM) to about 65% (10 mM of each component). To enhance the intrinsic affinity of the bead molecule for the thread on formation of the rotaxane complex, macrocycle **1b** was prepared. The presence of nitro groups in the *para*-positions of the pyridine rings greatly increased the stability of the complex: the association constant K_a between **1b** and **2c** was $(1.0 \pm 0.2) \times 10^4\,M^{-1}$ at $23\,^{\circ}C$ in $CDCl_3$, which is much greater than that between **1a** and **2c** ($\Delta\Delta G^0 = 1.7$ kcal mol^{-1}). When the macrocycle **1b** is employed as a bead component instead of **1a**, the equilibrium lies to side of the the rotaxane complex even at very low concentrations, for example, about 65% of the complex in a 0.5 mM solution.

Experimental Section

1a and **1b**: To a solution of the precursor bis-pyridyl ligands (ca. 0.1 g) in $CHCl_3$ (5–10 mL) were sequentially added 2,3-dimethyl-2-butene (ca. 1.1 equiv) and a 0.1 M solution of OsO_4 in toluene (ca. 1.1 equiv) in an ice–water bath. After the solution had been stirred for 10–30 min, the solvent was removed. The dark brown residue was repeatedly washed with diethyl ether and dried under vacuum to give the macrocycles **1a** or **1b** as dark brown solids in 81–86% yield.

1a: m.p. $> 150\,^{\circ}C$ (decomp); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 9.21$ (s, 2H, NH), 8.83 (s, 2H, NH), 8.63 (s, 4H, lutidyl H), 8.56 (d, $J = 7.8$ Hz, 2H, pyridyl H), 8.50 (d, $J = 7.8$ Hz, 2H, pyridyl H), 8.22 (t, $J = 7.8$ Hz, 2H, pyridyl H), 7.04 (s, 4H, anilinyl H), 2.31 (br s, 4H, cyclohexyl H), 2.25 (s, 12H, $ArCH_3$), 2.23 (s, 12H, $ArCH_3$), 1.64 (br s, 6H, cyclohexyl H), 1.50 (s, 12H, $OC(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 160.9$, 160.4, 149.0, 148.9, 148.2, 147.6, 145.9, 140.4, 134.9, 131.2, 130.3, 126.9, 126.3, 125.9, 90.3, 45.2, 36.1, 26.4, 24.7, 22.9, 19.2, 16.4; IR (KBr): $\tilde{\nu} = 3449$, 1684, 832 cm^{-1}; FAB-MS (*m*NBA matrix, based on ^{192}Os): $m/z = 1169.4$ (1.8%) $[M^+ - H]$, 1152.4 (3.3%) $[M^+ - O]$, 1052.4 (2.4%) $[M^+ - (O_2C_2(CH_3)_4)]$; elemental analysis calcd for $C_{56}H_{64}N_8O_8Os$: C 57.62, H 5.53, N 9.60; found: C 57.61, H 5.56, N 9.62.

1b: m.p. $> 150\,^{\circ}C$ (decomp); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 9.23$ (d, $J = 1.5$ Hz, 2H, pyridyl H), 9.19 (d, $J = 1.5$ Hz, 2H, pyridyl H), 9.06 (s, 2H, NH), 8.73 (s, 2H, NH), 8.66 (s, 4H, lutidyl H), 7.04 (s, 4H, anilinyl H), 2.31 (br s, 4H, cyclohexyl H), 2.25 (s, 12H, $ArCH_3$), 2.22 (s, 12H, $ArCH_3$), 1.65 (br s, 6H, cyclohexyl H), 1.50 (s, 12H, $OC(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 158.9$, 158.6, 157.5, 152.5, 151.0, 149.3, 148.4, 145.2, 134.9, 131.3, 129.9, 127.1, 119.5, 119.1, 90.5, 45.4, 36.1, 26.4, 24.8, 23.0, 19.2, 16.4; IR (KBr): $\tilde{\nu} =$ 3314, 1688, 831 cm^{-1}; FAB-MS (*m*NBA matrix, based on ^{192}Os) $m/z =$ 1259.4 (0.6%) $[M^+ - H]$, 1242.4 (1.9%) $[M^+ - O]$, 1142.4 (1.9%) $[M^+ - (O_2C_2(CH_3)_4)]$; elemental analysis calcd for $C_{56}H_{62}N_{10}O_{12}Os$: C 53.49, H 4.97, N 11.14; found: C 53.44, H 4.90, N 11.14.

The synthesis of threads **2a–c**, binding studies, and ^1H NMR experiments for determining activation barriers are described in the Supporting Information.

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[6] The ^{1}H NMR spectra of macrocycles **1a** and **1b** remained constant over a wide range of concentrations (0.25–10 mM) in $CDCl_3$, and this indicates that no aggregation or self-catenation occurs.

[7] Single crystals of **1a**·**2a** were grown by slow evaporation over about one week of a CH_2Cl_2/toluene/hexane solution containing an approximately 1:1 molar ratio of **1a** and **2a**. A dark brown crystal was selected under oil under ambient conditions, attached to the tip of a glass fiber, and transferred to a Bruker AXS SMART diffractometer/CCD area detector operating with ω scans. Crystal data: $C_{74}H_{100}N_{10}O_{10}Os \cdot$ hexane, crystal dimensions $0.36 \times 0.21 \times 0.14$ mm, monoclinic, $P2_1/n$, $a = 21.7391(4)$, $b = 16.9339(2)$, $c = 22.4259(2)$ Å, $\beta = 95.5360(10)^\circ$, $V = 8217.09(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.266$ g cm^{-3}, $F(000) = 3280$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 193(2)$ K, $2\theta = 46.5$, reflections collected/unique 48602/11617 (R(int) = 0.2205). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 891 parameters. All non-hydrogen atoms except for those of the disordered solvent molecules (hexane) were refined anisotropically. Hydrogen atoms were assigned to idealized positions. $R_1 = 0.1089$ ($I > 2\sigma(I)$), $wR_2 = 0.2122$ (all data), GOF 1.015; max./min. residual density 0.805/−0.479 e Å^{-3}. The high R value is partly due to the disorder of the solvent molecules, and poor quality of the crystal resulted from unavoidable loss of solvent during data acquisition. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137734. 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).

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[9] The association constants K_a were determined by the nonlinear least-squares fitting of the titration curves by plotting $\Delta\delta$ of the host (**1a**) NH signals against the number of molar equivalents of the guest **2a** or **2b**. All of the titration curves fitted well to the expression of a 1:1 binding isotherm; R. S. Macomber *J. Chem. Educ.* **1992**, *69*, 375–378.

[10] The association constant K_a was obtained from four separately prepared solutions of **1a** and **2c**, and concentrations of the free species and the complex in each solution were determined by ^{1}H NMR integration of well-resolved signals: two NH (**1a**), amide NH (**2c**), and NCH_2 (**2c**).

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Silole–Thiophene Alternating Copolymers with Narrow Band Gaps**

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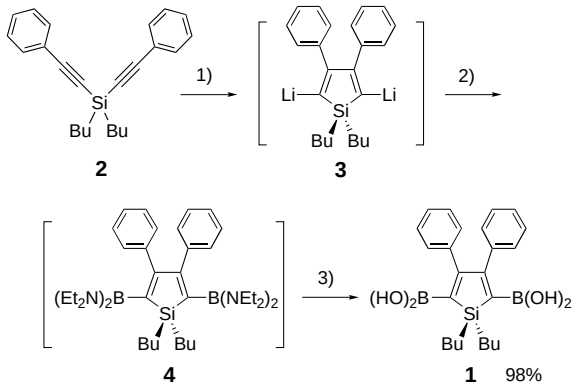
In the chemistry of π-conjugated polymers, the control of the band gap, which is necessary to obtain specific electrical and photophysical properties, is a fundamental goal.[1] Successful stratergies for creating a narrow band gap involve the construction of donor–acceptor type polymers,[2] planar ladder-type conjugated systems,[3] polymers based on fused-ring systems,[4] and copolymers with a specific combination of monomer units such as poly(thienylene–vinylene)s.[5] A new alternative to these approaches would be the modification of carbon π-conjugated systems with main group elements such as boron, silicon, and phosphorus.[6]

In this context, the silole–thiophene 1/1 alternating copolymer is an interesting target compound,[7] in which the ring silicon atoms fix the labile *s*-cis butadiene skeleton of the poly(thienylene–butadienylene) chain. In addition, the silicon atoms in the ring are expected to affect the electronic structure through unique orbital interactions such as σ*–π* conjugation.[8] Although its narrow band gap has been predicted theoretically[9, 10] and experimentally,[7c] its synthesis has been hampered by the limited availability of suitable 2,5-difunctionalized silole precursors.[11] These precursors should be isolable but sufficiently reactive towards coupling reactions for high molecular weight polymers to be obtained. We now report the preparation of silole-2,5-diboronic acid **1**, a suitable monomer,[12] and its use in a Suzuki–Miyaura coupling[13] for the first synthesis of silole–thiophene alternating copolymers.

The preparation of **1** is based on the intramolecular reductive cyclization of bis(phenylethynyl)silane **2**,[14] (Scheme 1). Reaction of the diyne **2** with four equivalents of



Scheme 1. Synthesis of **1**: 1) LiNaph (4 equiv), THF, room temperature (RT); 2) $(Et_2N)_2BCl$ (4 equiv), −78 °C ~ RT; 3) 1N HCl.

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