CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801289

A Modular "Toolbox" Approach to Flexible Branched Multimacrocyclic Hosts as Precursors for Multiply Interlocked Architectures

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Abstract: Tetralactam macrocycles can be functionalized by a variety of cross-coupling reactions. A modular "toolbox" strategy is presented that allows 1) several tetralactam macrocycles to be covalently connected with each other or with a central spacer, 2) the macrocycles to be substituted with or connected to different chromophores, and 3) metal-coordination sites to be attached to the macrocycles. With this approach a series of different oligomacrocyclic hosts was obtained with great structural diversity and enormous potential for further functionalization. Rotaxanes made on the basis of these macrocycles have been synthesized to demonstrate their utility in building more complex supramolecular architectures.

Keywords: coordination complexes · cross-coupling · interlocked molecules · supramolecular chemistry · tetralactam macrocycles

Introduction

In nature, complex architectures are assembled using a limited set of well-selected modules, for example, twenty amino acids, four nucleosides, and a series of monomeric carbohydrates, from which a sheer infinite variety of protein structures, nucleic acids, and linear or branched carbohydrate oligo- and polymers can be generated. This modular strategy is highly efficient in that it reduces the number of the required building blocks to a minimum, without restricting the structural diversity of the end products. However, biopolymers are not only diverse in structure, but also in function. The implementation of functions such as catalysis, information storage, or cell–cell communication has been realized in living organisms. However, it requires more than just a modular approach to structurally diverse architectures. Nature's approach also makes structures programmable and optimizable. The quite complex scaffolds of, for example, a large protein allow evolution to optimize by adjusting the structures gradually in small steps. These great achievements found in nature are a particularly stimulating source of inspiration to many chemists nowadays.

A realization of a similar modular strategy for the generation of structurally diverse, more complex artificial architectures is still a challenge. In the field of supramolecular chemistry, the application of this approach requires the design of modules that need to fulfill the following criteria: 1) The number of building blocks should be limited. 2) They should be synthetically accessible through inexpensive syntheses that provide high yields of the desired building blocks. 3) Chemistry needs to be identified or developed with which these units can be easily and flexibly combined into numerous supramolecular architectures with desired structures and functions, either through covalent or noncovalent bonding. Self-assembly may well be helpful in reducing the synthetic efforts.[1] Supramolecular chemists so far have often followed the strategy to identify a goal, for ex-

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ample, binding a guest molecule by a host through molecular recognition, followed by the design of a specific molecule that might fulfill the task. This molecule has then been evaluated and has often been found to be less than perfectly suited. A detailed analysis may then lead to a new design concept, which requires the synthesis of a new host through, by and large, a completely new synthetic route. This approach of finding one individual synthetic pathway for each target molecule is reasonable and often preferred when the number of targets is small. The modular route is a more process-oriented way of chemical thinking and provides much higher adaptability if a part of the specific target molecule design needs to be modified at a later stage. The modular approach has been explicitly described for various supramolecular assemblies, for example, receptors and capsules;[2] mechanically interlocked compounds,[3] such as rotaxanes or catenanes; metal–porphyrin complexes;[4] and artificial double helices.[5]

As one of the fundamental scaffolds in supramolecular chemistry, macrocyclic molecules have been widely used not only for the binding of small guest molecules,[6] but also for the fabrication of mechanically interlocked architectures such as rotaxanes or catenanes.[7] In recent years, assemblies consisting of several (at least two) host macrocycles linked to a single core,[8] which are shown in Figure 1a,b and which we decide to simply call "branched multimacrocyclic hosts", have attracted increasing interest among supramolecular researchers. The reason for this interest is the versatility of these hosts which can either interact with mono-[8a] or multivalent[8e] guests without threading, or contain mono-[8c–d] or multivalent[8b] guests threaded into them. In this contribution, we focus on hosts that open the gate to multiply mechanically interlocked architectures (MIAs). Among these hosts, we further distinguish flexible branched multimacrocyclic hosts (FBMHs), in which each of the bonds between macrocycle and core can rotate freely, from their rigid counterparts (e.g., triptycene-[8d] or triphenylene-based platforms[8b]), in which this rotation mode is disabled. Compared with the inflexible hosts, FBMHs have the advantage that 1) they can better adapt to the structures of multivalent guests, 2) they provide more possibilities for self-assembly, and 3) one single FBMH can serve as precursor for quite different MIAs (rotaxane-like as well as catenane-like MIAs), inherently complying with the modular philosophy of "few modules leading to many targets".

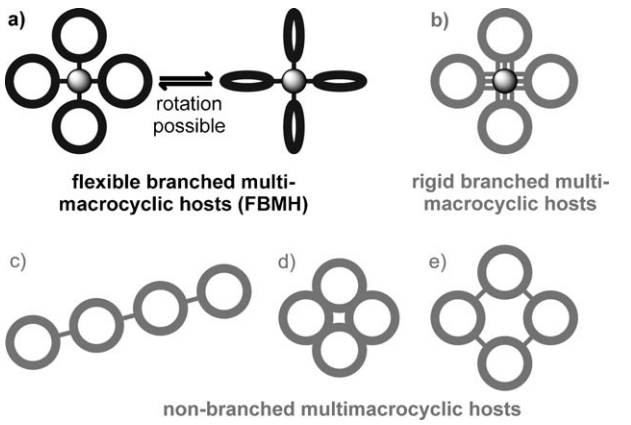


Figure 1. Generic structures of branched multimacrocyclic hosts that a) are connected to a common core through single bonds and can thus freely rotate or b) are rigidified through multiple connection to the core. c) to e) Examples for oligo-macrocycles that are not connected to a common core. In this contribution we focus on the group shown in part a.

FBMHs with this precursor function, which are rarely known as such,[8b] have not been obtained in great structural diversity through a modular approach so far. Herein, we describe the synthesis and characterization of a family of easily accessible, tetralactam-based FBMHs in which amide coupling, cross-coupling reactions, and metal templates are applied to combine the well-selected modules. We demonstrate that a broad structural variety is accessible, which encompasses covalently linked FBMHs as well as some examples for noncovalently linked analogues that are complexed to a metal core through rather weak coordinative bonds. On the other hand, chromophore-centered FBMHs are presented which relate to future functions through their photochemical properties. From some of the macrocyclic precursors, rotaxanes have been made either substituted with a chromophore or with a metal-binding site. As a proof of principle, the metal-coordination approach is applied to a rotaxane.

Results and Discussion

Our FBMHs are based on the well-known Hunter–Vögtle tetralactam macrocycle, which was reported by Hunter[9] and Vögtle et al.[10] Since these macrocycles provide four converging hydrogen bonds for interaction with guests,[11] they have been frequently applied in templated, high-yield syntheses of mechanically interlocked molecules, such as (pseudo-)rotaxanes and catenanes.[12,13] Another advantage is that tetralactam macrocycles provide high chemical stability under many reaction conditions.

We aim to functionalize the macrocycles with a broad selection of different groups. Two pathways can be imagined (Figure 2): One possibility is to introduce the functional

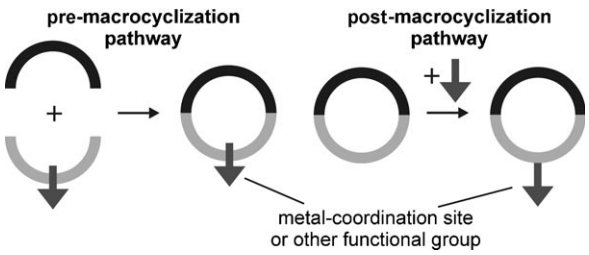
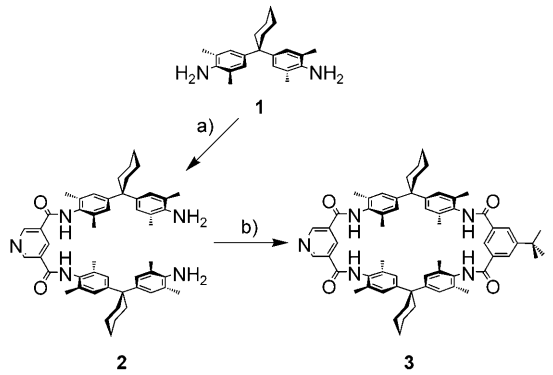


Figure 2. The pre- versus post-macrocyclization pathway used to arrive at macrocycles with specific ligand functions, for example, the pyridine moiety (indicated by the dark gray arrow). Note that for the pre-macrocyclization pathway, the ligand function is incorporated into the macrocycle.

group, for example, the metal-coordinating site mentioned in Figure 2, before macrocyclization. We call this route the pre-macrocyclization pathway. In an earlier study,[14] we reported bisquinoline-bearing macrocycles, catenanes, and rotaxanes that were synthesized according to this route. The alternative is to first perform the macrocyclization step followed by attachment of the desired functional group. This so-called post-macrocyclization pathway[15] has the advantage that functionalization can start from a common macrocyclic intermediate. A variety of functional groups can thus be introduced after the macrocyclization step—an approach that saves a significant amount of synthetic effort.

On the post-macrocyclization route to our FBMHs, a crucial key step is the connection of the macrocycles to a common core. To limit the flexibility in these target molecules to the rotation around the macrocycle core bond, cross-coupling reactions were chosen to realize this key step.

Synthesis of a tetralactam macrocycle through the pre-macrocyclization pathway: As illustrated in Scheme 1, the pyridine-containing tetralactam macrocycle **3** is accessible by



Scheme 1. Synthesis of tetralactam macrocycle **3**: a) pyridine-3,5-dicarbonyl dichloride, NEt_3, CH_2Cl_2, RT, 2 d, 64%; b) 5-*tert*-butylisophthaloyl dichloride, pyridine, NEt_3, CH_2Cl_2, high dilution, 40°C, 2 d, 41%.

well-known literature procedures in two steps starting from Hunter's diamine **1**.[9] The pyridine nitrogen is in an exocyclic position and thus can be utilized for metal coordination, through which several of these macrocycles can finally be connected (see below). The pyridine is incorporated into the corresponding building block before macrocyclization. The advantage of this strategy is that the synthetic route is analogous to that of other well-known tetralactam macrocycles and thus benefits from the experience that is available in the chemical literature. However, the reaction conditions still need to be significantly modified in the crucial and yield-determining macrocyclization step due to solubility problems with the intermediate extended diamine **2**. This optimization is quite time-consuming and such problems are likely to be encountered when other functional groups are attached to or incorporated into the building blocks. In our experience, small structural changes in the building blocks may significantly alter the macrocyclization yields. This makes the pre-macrocyclization pathway less flexible with respect to a toolbox approach. Consequently, the pre-macrocyclization pathway is quite limited.

Crystal structure of macrocycle 3: X-ray quality crystals of **3** were grown after four weeks at the interface of a biphasic system comprising a solution of **3** in dichloromethane and an acidic (pH 4) aqueous solution of K_2PtCl_4. Conformational isomorphism[16] is observed in the crystal structure: The unit cell contains one macrocycle in its "all-in" conformation (**3A**), in which all four amide protons converge into the macrocyclic cavity, and two macrocycles as the "two-in-two-out" conformer **3B**, in which the amide protons pointing into the macrocycle alternate with those pointing out of it (see arrows in Figure 3a,b). The presence of two different conformations of the macrocycle in the crystal indicates that both conformations are energetically not too distant from each other and can interconvert without being hampered by a high barrier. This is in excellent agreement with a previous theoretical study,[11a] which predicted both features for similar macrocycles. The reason why both conformers appear in the solid state presumably lies in crystal packing. In particular, intermolecular hydrogen bonds connect the macrocycles and generate an infinite ribbon (Figure 3c,d). In this ribbon, two macrocycles of **3B** connect two molecules in conformation **3A**. The latter macrocycle is disordered in the crystal with respect to the positions of the pyridine and the *tert*-butyl group. Either of the two possible orientations can occur. The N−O distances of the intermolecular N−H···O=C hydrogen bonds are 2.808 and 2.852 Å. In the crystal structure, the hydrogen-bonded assembly of one molecule of **3A** and two of **3B** serves as a noncovalent "monomer unit" for the twisted, ribbonlike, hydrogen-bonded polymer, in which two parallel strands of **3B** are interconnected by **3A** (Figure 3d).

Synthesis of key intermediates and synthesis of macrocyclic ligands using the post-macrocyclization pathway: To avoid the above-mentioned potential weaknesses of the pre-macrocyclization pathway, we explored the post-macrocyclization route to macrocyclic ligands. To be able to make use of the large potential for cross-coupling reactions, a series of key intermediates have been prepared that are already equipped with the functional groups needed for cross-coupling reactions (Scheme 2). From hydroxy-substituted macrocycle **9**, triflate **10** can be easily obtained with good yields. Similarly, iodo- and bromo-substituted analogues **11** and **14** are obtained when extended diamine **6** or **7** is treated under high-dilution conditions with the corresponding isophthaloyl dichloride. Two more cross-coupling precursors are available from the halogenated macrocycles: A Sonogashira coupling[17] followed by deprotection of the trimethylsilyl group with potassium hydroxide provides acetylene-substituted **13**, which may serve as a precursor in a second Sonogashira coupling. Besides this, it can also be employed in Glaser–Hay coupling reactions[18] (see below) or potentially in Huis-

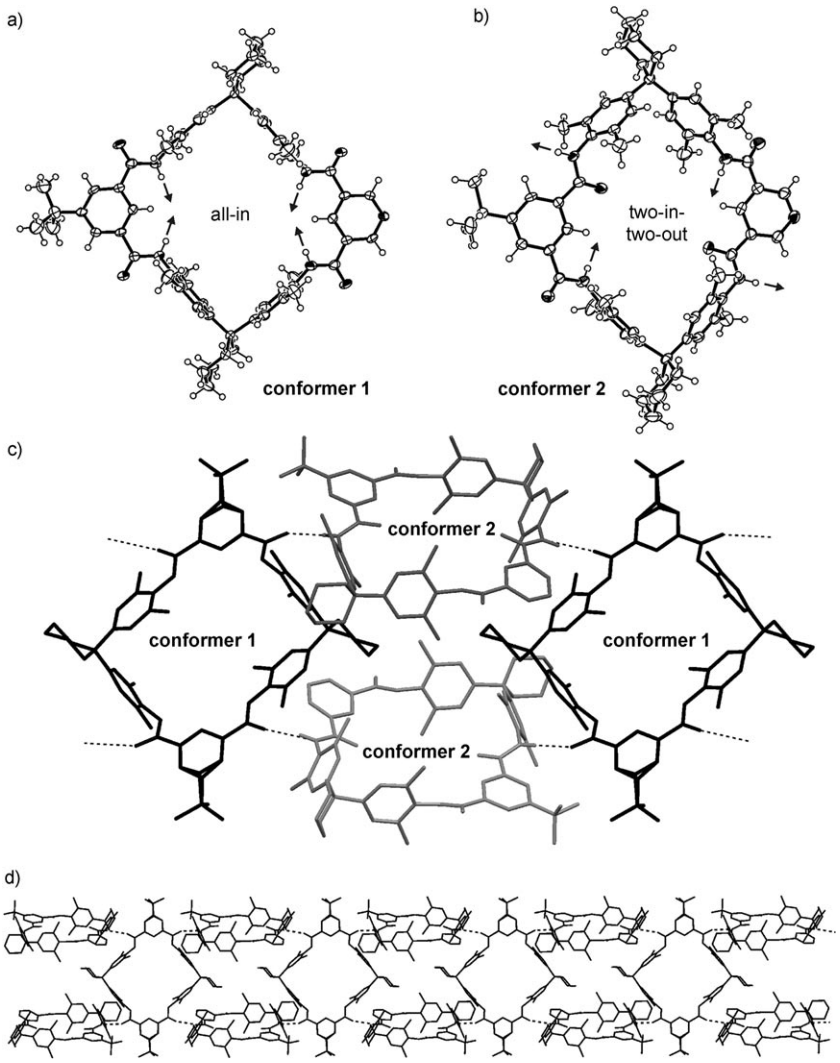


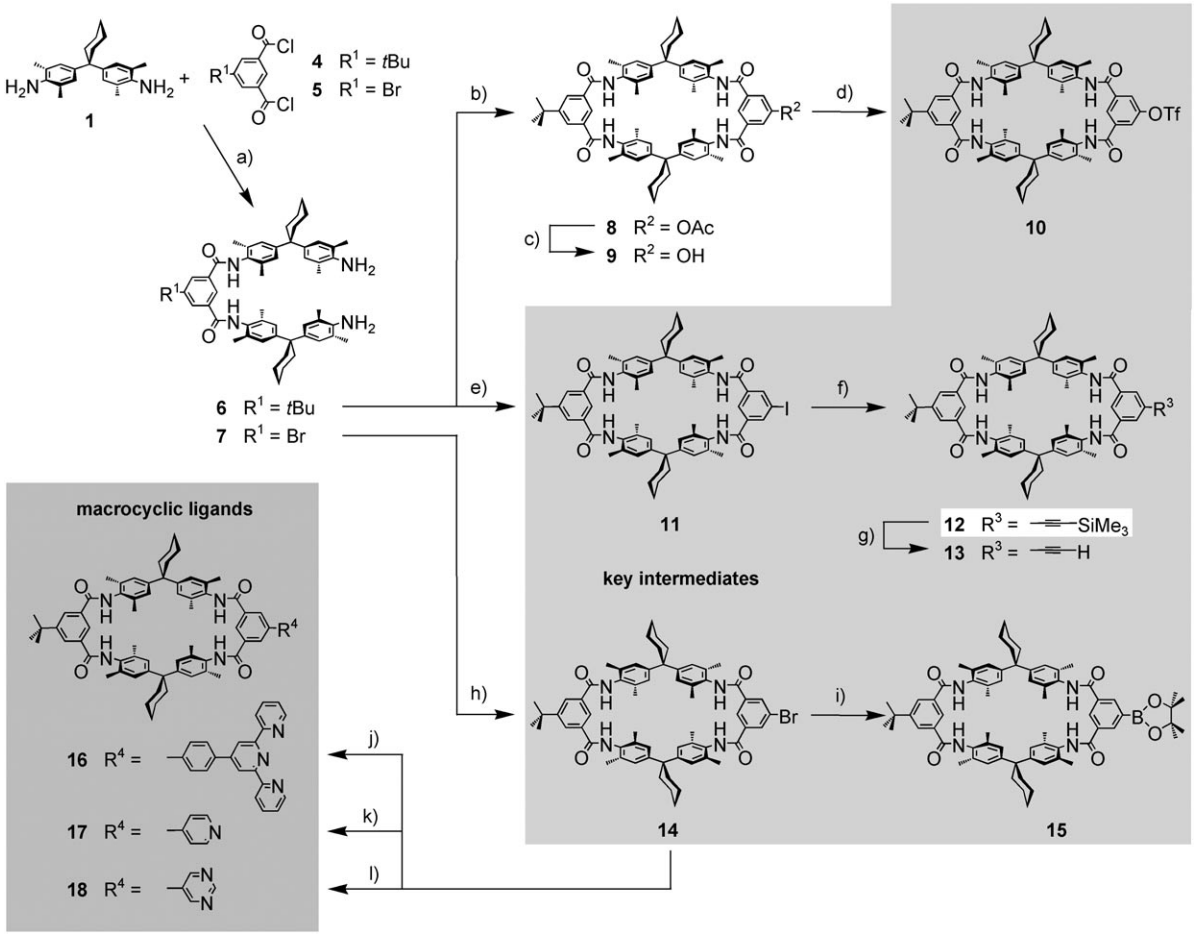
Figure 3. Crystal structure of **3**: a) ORTEP plot of all-in conformer **3A** (conformer 1). b) ORTEP plot of two-in-two-out conformer **3B** (conformer 2) (both conformers shown with 50% probability ellipsoids). c) Intermolecular hydrogen bonds (dashed) between **3A** (black) and **3B** (dark gray, gray) (hydrogen atoms omitted for clarity, except for the amide protons involved in hydrogen bonding). d) Visualization of the infinite molecular "chain" in the form of a twisted, ribbonlike, hydrogen-bonded polymer (all hydrogen atoms omitted for clarity).

gen–Sharpless–Meldal click chemistry[19] (not described herein). From **14**, pinacolato boronate-substituted macrocycle **15** is easily available through Miyaura borylation[20] and may, in addition to the two halogenated macrocycles **11** and **14**, serve as another key intermediate for Suzuki cross-coupling reactions.[21] The scope of the cross-coupling reactions mentioned herein can certainly be extended beyond the scope of the present study. Just to mention one example, which has not been explored in our study, boronates such as **15** may also be used in Chan–Lam[22] couplings. Consequently, the set of key intermediates **10**–**15** represents a very versatile and flexible, but at the same time compact, basis for further functionalization of the tetralactam macrocycles. This toolkit can be used for a broad spectrum of cross-coupling reactions with a vast range of coupling agents and is characterized, in accordance with the principles of modular approach, by its easy accessibility, great flexibility, and high adaptability.

A quick view at the cyclization yields again reveals them to be dependent on the substituent: Whereas **3** and **8** are obtained in similar yields of 41 and 43%, respectively, the yields are significantly lower in the case of halogenated analogues **11** (15%) and **14** (20%). The sometimes quite drastic effects might be rationalized not only by invoking different distributions of macrocycle and undesired oligomeric side products. Another major product usually found in substantial amounts is the corresponding catenane. It consists of two identical macrocycles that become intertwined during the macrocyclization by a hydrogen-bond-mediated template effect. This hydrogen-bonding pattern is rather sensitive to structural changes in the macrocycle structures.[11] Some of the catenanes have been isolated and fully characterized in the course of the present study. However, we refrain from describing them in detail herein, since unfortunately they turned out to be rather unreactive in cross-coupling reactions.

The first Suzuki cross-coupling reactions have been successfully performed with bromo-substituted **14** and the pinacolato boronates of phenyl terpyridine, pyridine, and pyrimidine as shown in Scheme 2. This approach turned out to be much more fruitful compared with the second possible variant, that is, Suzuki cross-coupling of **15** with the corresponding halogenated heterocycles.[23] The products of these coupling reactions (**16**–**18**) all carry heterocycles that can coordinate to transition-metal ions. This set of molecules can thus be connected to each other through the use of metal ions with their wide variety of coordination geometries.

Rotaxane synthesis: Scheme 3 shows attempts to synthesize rotaxanes with ether axles from some of the macrocycles following the anion-mediated template developed by Vögtle et al.[24] Again, two different routes were explored. To shift

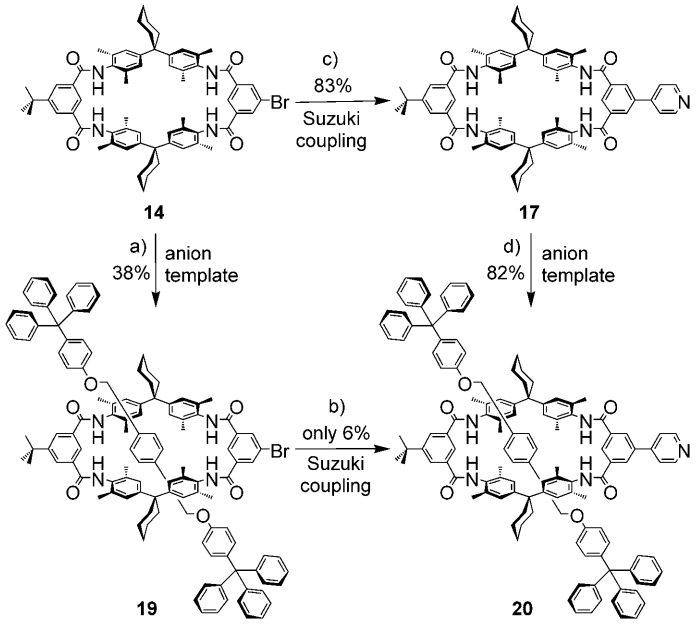


Scheme 2. Synthesis of key intermediates and macrocyclic ligands: a) NEt_3, CH_2Cl_2, RT, 1 d, 64% (**6**) or 74% (**7**); b) 5-acetoxyisophthaloyl dichloride, NEt_3, CH_2Cl_2, high dilution, RT, 1 d, 43%; c) KOH, dioxane, H_2O, reflux, 8 h, 95%; d) Tf_2O, pyridine, CH_2Cl_2, −25°C, 2 h, 87%; e) 5-iodoisophthaloyl dichloride, NEt_3, CH_2Cl_2, high dilution, RT, 1 d, 15%; f) trimethylsilyl acetylene, CuI, $[PdCl_2(PPh_3)_2]$, NEt_3, DMF, RT, 15 h, 41%; g) KOH, MeOH/CH_2Cl_2, RT, 75%; h) 5-*tert*-butylisophthaloyl dichloride, NEt_3, CH_2Cl_2, high dilution, RT, 1 d, 20%; i) B_2pin_2, $[PdCl_2(dppf)]$, KOAc, DMSO, 80°C, 6 h, 82%; j) 4-(2,2′;6′,2″-terpyridine-4′-yl)phenyl-B(pin), $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene/DMF, 120°C, 2 d, 66%; k) (pyridine-4-yl)B(pin), $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene/DMF, 120°C, 2 d, 83%; l) (pyrimidine-5-yl)B(pin), $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene/DMF, 120°C, 2 d, 83% (pin = pinacolato, dppf = 1,1′-bis(diphenylphosphino)ferrocene).

the macrocycle functionalization step to as a late state of the synthesis as possible, we first attempted to generate rotaxane **19** from bromo-substituted tetralactam macrocycle **14**. Then, rotaxane **19** may serve as a precursor for the attachment of a variety of different functional groups, such as a pyridine moiety, finally yielding rotaxane **20**. This approach would have another, practical advantage. Some of the macrocycles cause solubility problems. As soon as the axle is present, the resulting rotaxanes are usually soluble, since the interactions of macrocycles with each other in the crystal are disturbed by the stoppers protruding on both sides. Consequently, rotaxane **19** would help to circumvent solubility problems. From the Suzuki coupling of the pinacolato boronate of pyridine with **19**, only a disappointingly low yield of around 6% of rotaxane **20** has been obtained. The rotaxane can easily be identified by mass spectrometry[25] as well as by its ^1H NMR spectrum. Axle protons that are located inside the cavity of the macrocycle experience a significant upfield shift of up to $\Delta\delta = 1.8$ ppm[26] due to the anisotropy of the aromatic rings incorporated in the Hunter diamines.

One of the major side products of this reaction is the free axle. This finding may help to identify the reason for the low yield: Since the tritylphenol stoppers efficiently prevent deslipping of the axle, even at elevated temperatures,[27] such a process is certainly not the reason for this finding. Most likely, the cross-coupling catalyst activates the benzyl ether bond and causes it to open and close reversibly. Once it is cleaved, the mechanical bond is released and most of the rotaxane is thus destroyed.

In the second approach, the order of the two steps is reversed. The pyridine is attached first to macrocycle **14** to give **17** in an acceptable isolated yield of 83%. Rotaxane synthesis with **17** then provided rotaxane **20** in 82% yield. Thus, following this approach is by far superior compared with the first strategy—at least when targeting rotaxanes with ether axles. These experiments provide some insights into some limitations that may occur. However, these limita-

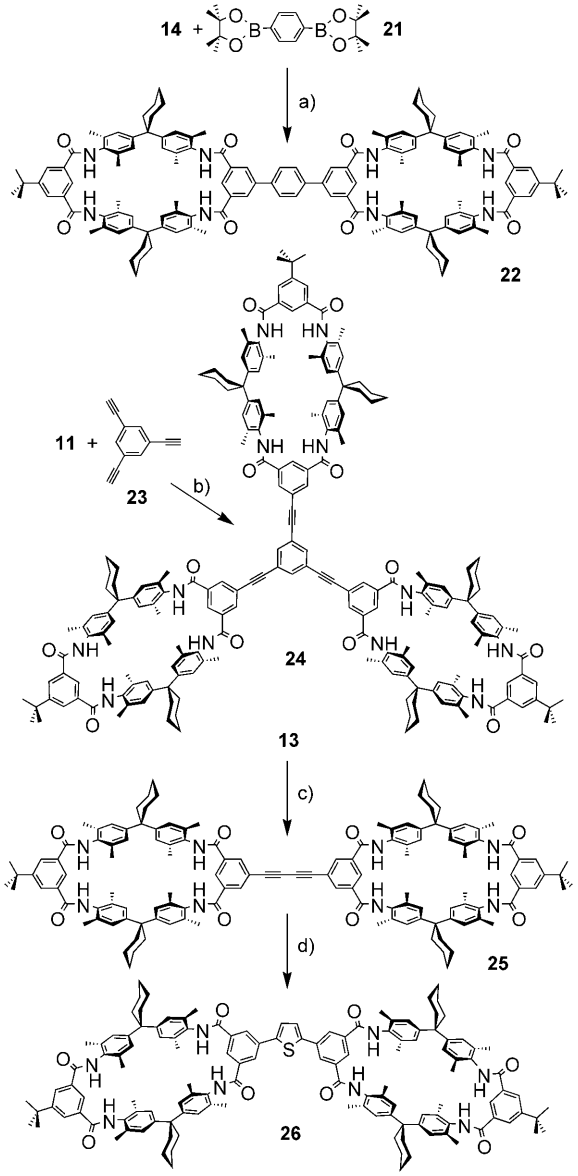


Scheme 3. Synthesis of pyridyl rotaxane **20** using two different routes: a) α,α′-dibromo-*p*-xylene, 4-tritylphenol, dibenzo[18]crown-6, K_2CO_3, CH_2Cl_2, RT, 7 d, 38%; b) (pyridin-4-yl)B(pin), $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene/DMF, 120°C, 2 d, 6%; c) (pyridin-4-yl)B(pin), $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene/DMF, 120°C, 2 d, 83%; d) α,α′-dibromo-*p*-xylene, 4-tritylphenol, dibenzo[18]crown-6, K_2CO_3, CH_2Cl_2, RT, 7 d, 82% (pin = pinacolato).

tions are not serious, if one considers that the tetralactam macrocycles can also serve as wheels for rotaxanes with more stable amide axles,[13] which can certainly be expected to survive the conditions of the cross-coupling reactions.

Synthesis of covalently linked, cross-coupled macrocycle dimers and trimers: In principle, the key intermediates described above can be converted into covalently linked FBMHs in two ways: 1) by coupling two or more macrocycles to a common core or 2) by homo- or heterocoupling of two or more of the key intermediates directly to each other, thus simultaneously building the joint core. According to the first alternative, divalent benzene-centered FBMH **22** (Scheme 4) has been afforded through a standard Suzuki coupling of bromo-substituted macrocycle **14** with diborylated benzene **21**, a readily available core component. The use of the brominated macrocycle requires elevated temperatures (ca. 120°C), but the yield of 90% is quite high. In a similar manner, trivalent benzene-centered FBMH **24** could be synthesized in a Sonogashira reaction between readily available triethynylbenzene **23** and iodomacrocycle **11**. No separate core component is required for the Glaser–Hay homocoupling of two acetylene-substituted macrocycles **13** to butadiyne-spacered dimer **25**. This reaction is an example for the second pathway described above.

The butadiyne product itself represents a functional group that permits further functionalization: In a preliminary experiment, we treated a few mg of **25** with Na_2S[28] and analyzed the raw product by mass spectrometry. In a fairly clean ESI mass spectrum (Figure 4), minor amounts of reactant **25** were observed together with product **26** (Scheme 4), which corresponds to the dominant signal. Such a transformation induces a change in the geometry of the tether connecting the two macrocycles.



Scheme 4. Synthesis of FBMHs **22**, **24**, and **25**: a) $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, DMF, 120°C, 1 d, 90%; b) CuI, PPh_3, $[Pd(PPh_3)_2Cl_2]$, NEt_3, DMF, RT, 40 h, 40%; c) CuCl, O_2, DMF, RT, 12 h, 26%; d) $Na_2S{\cdot}(H_2O)_x$, THF, 3 d, 60°C (pin = pinacolato).

These three examples of different coupling reactions, that is, the Suzuki, the Sonogashira, and the Glaser–Hay reactions, together with the possibility of postfunctionalization of the butadiyne spacer may suffice to provide evidence for the utility of our toolbox concept. In the following section, we now apply the concept to chromophore-substituted macrocycles and metal-coordination.

Synthesis of chromophore-substituted macrocycles: Scheme 5 shows the syntheses of chromophore-substituted

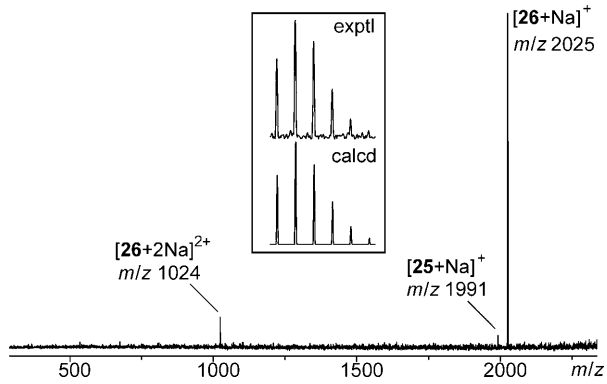


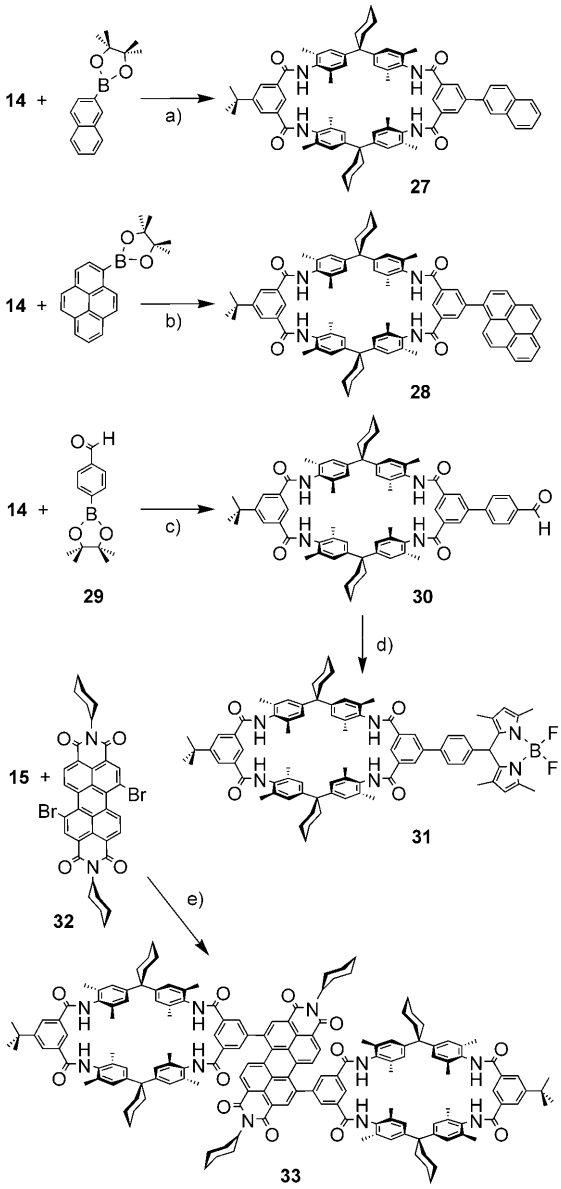
Figure 4. ESI-FTICR mass spectrum of the raw product obtained from the reaction of **25** with $Na_2S{\cdot}(H_2O)_x$ yielding thiophene-centered **26**.

macrocycles starting with either bromo-substituted macrocycle **14** or borylated analogue **15**. All cross-coupling reactions applied herein are Suzuki reactions. A naphthyl group is easily coupled in good yields to one of the isophthalic acid moieties of the macrocycle to provide easy access to **27**. Since pyrene boronic acid is commercially available, we initially attempted to use triflate-substituted macrocycle **10** together with pyrene boronic acid in an analogous Suzuki coupling. Indeed, compound **28** could be isolated from that reaction, but only with a disappointingly low yield of 19%. Consequently, the procedure that had been successful for naphthyl-attachment was applied and provided **28** in 87% yield.

Boron dipyrromethene (BODIPY) dyes are interesting chromophores because of their easy preparation, narrow absorption and emission bands, and high quantum yields, which is of great importance for energy transfer and sensing processes.[29] Thus, it seemed attractive to add a BODIPY-substituted macrocycle to the series of chromophore-substituted compounds presented herein. Again, a Suzuki cross-coupling reaction can be used to synthesize aldehyde precursor **30** from which target compound **31** is available in a three-step one-pot reaction.[30] The aldehyde is first converted into the corresponding dipyrromethane by an acid-catalyzed reaction with 2,4-dimethyl pyrrole. The dipyrromethane is oxidized to the dipyrromethene with *p*-chloranil without workup of the intermediate. Finally, addition of $BF_3{\cdot}Et_2O$ provides the desired product in 62% overall yield.

The last compound in the series of chromophore-substituted macrocycles (**33**) has a perylene as the core connecting two macrocycles. It can be most easily prepared from borylated macrocycle **15** and dibromo perylene **32**. The yield of 45% is somewhat lower than that for the other Suzuki reactions described so far and can be attributed to the rather low solubility of the monosubstituted intermediate.

The UV/Vis spectra for compounds **28**, **31**, and **33** (shown in Figure 5) display the typical absorbance patterns of the photoactive groups in the host macrocycles. The absorbance of the phenyl rings within the macrocycle body occurs up to 300 nm (the typical range is around 200 nm). In the case of pyrene and perylene macrocycles, the absorbance maxima in



Scheme 5. Synthesis of chromophore-substituted macrocycles **27**, **28**, and **31** and FBMH **33**. All coupling reactions are performed under standard Suzuki conditions ($[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, DMF, 120 °C, 1 d) and proceeded in the following yields: a) 76, b) 87, c) 84, and e) 45%. BODIPY-substituted macrocycle **31** was synthesized from **30** in a one-pot reaction with d) i) 2,4-dimethyl pyrrole, trifluoro acetic acid (cat.), ii) *p*-chloranil, iii) $BF_3{\cdot}Et_2O$, 62%.

the visible range are 348 and 548 nm respectively. The former maximum is not affected when the solvent was changed from CH_2Cl_2 to acetonitrile, whereas the latter shifts by about 10 nm, which is again expected from the solvatochromic behavior of 1,7-substituted perylene dyes.[31] The BODIPY macrocycle has the highest extinction coefficient (67200 $M^{-1}\,cm^{-1}$ at 498 nm) with the typical sharp peak shape.

Self-assembly of macrocyclic ligands to metal-centered FBMHs—pyridine coordination: Metal-directed self-assem-

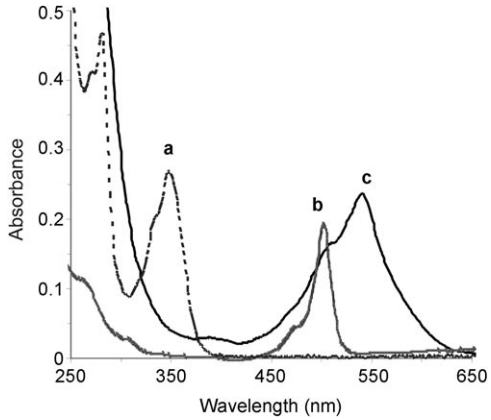
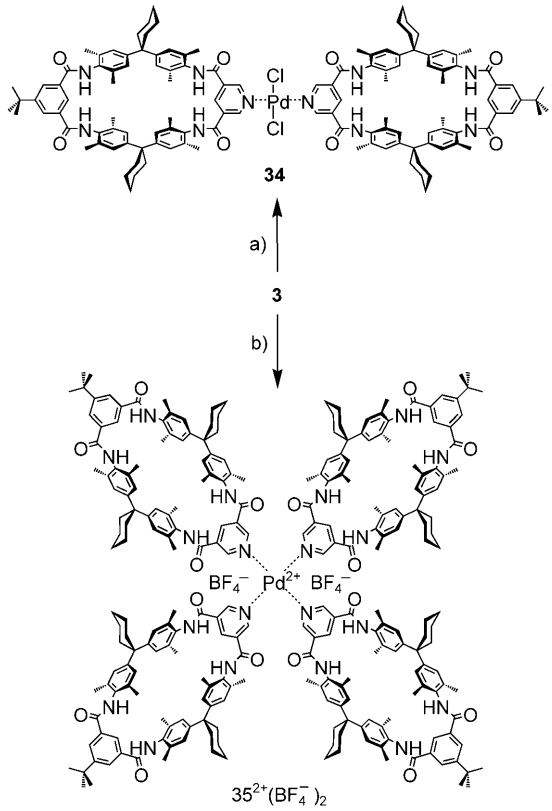


Figure 5. UV/Vis spectra of a) pyrene macrocycle **28** (1×10^{-6} M; multiplied by 10), b) BODIPY macrocycle **31** (5×10^{-6} M), and c) FBMH **33** (1.6×10^{-5} M) in CH_2Cl_2.

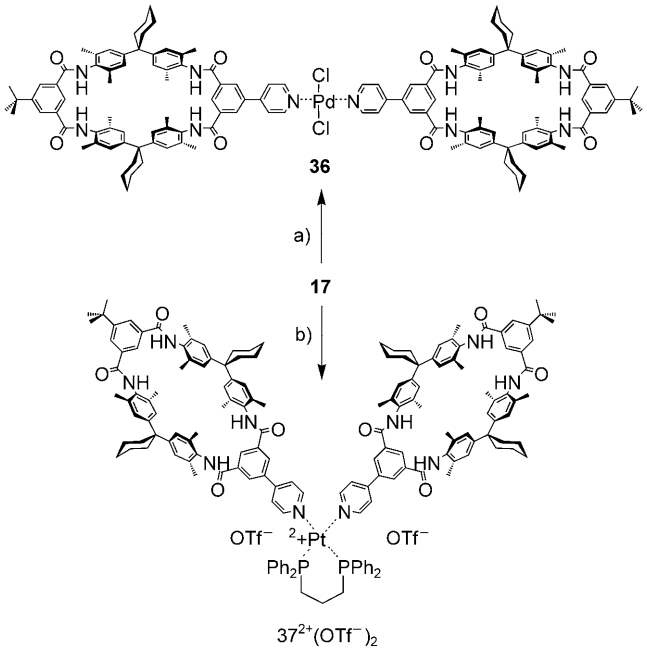
bly is a powerful approach to complex supramolecular structures with controllable, predefined sizes and geometries.[32] It significantly reduces the synthetic effort that would be required for the generation of a similarly complex covalent molecule. Other advantages of metal coordination complexes are the variety of coordination geometries available, the quite large range of accessible binding energies allowing for weakly bound complexes that form reversible bonds as well as for kinetically quite inert coordination.

Macrocycles **3** and **16–18** have been equipped with different metal coordination sites. Two of these ligands, **3** and **17**, carry monodentate pyridine moieties pointing away from the cavities of the macrocycles. Depending on the choice of the central metal complex, different number of macrocycles can be combined in different orientations. In this study, we have investigated the coordination to different d^8-metal centers: *trans*-$[PdCl_2]$, $[Pd(MeCN)_4](BF_4)_2$, and $(dppp)Pt(OTf)_2$. These metal centers provide access to quite different complex geometries.

When **3** was reacted with $[PdCl_2(PhCN)_2]$, which has two trans-oriented coordination sites blocked with chloride, divalent Pd-centered FBMH **34** precipitated as a pale-yellow solid (Scheme 6). Analogously, FBMH **36** (Scheme 7) was obtained from macrocyclic ligand **17**, which has a peripheral pyridine attached to one of the isophthalic acid moieties. Furthermore, tetravalent Pd-centered FBMH $\mathbf{35}^{2+}$ was afforded as the tetrafluoroborate salt upon addition of $[Pd(MeCN)_4](BF_4)_2$ to **3**. By utilizing the *cis*-blocked platinum corner $(dppp)Pt(OTf)_2$, a reagent applied for the assembly of metallosupramolecular squares,[33] we were able to obtain divalent Pt-centered FBMH $\mathbf{37}^{2+}$ in which the macrocyclic parts are almost perpendicular to each other. Since the pyridine rings prefer to coordinate to the metal in an orientation almost perpendicular to the plane defined by the four donor atoms around the metal center, compounds **3** and **17** result in different orientations of the macrocycles in the complex. In $\mathbf{35}^{2+}$, for example, the four macrocycles are likely to form a propeller-shaped arrangement with the cavities opening towards the neighbors. The analogous complex prepared



Scheme 6. Self-assembly of **34** and $\mathbf{35}^{2+}(BF_4^-)_2$: a) $[PdCl_2(PhCN)_2]$, CH_2Cl_2, RT, 9 h, 49%; b) $[Pd(MeCN)_4](BF_4)_2$, $CDCl_3/CD_3CN$, RT, 1 d, then cooling, 3 d, 33%.



Scheme 7. Self-assembly of **36** and $\mathbf{37}^{2+}(OTf^-)_2$: a) $[PdCl_2(PhCN)_2]$, CH_2Cl_2, RT, 16 h, then 40 °C, 1 h, 44%; b) $(dppp)Pt(OTf)_2$, DMF, 10 min, quantitative (dppp = 1,3-bis(diphenylphosphino)propane).

from **17** would result in an arrangement in which the pyridines obtain their preferred perpendicular orientation, whereas due to the aryl-aryl bond the macrocycles are in a more or less flat arrangement with their cavities opening to above and below the complex. Due to the larger macrocycle–metal distance, the rings are likely to be able to rotate without substantial rotation barriers caused by steric congestion.

The formation of metal-centered FBMHs is confirmed by ESIMS spectra and ^{1}H NMR spectra, in which the *ortho*-pyridine protons show downfield shifts due to metal coordination. The (dppp)Pt^{II} corner in **37**$^{2+}$ has the particular advantage that the Pt–P coupling constants are very sensitive to the coordination of the two pyridines. The coupling constant in **37**$^{2+}$ is ^1J(Pt,P) = 3023 Hz, whereas it is ^1J(Pt,P) = 3650 Hz in the (dppp)Pt(OTf)$_2$ precursor, thus clearly indicating the coordination of the pyridine rings.

Crystal structure of metal-centered FBMH 34:[34] When **34** was dissolved in approximately a 2:1:1 mixture of 1,4-dioxane, dichloromethane, and methanol and the solution was left to stand in a parafilm-closed test-tube for two months, pale-brown needlelike single-crystals of **34** were obtained. According to X-ray crystal structure analysis, two molecules of **3** are bound to the Pd center through their pyridine moieties, forming the expected square-planar *trans*-Pd-complex (Figure 6a). Since each corner of the unit cell, which is the crystallographic inversion center in the $P\bar{1}$ space group, is occupied by a Pd atom, compound **34** is a perfectly centrosymmetric molecule in the solid state. Compared with the crystal structure of **3**, the striking difference is that all macrocycles are arranged in the "all-in" conformation, which indicates that **34** is a suitable host for the formation of multiply interlocked architectures (MIAs). A highly interesting feature of the crystal packing is the existence of infinite channels passing through the macrocyclic cavities (Figure 6b). The channels, which are filled with quite disordered solvent molecules in the crystal, might be an interesting structural element for applications going beyond the use for MIA formation.

Synthesis and molecular modeling of MIA 40: As a proof-of-principle for the formation of multiply interlocked architectures through metal coordination, rotaxane **39** has been synthesized and subsequently coordinated to a *trans*-[PdCl$_2$] center (Scheme 8). The rotaxane can be easily made through our previously published anion-template procedure.[12c] Axle centerpiece **38** is deprotonated at the phenolic hydroxy group. The anion can—supported by one of the carbonyl groups—then form rather strong hydrogen bonds with tetralactam macrocycle **3**. The axle centerpiece is fixed inside the wheel in an orientation that ensures that triphenyl acetyl stoppers are attached to the two amino groups from opposite sides of the macrocycle. The axle is thus trapped in the cavity; a rotaxane forms. The mechanically interlocked structure of the rotaxane can be identified from strong upfield shifts of the ^{1}H NMR signals of those protons that are located in the macrocycle cavity. For **39**, the methylene spacers between the stoppers and the central phenol are af-

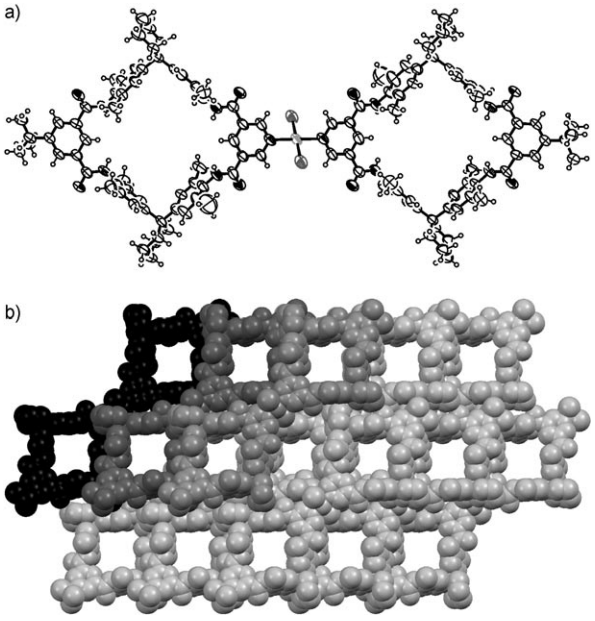
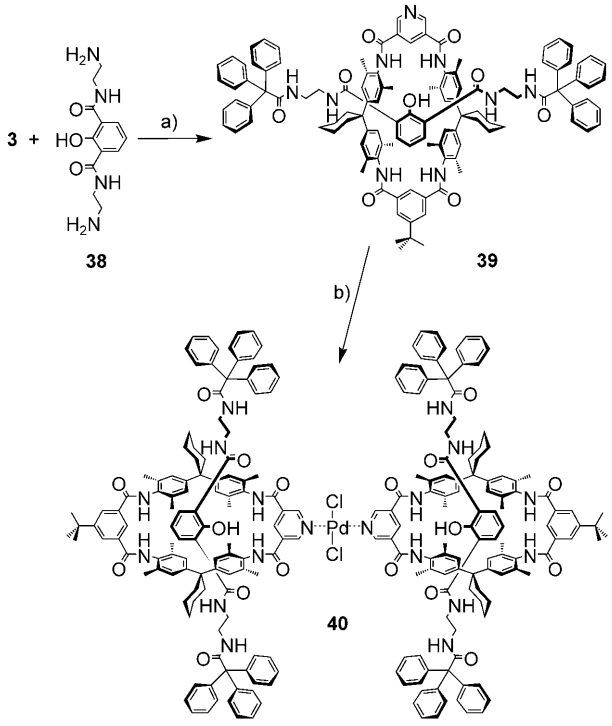


Figure 6. Crystal structure of **34** (solvent molecules are omitted for clarity): a) ORTEP plot (shown with 50% probability ellipsoids). b) Crystal packing, space-filling view along the diagonal between the crystallographic *a* and *c* axes, showing the infinite channels.



Scheme 8. Synthesis of rotaxane **39** and assembly of MIA **40**: a) *tert*-butylimino-tris(dimethylamino)phosphorane (P_1 base), NEt_3, triphenylacetyl chloride, CH_2Cl_2, RT, 3 d, 14%; b) $PdCl_2(PhCN)_2$, CH_2Cl_2, RT, 1 d, then cooling, 7 d, 11%.

fected most ($\Delta\delta = 0.9$–1.0 ppm; see analytical data below). The threaded topology can be also determined from tandem MS experiments. In these experiments, fragmentations are induced by collisions of the mass-selected rotaxane ions with a collision gas (Ar) in an FTICR mass spectrometer. Mass-selected **39** was thus subjected to this experiment. The same experiment was then conducted under exactly the same conditions with a 1:1 mixture of macrocycle **3** and the free, stoppered axle. During ionization these two components form a non-interlocked, hydrogen-bonded complex with the same *m*/*z* value as **39**. The two MS/MS spectra differ much: The MS/MS spectrum of **39** still shows the rotaxane ion as the base peak, whereas the free axle appears as a fragment with around 30% relative intensity accompanied by axle fragments. In the same experiment conducted with the hydrogen-bonded complex, all parent ions have dissociated and the free axle is the only fragment visible. This indicates that it is energetically much easier to dissociate the hydrogen-bonded complex than to fragment the rotaxane, in which a covalent bond needs to be broken to release the mechanical bond. We have reported similar experiments on an analogous rotaxane before with a similar outcome.[12c,25] Consequently, the rotaxane has unambiguously formed.

Subsequently, compound **39** was treated with $[PdCl_2(PhCN)_2]$ to give MIA **40** through metal-directed self-assembly. In the ESI-FTICR mass spectrum of **40**, the only intense ion observed is the sodium adduct of **40**, which shows the fairly high stability of this rotaxane dimer (Figure 7). The characteristic isotope pattern confirms the presence of the $PdCl_2$ unit. Compared to **39**, a downfield shift of the *ortho*-pyridine protons was found in the ^{1}H NMR spectrum of **40**. To obtain at least a rough idea of the structure of **40**, molecular modeling calculations were performed with the augmented MM2 force field implemented in the CAChe 5.0 program.[35] Figure 8 shows one example out of many possible low-energy conformations of **40**.

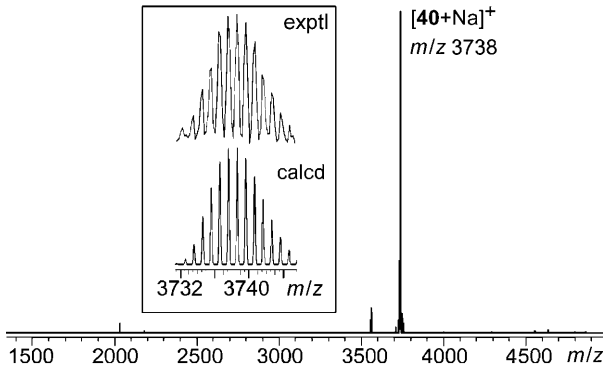


Figure 7. ESI-FTICR-MS spectrum of MIA **40**.

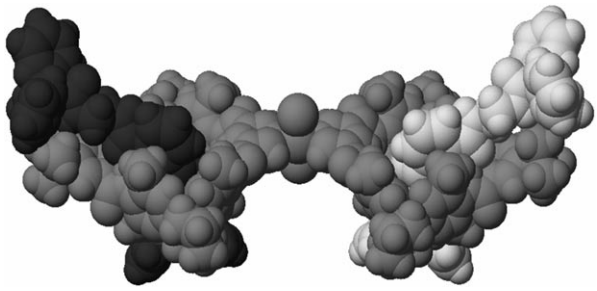
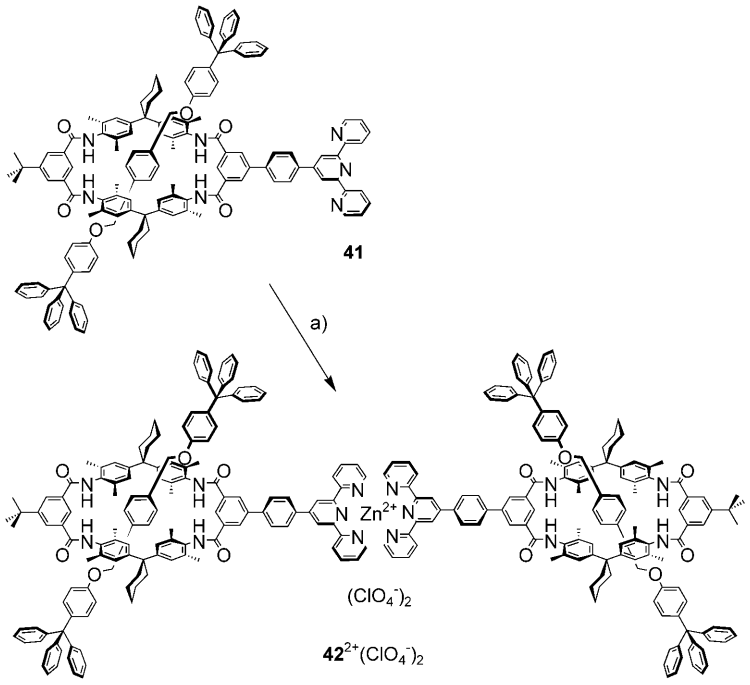


Figure 8. Space-filling representation of one example out of many possible low-energy conformations of MIA **40** calculated at the MM2 level (dark gray: FBMH part of the MIA, black and light gray: axle components).

Self-assembly of macrocyclic ligands to metal-centered FBMHs–terpyridine coordination: From terpyridine-substituted macrocycle **16**, rotaxane **41** (Scheme 9) was synthesized by the same procedure as that used for **19**. Again, rotaxane synthesis was successful if carried out after cross-coupling the terpyridine moiety to bromo-macrocycle **14**. Figure 9 (top) shows the aromatic region of the ^{1}H NMR spectrum of **41**. The threaded topology of the rotaxane can easily be determined from the unusual upfield



Scheme 9. Synthesis of the dimeric Zn^{II}-complex $\mathbf{42}^{2+}$ of rotaxane **41**. a) $Zn(ClO_4)_2 \cdot 6H_2O$, $CDCl_3$, RT, quant.

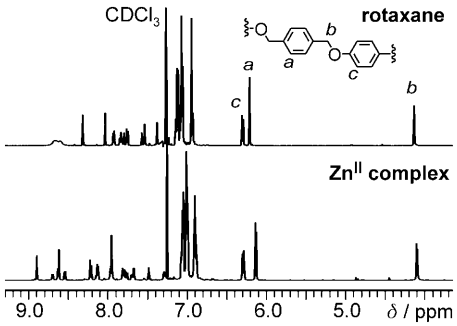


Figure 9. Top: Partial ^{1}H NMR spectrum of the rotaxane **41** synthesized from terpyridine-substituted macrocycle **16**. The unusual upfield shifts of protons *a*, *b*, and *c* of the axle centerpiece indicate rotaxane formation. Bottom: Partial ^{1}H NMR spectrum of dimeric Zn^{II}-complex $\mathbf{42}^{2+}$ of this rotaxane. The appearance of one set of sharp signals at positions shifted relative to those observed for the rotaxane indicates quantitative complex formation.

shifts of the protons located at the axle centerpiece (labeled *a*, *b*, and *c*). They experience the anisotropy of the macrocycle's aromatic rings. In comparison to the signals of the free axle, proton *a* shifts by around 1.7 ppm to higher field.

When half an equivalent of zinc perchlorate is added to the solution of rotaxane **41**, a ^{1}H NMR spectrum is obtained that contains only one set of well-resolved signals and thus indicates that only one complex, that is, the Zn^{II}-bridged dimer of the rotaxane, is almost quantitatively formed. Most of the signals in the aromatic region are shifted to some extent upon complexation of the rotaxane to the metal ion.

Conclusion

In this study, we have developed a toolbox of building blocks on the basis of tetralactam macrocycles for the supramolecular assembly of more complex, multiply interlocked architectures. We can draw the following conclusions:

1) A quite limited set of five key intermediates, that is, macrocycles with substituents suitable for cross-coupling reactions, serves as the basis for quite different purposes. Simple organic spacers can be used to connect several macrocycles around a common core to provide access to multivalent host molecules. Photoactive groups can be attached and may have potential for future energy-transfer studies. Metal-binding sites are easily coupled to the macrocycles, which can then coordinate to a metal center serving as a noncovalent core. Consequently, a large variety of different structures is now available based on the small set of key intermediates.
2) Different key intermediates open the opportunity to use almost any kind of cross-coupling reaction. Iodinated, brominated, and borylated macrocycles have proven to be excellent precursors for Suzuki cross-coupling reactions. Iodinated and ethynyl derivatives can be utilized in Glaser–Hay or Sonogashira reactions. Even the tosylated macrocycle reacted in coupling reactions, however, with unsatisfactory yields. This variety of different reactions increases the range of accessible structures drastically.
3) Although only shown for one example, some of the cross-coupling products can be converted into different functional groups after the cross-coupling reaction, again providing access to different geometries.
4) Rotaxanes can be made from almost all macrocycles reported in this study—maybe with the exception of the borylated macrocycle **15**, which we did not test in the threading reaction. As a proof of principle, we synthesized two types of rotaxanes, one of which has benzyl ether axles, the other one an amide axle. The benzyl ethers do not survive a Suzuki coupling due to the Lewis acidity of the catalyst. This finding points to a limitation of our approach that, however, can be circumvented by the use of other, more stable axles.
5) The formation of metal complexes has been demonstrated up to a tetravalent complex of the pyridine macrocycle. These studies also include metal-bridged rotaxane dimers.

The present toolbox approach to macrocyclic and interlocked molecules is thus extremely versatile in several different aspects and opens a new playground for supramolecular synthesis that can rely on a large set of different structures accessible from our five key intermediates. The synthetic approach is a convergent one, since more complex substituents that are to be coupled to the macrocycles can be prepared independently from the macrocycle synthesis and then coupled to it afterwards.

Experimental Section

General methods: Reagents were purchased from Aldrich, ACROS, or Fluka and used without further purification. Hunter's diamine **1**,[9,12a] extended diamines **6** and **7**,[9,12a] 4-(2,2′;6′,2″-terpyridine-4′-yl)phenylboronic acid pinacol ester,[23] and perylene **32**[36] were synthesized according to literature procedures. All acid chlorides were obtained from the corresponding isophthalic acids by reaction with $SOCl_2$.[37] The only exception was 5-iodoisophthaloyl dichloride, which was synthesized in two steps from 5-aminoisophthalic acid. First, the amino group is converted into the iodine substituent by a Schiemann reaction,[38] then the 5-iodoisophthalic acid is converted into the acid chloride with oxalyl chloride.[39] CH_2Cl_2, MeOH, EtOAc, and toluene were dried and distilled prior to use by usual laboratory methods, whereas all other solvents were used from commercial sources.

Thin-layer chromatography (TLC) was performed on precoated silica gel $60/F_{254}$ plates (Merck KGaA). Silica gel (0.04–0.063, 0.63–0.100 mm; Merck) and Al_2O_3 (neutral; Riedel de Haën) were used for column chromatography.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker ECX 400, DPX 400, DRX 500, or Jeol Eclipse 500 instruments. All chemical shifts are reported in ppm with solvent signals taken as internal standards; coupling constants are in Hertz. Mass spectra were recorded with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a micromass Z-spray ESI ion source, a Micromass Q-TOF2 mass spectrometer equipped with a Z geometry nanospray ion source, or a Bruker APEX IV Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with an Apollo ESI ion source equipped with an off-axis 70° spray needle.

Elemental analyses of the macrocyclic compounds reported herein almost always fail due to solvent molecules that are encapsulated inside the cavities of the macrocycles. These solvents cannot be removed by high vacuum, not even when the substances are heated. They appear in the NMR spectra and are also visible in the crystal structures with some disorder. Therefore, elemental compositions were assessed by isotope pattern analysis of the corresponding ions observed in the mass spectra and/or by exact mass measurements.

The following abbreviations are used: Ar = aryl, Cy = cyclohexyl, dppf = 1,1′-bis(diphenylphosphino)ferrocene, dppp = 1,3-bis(diphenylphosphino)-propane, isophth = isophthalamide moiety, naph = naphthyl, pin = pinacolato, py = pyridyl, pyr = pyrimidyl, tpy = 2,2′;6′2″-terpyridyl.

Extended diamine 2: At room temperature, a solution of pyridine-3,5-dicarbonyl dichloride (1.0 g, 5.0 mmol) in CH_2Cl_2 (150 mL) was slowly added over 5 h to a solution of **1** (10.2 g, 31.6 mmol) in CH_2Cl_2 (50 mL) and NEt_3 (2 mL). The mixture was left stirring at room temperature for 48 h. The solvents were then evaporated and the product was isolated by column chromatography (silica gel, elution with a (1:2) CH_2Cl_2/EtOAc mixture) as a white solid (2.5 g, 64%). $R_f = 0.4$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.43$–1.53 (m, 20H; CH_2), 2.13–2.16 (m, 24H; CH_3), 6.83 (s, 4H; ArH), 6.99 (s, 4H; ArH), 7.57 (s, 2H; NH), 8.70–8.71 (m, 1H; ArH(py)), 9.17 ppm (d, $J = 2.0$ Hz, 1H; ArH(py)); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.2$, 19.0, 23.2, 26.7, 37.4, 45.2, 121.7, 127.3, 127.4, 130.4, 130.6, 134.3, 134.8, 137.7, 140.4, 149.5, 150.9, 163.4 ppm; ESIMS: m/z (%): 776 (100) $[M+H]^+$, 798 (49) $[M+Na]^+$; HRMS (ESI$^-$): m/z calcd for $C_{51}H_{60}N_5O_2^-$: 774.4752 $[M-H]^-$; found: 774.4792.

Macrocycle 3: A suspension that was obtained from adding **2** (2.44 g, 3.1 mmol) to a solvent mixture of CH_2Cl_2 (500 mL), pyridine (10 mL), and NEt_3 (0.3 mL) was stirred in an ultrasonic bath for 1 h to afford a clear, light green solution. This solution and a solution of 5-*tert*-butylisophthaloyl dichloride (0.77 g, 3.0 mmol) were simultaneously added over 24 h to a flask containing CH_2Cl_2 (2000 mL) heated at reflux by using an automatic solvent pump. The reaction mixture was heated at reflux for another 24 h. The solvents were then evaporated and the residue was purified by column chromatography (silica gel, eluting with a 50:50:3 mixture of CH_2Cl_2/EtOAc/pyridine). The solid obtained from the purification was redissolved in toluene and the solvent was evaporated; this was done two more times. The product was again purified by column chromatography (silica gel, elution with a (14:2:1) CH_2Cl_2/EtOAc/MeOH mixture) to afford **3** as a white solid (0.93 g, 31%). $R_f = 0.54$ (CH_2Cl_2/EtOAc/MeOH 14:2:1); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD (5:1)): $\delta =$ 1.24 (s, 9H; C(CH_3)$_3$), 1.34–1.35 (br, 4H; CH_2), 1.47 (br, 8H; CH_2), 2.00 (s, 24H; ArCH_3), 2.16 (br, 8H; CH_2), 6.82 (s, 8H; ArH), 7.97 (br, 1H; ArH), 8.01 (d, $J = 1.4$ Hz, 2H; ArH), 8.74 (br, 1H; ArH(py)), 9.07 ppm (d, $J = 1.9$ Hz, 2H; ArH(py)); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD (5:1)): $\delta = 18.3$, 22.8, 26.2, 30.9, 35.0, 35.1, 45.0, 123.8, 126.1, 126.2, 128.3, 130.67, 130.73, 131.3, 134.0, 134.7, 134.9, 137.0, 147.8, 148.2, 149.5, 153.2, 163.6, 166.9 ppm; ESIMS: m/z (%): 960 (100) $[M-H]^-$; HRMS (ESI$^-$): m/z calcd for $C_{63}H_{70}N_5O_4^-$: 960.5433 $[M-H]^-$; found: 960.5396.

Macrocycle 8: A solution of 5-acetoxyisophthaloyl dichloride (0.8 g, 3.1 mmol) in dry CH_2Cl_2 (250 mL) and a mixture of **6** (2.6 g, 3.1 mmol) and triethylamine (1 mL) in dry CH_2Cl_2 (250 mL) were simultaneously added dropwise to dry CH_2Cl_2 (1000 mL) from separate dropping funnels, while the system was kept under argon atmosphere. The addition was completed after 8 h, and the solution was stirred at room temperature for another 12 h. The solvents were evaporated under reduced pressure. The residue was subjected to column chromatography (silica gel, eluting with a (6:1) CH_2Cl_2/EtOAc mixture) to obtain **8** as a white product (1.4 g, 43%). $R_f = 0.40$; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.40$ (s, 9H; C(CH_3)$_3$), 1.52 (br, 4H; CH_2), 1.65 (br, 8H; CH_2), 2.05 (br, 3H; CH_3), 2.17 (br, 24H; CH_3), 2.33 (br, 8H; CH_2), 6.96 (br, 8H; ArH), 7.56 (br, 4H; NH), 7.87 (s, 2H; ArH), 8.04 (s, 1H; ArH), 8.12 (s, 1H; ArH), 8.19 ppm (s, 2H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.91$, 18.92, 20.9, 22.9, 26.3, 31.2, 35.3, 45.1, 59.3, 122.8, 122.9, 124.8, 126.4, 126.5, 128.6, 130.8, 131.1, 134.7, 134.7, 136.4, 147.4, 148.1, 148.1, 151.9, 153.9, 164.2, 165.7, 171.3 ppm; ESIMS: m/z: 1020 $[M+H]^+$.

Macrocycle 9: Macrocycle **8** (1.20 g, 1.18 mmol) was dissolved in a dioxane (30 mL)/water (20 mL) mixture together with KOH (1.46 g, 26 mmol). The mixture was heated at reflux for 8 h. The solvents were removed in vacuo and the remaining solid was suspended in water (2 mL). The free acid was generated by dropwise addition of concd HCl. The product was collected by filtration and washed several times with water (1.04 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (s, 9H; C(CH_3)$_3$), 1.46 (br, 4H; CH_2), 1.57 (br, 8H; CH_2), 2.09 (s, 12H; CH_3), 2.10 (s, 12H; CH_3), 2.26 (br, 8H; CH_2), 6.92 (br, 8H; ArH), 7.44 (s, 2H; ArH), 7.50 (s, 1H; ArH), 7.73 (s, 1H; ArH), 8.11 ppm (s, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.6$, 24.3, 27.7, 32.2, 36.5, 36.8, 46.5, 119.1, 119.4, 125.4, 126.4, 127.7, 132.7, 132.8, 135.6, 136.42, 136.43, 137.3, 149.5, 149.6, 154.8, 160.0, 168.5, 168.7 ppm; ESIMS: m/z (%): 978 (6) $[M+H]^+$, 1000 (100) $[M+Na]^+$, 1016 (18) $[M+K]^+$, 1977 (16) $[M+Na^+]$.

Macrocycle 10: A solution of **9** (1,15 g; 1,18 mmol) in CH_2Cl_2 (20 mL) and pyridine (30 mL) was cooled to −30 °C. Trifluoromethanesulfonic acid anhydride (0.78 mL) was added dropwise over 1 h taking care that the temperature does not exceed −25 °C. After the mixture was then stirred for 5 h at 0 °C, it was poured into ice (100 mL). The aqueous phase was extracted two times with toluene and the combined organic phases were washed with water, dried over $MgSO_4$, and evaporated in vacuo. The solid was purified by column chromatography (silica gel, elution with a (8:1) CH_2Cl_2/EtOAc mixture) to give **10** as a beige solid (275 mg, 21%). $R_f = 0.50$; ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD): $\delta = 1.26$ (s, 9H; C(CH_3)$_3$), 1.36 (br, 4H; CH_2), 1.49 (br, 8H; CH_2), 2.01 (s, 24H; CH_3), 2.17 (br, 8H; CH_2), 6.82 (s, 4H; ArH), 6.83 (s, 4H; ArH), 7.91 (s, 2H; 4,6-*OTf*-isophth$H$), 7.99 (s, 1H; 2-*OTf*-isophth$H$), 8.02 (s, 2H; 4,6-*t*-Bu-isophth$H$), 8.30 ppm (s, 1H; 2-*t*-Bu-isophth$H$); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD): $\delta = 18.11$, 18.12, 22.6, 26.0, 30.7, 35.0, 44.9, 60.3, 116.8, 123.7, 123.8, 126.0, 126.3, 126.4, 128.1, 130.7, 131.1, 133.9, 134.72, 134.73, 136.8, 147.7, 148.0, 148.1, 149.9, 153.2, 164.1, 166.8 ppm; ESIMS: m/z (%): 1110 (51) $[M+H]^+$, 1131 (100) $[M+Na]^+$, 1147 (5) $[M+K]^+$; HRMS (ESI$^-$): m/z calcd for $C_{65}H_{72}F_3N_4O_7S_1^+$: 1109.507 $[M+H]^+$; found: 1109.503.

Macrocycle 11: A solution of 5-iodoisophthaloyl dichloride (0.33 g, 1 mmol) in dry CH_2Cl_2 (250 mL) and a mixture of **7** (0.83 g, 1 mmol) and triethylamine (2 mL) in dry CH_2Cl_2 (250 mL) were simultaneously added dropwise to dry CH_2Cl_2 (1200 mL) from separate dropping funnels, while the system was kept under argon atmosphere. The addition was completed after 8 h and the solution was stirred at room temperature for another 72 h. The solvents were evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, eluting with a (6:1) CH_2Cl_2/EtOAC mixture) to give **11** as a white solid (0.12 g, 11%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.36$ (s, 9H; C(CH_3)$_3$), 1.40–1.50 (br, 4H; CH_2) 1.51–1.63 (br, 8H; CH_2), 2.08–2.11 (br, 24H; ArCH_3), 2.27 (br, 8H; CH_2), 6.92 (s, 8H; ArH), 8.03 (s, 1H; 2-*t*-Bu-isophth$H$), 8.12 (s, 2H; 4,6-*I*-isophth$H$), 8.20 (s, H; 2-*I*-isophth$H$), 8.41 ppm (s, 2H; 4,6-*t*-Bu -isophth$H$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 19.0$, 23.0, 26.4, 31.3, 35.0, 45.2, 95.5, 122.9, 126.4, 128.5, 130.8, 131.1, 134.7, 135.4, 136.4, 139.9, 148.0, 148.3, 153.9, 163.9 ppm; ESIMS: m/z (%): 1087 (40) $[M+H]^+$, 1109 (100) $[M+Na]^+$; HRMS (ESI$^+$): m/z calcd for $C_{64}H_{71}IN_4O_4Na^+$: 1109.4412 $[M+Na]^+$; found: 1109.4221.

Macrocycle 12: Macrocycle **11** (0.05 g, 0.046 mmol), $[PdCl_2(PPh_3)_2]$ (0.0064 g, 0.001 mmol) and CuI (0.0017 g, 0.001 mmol) were dissolved in dry DMF (5 mL) under an argon atmosphere. After the addition of triethylamine (5 mL), trimethylsilyl acetylene (20 μL 0.14 mmol) was added dropwise to the reaction mixture. After stirring for 15 h under an argon atmosphere at room temperature the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, eluting with a (15:1) CH_2Cl_2/EtOAc mixture) to give **12** as a white solid (0.018 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.26$ (s, 9H; SiC(CH_3)$_3$), 1.42 (s, 9H; C(CH_3)$_3$), 1.52–1.55 (br, 4H; CH_2), 1.62–1.65 (br, 8H; CH_2), 2.15–2.18 (br, 24H; ArCH_3), 2.30–2.32 (br, 8H; CH_2), 6.98 (br, 8H; ArH), 7.57 (br, 2H; 4,6-*t*-Bu-isophth$H$), 7.64 (br, 2H; 4,6-acetylene-isophth$H$), 7.75 (s, H; 2-*t*-Bu-isophth$H$), 8.08 ppm (s, H; 2-acetylene-isophth$H$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -0.1$, 19.1, 23.0, 26.4, 31.3, 35.4, 45.2, 97.5, 103.0, 122.9, 126.4, 128.7, 131.1, 131.3, 134.2, 134.8, 135.1, 148.1, 148.2, 153.9, 165.9 ppm; ESIMS: m/z (%): 1057 (100) $[M+H]^+$, 1079 (90) $[M+Na]^+$.

Macrocycle 13: Macrocycle **12** (0.02 g, 0.019 mmol) was dissolved in a 1:1 mixture of CH_2Cl_2/CH_3OH. KOH (0.005 g, 0.095 mmol) was added and the reaction mixture was stirred at room temperature for 12 h. Half of the solvent was evaporated under reduced pressure and the remaining organic phase was washed three times with H_2O. The organic phases were collected, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. Macrocycle **13** was obtained as a yellowish-white solid (0.014 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.42 (s, 9H; C(CH_3)$_3$), 1.52–1.55 (br, 4H; CH_3), 1.62–1.66 (br, 8H; CH_2), 2.16–2.18 (br, 24H; ArCH_3), 2.30–2.32 (br, 8H; CH_2), 6.97 (br, 8H; Ar*H*), 7.34 (br, 2H; 4,6-*t*-Bu-isophth*H*), 7.43 (br, 3H; 4,6-acetylene-isophth*H*, 2-*t*-Bu-isophth*H*), 7.99 ppm (s, H; 2-acetylene-isophth*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 19.0, 23.0, 26.5, 31.3, 35.4, 45.2, 79.9, 81.7, 122.9, 126.6, 128.6, 130.9, 131.1, 134.4, 134.7, 135.4, 148.1, 148.3, 154.0, 165.7 ppm; ESIMS: *m*/*z* (%): 985 (15) [*M*+H]$^+$, 1007 (100) [*M*+Na]$^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{66}H_{72}N_4NaO_4^+$: 1007.5446 [*M*+Na]$^+$; found: 1007.5360.

Macrocycle 14: A solution of 5-*tert*-butyl isophthaloyl dichloride (0.26 g, 1 mmol) in dry CH_2Cl_2 (250 mL) and a mixture of **7** (0.85 g, 1 mmol) and NEt_3 (2 mL) were simultaneously added dropwise to dry CH_2Cl_2 (1200 mL) over 8 h by using an automatic solvent pump, while the system was kept under an argon atmosphere. The cloudy solution was stirred at room temperature overnight. The solvents were then evaporated and the product was isolated by column chromatography (silica gel, eluting with a (15:1→6:1) CH_2Cl_2/EtOAc mixture) as a white solid (0.21 g, 20%). ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD (5:1)): δ=1.33 (s, 9H; C(CH_3)$_3$), 1.43–1.44 (br, 4H; CH_2), 1.55–1.56 (br, 8H; CH_2), 2.08–2.10 (br, 24H; ArCH_3), 2.24 (br, 8H; CH_2), 6.90 (s, 8H; Ar*H*), 8.07 (s, H; 2-*t*-Bu-isophth*H*), 8.10 (s, 2H; 4,6-Br-isophth*H*), 8.19 (s, 2H; 4,6-*t*-Bu-isophth*H*), 8.21 (s, H; 2-Br-isophth*H*), 8.65 (s, 2H; N*H*), 8.86 ppm (s, 2H; N*H*); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD (5:1)): δ=18.5, 31.1, 22.9, 26.4, 35.0, 45.1, 123.6, 126.0, 128.3, 131.2, 131.5, 133.9, 134.4, 135.3, 135.4, 136.1, 148.0, 148.2, 153.3, 164.9 ppm; ESIMS: *m*/*z* (%): 1041.5 (6) [*M*+H]$^+$, 1063.4 (52) [*M*+Na]$^+$, 2081.9 (8)[2*M*+H$^+$], 2102.9 (100) [2*M*+Na$^+$].

Macrocycle 15: Macrocycle **14** (360 mg, 0.345 mmol), bis(pinacolato)diboron (92.4 mg, 0.362 mmol), [$PdCl_2$(dppf)] (14.1 mg, 0.0173 mmol), and dried potassium acetate (101.7 mg, 1.035 mmol) were added to dried and argon-bubbled DMSO (10 mL). The mixture was kept at 80°C overnight under an argon atmosphere. After cooling to room temperature, CH_2Cl_2 (20 mL) and water (20 mL) were added and the product was extracted into the organic phase, which was washed three times with water (20 mL). The combined organic phases were dried in vacuo and the residue was examined by TLC. No bromo macrocycle starting material was detected on the TLC plate, so the residue was applied to a 10 cm column (silica gel, eluting with a (1:1) CH2L2/EtOAc mixture). The only band was collected and dried to give **15** as a white solid (308 mg, 82%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.35 (s, 12H CH_3 (pinacol)), 1.40 (s, 9H; C(CH_3)$_3$), 1.45–1.69 (b, 12H; CH_2), 2.14 (s, 12H; ArCH_3), 2.16 (s, 12H; ArCH_3), 2.38 (b, 8H; CH_2), 6.94 (s, 8H; Ar*H*), 7.94 (s, 1H; 2-isophth*H*), 8.19 (s, 2H; 4,6-isophth*H*), 8.31 (s, 1H; 2-isophth*H*), 8.51 ppm (s, 2H; 4,6-isophth*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=18.7, 22.7, 24.7, 26.2, 29.5, 31.0, 35.2, 45.0, 121.9, 126.2, 128.4, 128.8, 130.8, 134.2, 134.5, 136.5, 147.8, 153.7, 165.3 ppm; ESIMS: *m*/*z* (%): 1087.56 (100) [*M*+H]$^+$, 1109.54 (30) [*M*+Na]$^+$, 1125.51 (46) [*M*+K]$^+$.

Macrocycle 16: 4-(2,2′;6′,2″-Terpyridine-4′-yl)phenylboronic acid pinacol ester (52.3 mg, 0.120 mmol) was poured into a mixture of **14** (100 mg, 0.096 mmol), [Pd(PPh_3)$_4$] (3.45 mg, 0.003 mmol), and Cs_2CO_3 (46.9 mg, 0.144 mmol) in dry toluene (10 mL) and dry DMF (10 mL). The temperature was raised to 100°C whilst argon was bubbled through the solution and then it was heated at 120–130°C for 2 d under argon before the solvents were removed at reduced pressure. The remaining pale-pink solid was first examined by TLC on silica gel with a 95:5 mixture of CH_2Cl_2/CH_3OH to show that no appreciable amount of starting material remained. The residue was purified by column chromatography (neutral Al_2O_3, eluting with 1% CH_3OH in CH_2Cl_2) to give the product as a white powder (80.2 mg, 66%). R_f=0.88; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.35 (s, 9H; C(CH_3)$_3$), 1.40–1.65 (br, 12H; CH_2), 2.07 (s, 12H; ArCH_3), 2.09 (s, 12H; ArCH_3), 2.26 (br, 8H; CH_2), 6.92 (s, 8H; Ar*H*), 7.24–7.28 (m, 2H; Ar*H*(5,5″-tpy)), 7.74 (d, *J*=8.3 Hz, 2H; Ar*H*), 7.76–7.81 (m, 2H; Ar*H*(4,4″-tpy)), 7.91 (d, *J*=8.3 Hz, 2H; Ar*H*), 8.09 (s, 2H; 4,6-*t*-Bu isophth*H*), 8.13 (s, 1H; 2-*t*-Bu isophth*H*), 8.17 (s, 2H; 4,6-isophth*H*), 8.37 (s, 1H; 2-isophth*H*), 8.43 (s, 4H; N*H*), 8.54 (d, *J*=8 Hz, 2H; Ar*H*(3,3″-tpy)), 8.64 (d, *J*=4.6 Hz, 2H; Ar*H*(6,6″-tpy)), 8.71 ppm (s, 2H; Ar*H*(3′,5′-tpy)); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD (4:1)): δ= 18.6, 22.9, 26.3, 31.1, 35.2, 36.6, 45.2, 118.8, 121.9, 123.7, 124.2, 126.2, 127.7, 127.9, 128.5, 128.6, 128.7, 129.5, 130.9, 131.4, 131.5, 131.9, 132.0, 132.3, 134.2, 135.0, 135.2, 137.4, 138.0, 140.0, 142.1, 148.0, 148.1, 148.9, 149.7, 153.4, 155.9, 156.0, 163.1, 166.4, 166.8 ppm; ESIMS: *m*/*z* (%): 1268 (100) [*M*+H]$^+$.

Macrocycle 17: Pyridine-4-boronic acid pinacol ester (0.025 g, 0.120 mmol) was poured into a mixture of **14** (0.1 g, 0.096 mmol), [Pd(PPh_3)$_4$] (0.0035 g, 0.003 mmol), and Cs_2CO_3 (0.047 g, 0.144 mmol) in dry toluene (10 mL) and dry DMF (10 mL). The temperature was raised to 100°C whilst argon was bubbled through the solution and then it was heated at 120–130°C for 2 d under argon before the solvents were removed at reduced pressure. The residue was purified by column chromatography (silica gel, eluting with a 95:5 mixture of CH_2Cl_2/CH_3OH) to give **10** as a white solid (82 mg, 83.4%). ^{1}H NMR (400 MHz, [D_7]DMF): δ=1.41 (s, 9H; C(CH_3)$_3$), 1.52–1.54 (br, 4H; CH_2), 1.62–1.64 (br, 8H; CH_2), 2.18 (s, 12H; ArCH_3), 2.20 (s, 12H; ArCH_3), 2.47 (br, 8H; CH_2), 7.23 (s, 8H; Ar*H*), 7.87 (d, *J*=6.1 Hz, 2H; Ar*H*(py)), 8.21 (s, 2H; 4,6-*t*-Bu-isophth*H*), 8.49 (s, 2H; 4,6-py isophth*H*), 8.77 (s, H; 2-*t*-Bu-isophth*H*), 8.78 (d, *J*=6.1 Hz, 2H; Ar*H*(py)), 8.92 (s, H; 2-py-isophth*H*), 9.30 (s, 2H; NH), 9.47 ppm (s, 2H; NH); ^{13}C NMR ($CDCl_3$): δ=18.9, 19.0, 22.9, 24.7, 26.4, 31.1, 31.3, 35.4, 36.5, 45.2, 121.7, 126.5, 128.5, 129.9, 131.2, 134.7, 134.9, 135.7, 150.3, 162.6, 164.7 ppm; ESIMS: *m*/*z* (%): 1038 (100) [*M*+H]$^+$.

Macrocycle 18: Pyrimidine-5-boronic acid pinacol ester (51.5 mg, 0.250 mmol) was added to a mixture of **14** (208 mg, 0.200 mmol), [Pd(PPh_3)$_4$] (6.93 mg, 6.0 μmol), and Cs_2CO_3 (97.8 g, 0.300 mmol) in dry toluene (10 mL) and dry DMF (10 mL) under argon. The reaction was heated at 120°C for 2 d. All solvents were evaporated and the crude product was purified by column chromatography (silica gel, eluting with a (95:5) CH_2Cl_2/CH_3OH). The product, obtained as the second band from the column, was dried at high vacuum (166 mg, 83%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.38 (s, 9H; C(CH_3)$_3$), 1.42–1.65 (b, 12H; CH_2), 2.14 (s, 24H; ArCH_3), 2.34 (b, 8H; CH_2), 6.97 (s, 8H; Ar*H*), 7.96 (s, 2H; N*H*), 8.15 (s, 1H; 2-isophth*H*), 8.19 (s, 2H; 4,6-isophth*H*); 8.40 (s, 2H; 4,6-isophth*H*), 8.56 (s, 2H; N*H*), 8.64 (s, 1H; 2-isophth*H*), 9.04 (s, 2H; Ar*H*(pyr)), 9.16 ppm (s, 1H; Ar*H*(pyr)) (the spectrum always showed that there were two equivalents of DMF associated with the macrocycle even after extensive drying); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=18.7, 18.8, 22.6, 26.1, 29.5, 30.6, 31.0, 35.1, 36.2, 44.8, 122.9, 125.9, 126.1, 128.2, 128.4, 128.5, 129.7, 131.1, 131.3, 131.4, 131.5, 131.9, 132.8, 134.2, 134.5, 134.7, 135.7, 147.7, 148.2, 153.6, 154.8, 157.5, 162.4, 164.3, 165.5 ppm; ESIMS: *m*/*z* (%): 1039.6 [*M*+H]$^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{68}H_{75}N_6O_4^+$: 1039.5844 [*M*+H]$^+$; found: 1039.579.

Rotaxane 19: Dibenzo[18]crown-6 (13.0 mg, 0.036 mmol), **14** (150 mg, 0.144 mmol), potassium carbonate (198 mg, 1.44 mmol), α,α′-dibromo-*p*-xylene (38.0 mg, 0.144 mmol), and tritylphenol (96.9 mg, 0.288 mmol) were stirred in dry CH_2Cl_2 (20 mL) for a week. The solvent was then evaporated and the residue was eluted on a silica column with 2% methanol in CH_2Cl_2. The second band was collected as the pure rotaxane (100 mg, 38%). R_f=0.5; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.27 (s, 9H; C-(CH_3)$_3$), 1.40–1.65 (br, 12H; CyCH_2), 1.81 (s, 12H; PhCH_3), 1.83 (s, 12H; PhCH_3), 2.26 (br, 8H; CyCH_2), 4.22 (s, 4H; OCH_2), 5.98 (s, 4H; PhH_{axle}), 6.34 (d, *J*=4.5 Hz, 4H; Ph$H_{stopper}$), 6.96 (s, 8H; Ph*H*), 6.98 (d, *J*=4.5 Hz, 4H; Ph$H_{stopper}$), 7.07–7.18 (m, 30H; Ph$H_{stopper}$), 7.46 (s, 1H; 2-isophth*H*), 7.63 (s, 1H; 2-isophth*H*), 8.05 (s, 2H; 4,6-isophth*H*), 8.14 ppm (s, 2H; 4,6-isophth*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$+2 drops of CD_3OD): δ= 18.3, 30.8, 35.0, 64.0, 110.5, 112.9, 113.1, 125.6, 125.8, 126.4, 126.5, 127.1, 127.2, 127.3, 127.4, 130.5, 130.6, 130.7, 130.8, 132.3, 134.7, 134.8, 135.9, 140.8, 140.3, 161.6 ppm; HRMS (ESI$^+$): *m*/*z* calcd for $C_{128}H_{133}BrN_5O_6^+$: 1914.9434 [*M*+HNEt$_3$]$^+$; found: 1914.9560.

Rotaxane 20 (Synthesis starting from macrocycle 17): Dibenzo[18]crown-6 (31.1 mg, 0.0863 mmol), **17** (367 mg, 0.345 mmol), potassium carbonate

(476 mg, 3.45 mmol), α,α′-dibromo-*p*-xylene (91.0 mg, 0.345 mmol), and tritylphenol (232 mg, 0.690 mmol) were stirred in dry CH_2Cl_2 (20 mL) for a week. The solvent was then evaporated and the residue was eluted on a silica column with 2% methanol in CH_2Cl_2. The second band collected was the pure rotaxane (512 mg, 82%). R_f = 0.23; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.40 (s, 9H; C(CH_3)$_3$), 1.49–1.72 (br, 12H; CyCH_2), 1.88 (s, 24H; PhCH_3), 2.32 (br, 8H; CyCH_2), 4.34 (s, 4H; OCH_2), 5.89 (s, 4H; PhH_{axle}), 6.38 (d, J = 9.1 Hz, 4H; Ph$H_{stopper}$), 6.96 (d, J = 9.1 Hz, 4H; Ph$H_{stopper}$), 7.00 (s, 8H; Ph*H*), 7.01–7.22 (m, 30H; Ph$H_{stopper}$), 7.36 (s, 2H; 4,6-isoph*H*), 7.53 (d, J = 6.4, 2H; H_{py}), 7.82 (s, 1H; 2-isophth*H*), 8.17 (s, 1H; 2-isophth*H*), 8.37 (s, 2H; 4,6-isophth*H*). 8.59 ppm (d, J = 6.4 Hz, 2H; H_{py}); ^{13}C NMR (62.5 MHz, $CDCl_3$ + 2 drops of CD_3OD): δ = 18.4, 22.7, 29.4, 30.8, 35.3, 45.1, 64.0, 70.3, 113.1, 122.5, 125.9, 126.5, 127.3, 128.9, 130.7, 130.8, 131.9, 132.4, 132.6, 134.7, 134.8, 135.6, 140.9, 146.3, 148.5, 148.9, 153.4, 160.6, 165.9 ppm; ESIMS: m/z: 1813 $[M+H]^+$.

Rotaxane 20 (Synthesis starting from rotaxane 19): Pyridine boronic acid pinacol ester (11.3 mg, 0.055 mmol) was added to a mixture of rotaxane **19** (80 mg, 0.044 mmol), [Pd(PPh_3)$_4$] (1.53 mg, 1.32 μmol), and Cs_2CO_3 (21.5 mg, 0.066 mmol) in dry toluene (5 mL) and dry DMF (5 mL) under argon. The reaction was continued at 120°C for 2 d. All solvents were evaporated and the crude product was purified by column chromatography (silica, eluting with 2% methanol in CH_2Cl_2). The product was obtained as the third band from the column and dried at high vacuum (4.8 mg, 6%). For NMR and MS characterization see above.

FBMH 22: 1,4-Benzene diboronic acid pinacol ester (33.0 mg, 0.100 mmol) was added to a mixture of **14** (208 mg, 0.200 mmol), [Pd(PPh_3)$_4$] (7.0 mg, 6.0 μmol), and Cs_2CO_3 (97.8, 0.300 mmol) in dry toluene (10 mL) and dry DMF (10 mL) under argon. The reaction was continued at 120°C for 1 d. All solvents were evaporated and the crude product was purified by column chromatography (silica gel, eluting with a 10:1 mixture of CH_2Cl_2/CH_3OH). The product, obtained as the first band from the column, was dried at high vacuum. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD (2:1)): δ = 1.39 (s, 18H; C(CH_3)$_3$), 1.45–1.65 (br, 24H; CH_2), 2.16 (s, 24H; ArCH_3), 2.18 (s, 24H; ArCH_3), 2.31 (br, 16H; CH_2), 6.98 (s, 16H; Ar*H*), 7.86 (s, 2H; Ar*H*), 8.16 (s, 4H; 4,6-*t*-Bu-isophth*H*), 8.17 (s, 2H; 2-isophth*H*), 8.37 (s, 2H; 4,6-*t*-Bu-isophth*H*), 8.43 ppm (s, 4H; 4,6-isophth*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$/CD_3OD (2:1)): δ = 15.8, 17.9, 22.4, 25.9, 30.5, 34.7, 34.8, 44.7, 127.3, 128.1, 128.2, 128.4, 129.1, 131.0, 131.4, 131.5, 132.0, 133.7, 134.6, 141.6, 147.6, 147.7, 152.9, 160.7, 166.3, 166.7 ppm; ESIMS: m/z: 1997.151; HRMS (ESI$^+$): m/z calcd for $C_{134}H_{147}N_8O_8^+$: 1996.1336 $[M+H]^+$; found: 1996.151.

FBMH 24: Macrocycle **11** (0.112 g 0.103 mmol) was placed under argon atmosphere in a three-necked flask. Compound **23** (0.05 g, 0.033 mmol), dry DMF (10 mL), and dry triethylamine (0.15 mL) were added. The suspension was stirred until all of the starting material had dissolved, then PPh_3 (0.003 g, 0.099 mmol), [Pd(PPh_3)$_2$Cl$_2$] (0.004 g, 0.005 mmol), and CuI (0.001 g, 0.005 mmol) were added. After stirring for 40 h at room temperature, the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography (silica gel, eluting with a 20:1 mixture of CH_2Cl_2/CH_3OH) to obtain **24** as a dark yellowish solid (0.04 g, 40%). ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3OD (10:1)): δ = 1.38 (s, 27H; C(CH_3)$_3$), 1.51–1.53 (br, 12H; CH_2), 1.62–1.65 (br, 24H; CH_2), 2.14–2.16 (br, 72H; ArCH_3), 2.30–2.34 (br, 24H; CH_2), 6.97 (br, 24H; Ar*H*), 7.73 (s, 3H; Ar*H*), 8.11 (br, 3H; 2-*t*-Bu-isophth*H*), 8.14 (br, 6H; 4,6-*t*-Bu-isophth*H*), 8.27 (br, 6H; 4,6-acetylene-isophth*H*), 8.30 ppm (s, H; 2-acetylene-isophth*H*); ^{13}C NMR (125 MHz, CD_2Cl_2/CD_3OD (10:1)): δ = 15.8, 23.8, 27.1, 32.6, 42.7, 91.2, 123.7, 125.7, 128.9, 129.1, 131.8, 132.6, 132.7, 145.6, 152.4, 164.0 ppm; ESIMS: m/z (%): 1536 (50)[2M+Na]$^{2+}$, 3027 (25) $[M+H]^+$, 3050 (100) $[M+Na]^+$; HRMS (ESI$^+$): m/z calcd for $C_{204}H_{216}N_{12}NaO_{12}^+$: 3050.6618 $[M+Na]^+$; found: 3050.5579.

FBMH 25: Macrocycle **13** (0.014 g, 0.014 mmol) and CuCl (0.004 g, 0.0042 mmol) were dissolved in dry DMF (2 mL). After 12 h stirring at room temperature the solvents were evaporated under reduced pressure. The residue was purified by preparative TLC (silica gel, eluting with a 25:1 mixture of CH_2Cl_2/CH_3OH) to obtain **25** as a white solid (0.007 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD (10:1)): δ = 1.31 (s, 18H; C-(CH_3)$_3$), 1.41–1.43 (br, 8H; CH_2), 1.52–1.55 (br, 16H; CH_2), 2.06–2.08 (br, 48H; ArCH_3), 2.22–2.24 (br, 16H; CH_2), 6.9 (br, 16H; Ar*H*), 8.09 (br, 3H; 4,6-*t*-Bu-isophth*H*, 2-*t*-Bu-isophth*H*), 8.17 (s, 4H; 4,6-acetylene-isophth*H*), 8.30 ppm (s, 2H; 2-acetylene-isophth*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.6, 22.7, 26.6, 31.1, 35.2, 45.2, 71.2, 71.9, 126.3, 127.6, 131.2, 131.4, 134.2, 134.7, 135.1, 147.6, 148.1, 153.4, 165.4 ppm; ESIMS: m/z (%): 1969 (10) $[M+H]^+$, 1991 (100) $[M+Na]^+$; HRMS (ESI$^+$): m/z calcd for $C_{132}H_{142}N_8NaO_8^+$: 1991.0876 $[M+Na]^+$; found: 1991.0860.

Macrocycle 27: 2-Naphthyl boronic acid pinacol ester (0.120 mmol) was poured into an argon-purged mixture of bromo macrocycle **14** (100 mg, 0.096 mmol), [Pd(PPh_3)$_4$] (3.45 mg, 0.003 mmol), Cs_2CO_3 (46.9, 0.144 mmol) in dry toluene (10 mL) and dry DMF (10 mL) at 100°C. Then it was kept at 120–130°C for 2 d under argon. The solvents were evaporated at reduced pressure to dryness. After column chromatography on silica eluting with CH_2Cl_2/ethyl acetate (6:1), macrocycle **27** was obtained as the first band from the column dried at high vacuum (80.0 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$ + 2 drops CD_3OD): δ = 1.32 (s, 9H; C(CH_3)$_3$), 1.40–1.62 (br, 12H; CH_2), 2.09 (s, 12H; PhCH_3), 2.11 (s, 12H; PhCH_3), 2.27 (br, 8H; CH_2), 6.93 (s, 8H; Ph*H*), 7.37–7.48 (m, 3H; ArH_{naph}), 7.71–7.79 (m, 4H; ArH_{naph}), 8.09 (s, 1H; 2-isophth*H*), 8.12 (s, 2H; 4,6-isophth*H*), 8.24 (s, 1H; 2-isophth*H*), 8.44 (s, 2H; 4,6-isophth*H*), 8.62 (s, 2H; N*H*), 8.80 ppm (s, 2H; N*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$ + 2 drops CD_3OD): δ = 18.4, 22.7, 26.1, 30.9, 34.9, 35.0, 44.9, 124.7, 125.9, 126.0, 126.3, 127.4, 128.1, 128.2, 128.5, 129.6, 131.1, 132.7, 133.3, 133.9, 134.9, 142.5, 147.7, 153.1, 166.4, 166.1 ppm; ESIMS: m/z (%): 1088.61 (100) $[M+H]^+$, 544.31 (52) $[M+2H]^{2+}$; HRMS (ESI$^+$): m/z calcd for $C_{74}H_{80}N_4O_4^{2+}$: 544.3084 $[M+2H]^{2+}$; found: 544.3072.

Macrocycle 28: 1-Pyrenyl boronic acid pinacol ester (0.120 mmol) was poured into an argon-purged mixture of bromo macrocycle **14** (100 mg, 0.096 mmol), [Pd(PPh_3)$_4$](3.45 mg, 0.003 mmol), Cs_2CO_3 (46.9, 0.144 mmol) in dry toluene (10 mL) and dry DMF (10 mL) at 100°C. Then it was kept at 120–130°C for 2 d under argon. The solvents were evaporated at reduced pressure to dryness. After column chromatography on silica eluting with CH_2Cl_2/ethyl acetate (8:1), macrocycle **28** was obtained as the second band from the column and dried at high vacuum (97.0 mg, 87%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.44 (s, 9H; C(CH_3)$_3$), 1.51–1.70 (br, 12H; CH_2), 2.20 (s, 12H; PhCH_3), 2.24 (s, 12H; PhCH_3), 2.40 (br, 8H; CH_2), 7.09 (s, 8H; Ph*H*), 7.44 (s, 2H; 4,6-isophth*H*), 7.59 (s, 2H; 4,6-isophth*H*), 8.03–8.30 (m, ArH_{pyrene}), 8.37 ppm (s, 4H; N*H*); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 18.5, 19.1, 23.0, 26.4, 31.3, 35.5, 45.3, 58.5, 124.5, 124.8, 124.8, 125.0, 125.3, 125.6, 126.3, 126.6, 126.7, 127.4, 127.6, 128.0, 128.4, 128.5, 128.7, 130.9, 131.0, 131.3, 131.5, 133.1, 134.7, 134.8, 135.0, 135.3, 135.4, 143.8, 148.2, 154.1, 165.3, 165.7 ppm; ESIMS: m/z (%): 1162 (100) $[M+H]^+$.

Macrocycle 30: 4-Formyl benzene boronic acid pinacol ester (0.120 mmol) was poured into an argon-purged mixture of bromo macrocycle **14** (100 mg, 0.096 mmol), [Pd(PPh_3)$_4$] (3.45 mg, 0.003 mmol), Cs_2CO_3 (46.9, 0.144 mmol) in dry toluene (10 ml) and dry DMF (10 mL) at 100°C. Then it was kept at 120–130°C for 2 d under argon. The solvents were evaporated at reduced pressure to dryness. After column chromatography on silica eluting with CH_2Cl_2/CH_3OH (7:1), macrocycle **30** was obtained as a white powder (85.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 9H; C(CH_3)$_3$), 1.47–1.70 (br, 12H; CH_2), 2.12 (s, 24H; PhCH_3), 2.31 (br, 8H; CH_2), 6.97 (s, 8H; Ph*H*), 7.48 (br, 4H; N*H*), 7.68 (d, J = 10.3 Hz, 2H; Ph*H*), 7.75 (d, J = 10.3 Hz, 2H; Ph*H*), 7.99 (s, 1H; 2-isophth*H*), 8.14 (s, 2H; 4,6-isophth*H*), 8.25 (s, 1H; 2-isophth*H*), 8.37 (s, 2H; 4,6-isophth*H*), 9.93 ppm (s, 1H; C*H*O); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 19.1, 23.0, 26.4, 30.8, 31.3, 35.5, 45.3, 65.9, 122.7, 126.66, 126.74, 128.0, 128.6, 130.1, 130.4, 130.9, 131.1, 134.6, 134.8, 134.9, 135.1, 135.2, 135.3, 135.9, 141.9, 145.0, 148.1, 148.4, 154.1, 164.9, 165.8, 192.1 ppm; ESIMS: m/z (%): 1166.7 (100) $[M+HNEt_3]^+$ (ionization turned out to be significantly easier, when 0.5% of NEt_3 were added which forms a complex with the macrocycle in high abundances).

Macrocycle 31: 2,4-Dimethyl pyrrole (19 mg, 0.2 mmol, 17μL) and aldehyde **30** (106.5 mg, 0.1 mmol) were dissolved in dry CH_2Cl_2 (15 mL; argon was bubbled for 10 min) under argon. One drop of trifluoroacetic acid was added and the solution was stirred at room temperature for 4 h. A solution of *p*-chloranil (24.5 mg, 0.1 mmol) in dry CH_2Cl_2 (5 mL) was added and stirring was continued for 30 min. Then, BF_3·Et_2O was added and the reaction mixture was stirred for another 30 min. The reaction

mixture was washed three times with water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography eluting with CH_2Cl_2 (79.4 mg, 62%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.39$ (s, 9H; C(CH_3)$_3$), 1.41 (s, 6H; CH_3 of BODIPY), 1.45–1.65 (br, 12H; CH_2), 2.30 (br, 8H; CH_2), 2.47 (s, 24H; PhCH_3), 2.52 (s, 6H; CH_3 of BODIPY), 5.97 (s, 2H; Pyrrole*H* of BODIPY), 6.97 (s, 8H; Ph*H*), 7.38 (d, $J = 7.7$ Hz, 2H; Ph*H*), 7.38 (d, $J = 7.7$ Hz, 2H; Ph*H*), 7.96 (s, 1H; 2-isophth*H*), 8.20 (s, 2H; 4,6-isophth*H*), 8.30 (s, 1H; 2-isophth*H*), 8.49 ppm (s, 2H 4,6-isophth*H*) (the spectrum always shows three equivalents of DMF associated with the macrocycle even after extensive drying); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 14.4$, 18.8, 22.6, 30.8, 31.0, 35.1, 36.2, 44.8, 121.1, 126.1, 127.8, 128.5, 131.2, 131.3, 134.2, 134.47, 134.54, 134.7, 135.1, 162.4 ppm; ESIMS: *m*/*z* (%): 1306.7 (28) $[M+Na]^+$, 1321.9 (100) $[M+K]^+$, 1384.9 (18) $[M+HNEt_3]^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{89}H_{106}BF_2N_7O_4$: 1384.8404 $[M+HNEt_3]^+$; found: 1384.854 (ionization turned out to be significantly easier when 0.5% NEt_3 was added to form a complex with the macrocycle in high abundances).

FBMH 33: 1,7-Dibromoperylene-3,4,9,10-tetracarbonic acid cyclohexylbisimide (71.2 mg, 0.100 mmol) was added to a mixture of **15** (219.5 mg, 0.2 mmol), $[Pd(PPh_3)_4]$ (6.93 mg, 6.0 μmol), and Cs_2CO_3 (97.8, 0.3 mmol) in dry toluene (10 mL) and dry DMF (10 mL) under argon. The reaction was continued at 120°C for 2 d. All solvents were evaporated and the crude product was purified by column chromatography (silica gel, eluting with a 5:95 mixture of CH_3OH/CH_2Cl_2). The product obtained was analyzed by ^{1}H NMR spectroscopy and ESIMS and was found to be contaminated with bismacrocycle. Thus, a second column was employed to yield the product (112 mg, 45%; after second column). ^{1}H NMR (250 MHz, $CDCl_3/CD_3OD$ (10:1)) $\delta = 1.32$ (s, 18H; C(CH_3)$_3$), 1.40–155 (br, 48H; CH_2), 2.07 (s, 48H; ArCH_3), 2.23 (br, 16H; CH_2), 6.88 (s, 16H; Ar*H*), 8.02 (s, 2H; 2-isophth*H*), 8.05 (s, 4H; 4,6-isophth*H*), 8.10 (s, 4H; 4,6-isophth*H*), 8.23 (s, 2H; 2-isophth*H*), 8.40 (d, $J = 8.3$ Hz, 2H; Ar$H_{perylene}$), 8.51 (s, 2H; Ar$H_{perylene}$), 8.62 ppm (d, $J = 8.3$ Hz, 2H; Ar$H_{perylene}$); due to the poor solubility of **33**, no ^{13}C NMR could be measured; ESIMS: m/z (%): 2574 (8) $[M+HNEt_3]^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{170}H_{186}N_{11}O_{12}^+$: 2573.428 $[M+HNEt_3]^+$; found: 2573.440 (ionization turned out to be significantly easier when 0.5% NEt_3 was added to form a complex with the macrocycle in high abundances).

FBMH 34: Under an argon atmosphere, a solution of **3** (25.9 mg, 0.027 mmol) was slowly added to a solution of bis(benzonitrile)palladium(II)chloride (4.8 mg, 0.013 mmol). After stirring for 9 h, pale-yellow precipitate was filtered and dried (13.5 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ (5:1)): $\delta = 1.31$ (s, 18H; C(CH_3)$_3$), 1.43 (br, 8H; CH_2), 1.55 (br, 16H; CH_2), 2.06 (br, 48H; ArCH_3), 2.24 (br, 16H; CH_2), 6.88–6.89 (m, 16H; Ar*H*), 8.03 (br, 2H; Ar*H*), 8.08 (br, 4H; Ar*H*), 8.64 (br, 2H; Ar*H* (py)), 9.38 ppm (br, 4H; Ar*H*(py)); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (5:1)): $\delta = 18.4$, 22.9, 26.3, 31.0, 35.0, 35.2, 45.1, 123.8, 126.1, 126.3, 128.3, 130.8, 131.3, 131.7, 134.0, 134.8, 135.0, 137.7, 147.9, 148.3, 153.3, 154.4, 162.1, 166.8 ppm; ESIMS: *m*/*z* (%): 2122 (100) $[M+Na]^+$, 2138 (60) $[M+K]^+$; HRMS (ESI$^-$): *m*/*z* calcd for $C_{126}H_{141}Cl_2N_{10}O_8Pd^-$: 2099.9382 $[M-H]^+$; found: 2099.9416.

FBMH 35^{2+}(BF$_4^-$)$_2$: A solution of **3** (27.3 mg, 0.028 mmol) was dissolved in $CDCl_3$ (500 μL) before a solution of tetra(acetonitrile)palladium(II) tetrafluoroborate (2.6 mg, 0.006 mmol) in CD_3CN (60 μL) was slowly added under an argon atmosphere. After $CDCl_3$ (400 μL) was added to the mixture, it was stirred for a day and then stored in the refrigerator. After 3 d the white precipitate obtained was filtered to give the product (9 mg, 33%). ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (5:1)): $\delta = 1.31$ (s, 36H; C(CH_3)$_3$), 1.43 (br, 16H; CH_2), 1.55 (br, 32H; CH_2), 2.00–2.06 (br, 96H; ArCH_3), 2.22 (br, 32H; CH_2), 6.85–6.90 (m, 32H; Ar*H*), 8.00 (br, 4H; Ar*H*), 8.08 (d, $J = 1.6$ Hz, 8H; Ar*H*), 8.55 (br, 4H; Ar*H*(py)), 9.71 ppm (d, $J = 1.7$ Hz, 8H; Ar*H*(py)); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (5:1)): $\delta = 18.4$, 22.9, 26.3, 31.0, 35.1, 35.2, 45.1, 123.6, 126.2, 126.4, 128.3, 128.5, 130.4, 131.3, 134.1, 134.6, 134.8, 134.9, 147.9, 148.5, 152.2, 153.4, 162.1, 166.8 ppm; ESIMS: *m*/*z* (%): 3051 (100) $[M-$macrocycle$+CH_3COO]^+$, 4014 (33) $[M+CH_3COO]^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{254}H_{287}N_{20}O_{18}Pd^+$: 4010.1222 $[M+CH_3COO]^+$; found: 4010.1530.

FBMH 36: Macrocycle **17** (0.021 g, 0.02 mmol) and bis(benzonitrile)palladiumdichloride (0.004 g, 0.01 mmol) were dissolved in CH_2Cl_2 (20 mL) under an argon atmosphere. After stirring for 16 h at room temperature, the temperature was raised to 40°C for 1 h. Two thirds of the solvent was evaporated under reduced pressure and diethyl ether was slowly added. The suspension was filtered and the crude product was recrystallized from acetone/diethyl ether to give **36** as a brownish solid (0.010 g, 44%). ^{1}H NMR (500 MHz, [D$_7$]DMF): $\delta = 1.41$ (s, 18H; C(CH_3)$_3$), 1.52–1.55 (br, 8H; CH_2), 1.62–1.67 (br, 16H; CH_2), 2.19 (s, 24H; ArCH_3), 2.21 (s, 24H; ArCH_3), 2.48 (br, 14H; CH_2), 7.23 (s, 16H; Ar*H*), 8.15 (d, $J = 6.1$ Hz, 4H; Ar*H*(py)), 8.20 (s, 4H; 4,6-*t*-Bu-isophth*H*), 8.57 (s, 4H; 4,6-py-isophth*H*), 8.71 (s, 2H; 2-*t*-Bu-isophth*H*), 8.99 (s, H; 2-py-isophth*H*), 9.02 (d, $J = 6.1$ Hz, 4H; Ar*H*(py)), 9.35 (s, 4H; N*H*), 9.58 ppm (s, 4H; NH); ^{13}C NMR (125 MHz, [D$_7$]DMF): $\delta = 19.1$, 23.8, 27.1, 27.6, 31.6, 45.1, 124.0, 126.8, 128.7, 130.1, 133.7, 133.9, 135.8, 135.9, 137.3, 147.9, 148.1, 165.2, 166.0 ppm; ESIMS: *m*/*z* (%): 2216.04 (100) $[M-Cl]^+$, 2254.25 (50) $[M-H]^+$.

FBMH 37^{2+}(OTf$^-$)$_2$: [Pt(dppp)(OTf)$_2$] (0.011 g, 0.012 mmol) and **10** (0.025 g, 0.024 mmol) were dissolved in DMF (0.5 mL) and stirred for 10 min at room temperature. The solvents were evaporated under reduced pressure to obtain the product as a green solid in quantitative yield. ^{1}H NMR (500 MHz, [D$_7$]DMF): $\delta = 1.39$ (s, 18H; C(CH_3)$_3$), 1.52–1.61 (br, 24H; CH_2), 2.15 (s, 48H; ArCH_3), 2.23 (br, 4H; P-CH_2), 2.45 (br, 16H; CH_2), 3.45 (br, 2H; P-CH_2), 7.20–7.22 (br, 16H; Ar*H*), 7.47–7.51 (br, 20H; PtAr*H*), 7.85–7.88 (br, 4H; Ar*H*(py)), 8.20 (br, 4H; 4,6-*t*-Bu-isophth*H*), 8.30 (br, 4H; 4,6-*t*-Bu-isophth*H*), 8.66 (s, 2H; 2-*t*-Bu-isophth*H*), 8.94 (s, 2H; 2-py-isophth*H*), 9.15–9.17 (br, 2H; Ar*H*(py)), 9.25 (s, 4H; N*H*), 9.43 ppm (s, 4H; N*H*); ^{13}C NMR (125 MHz, [D$_7$]DMF): $\delta = 19.2$, 31.8, 24.0, 25.6, 27.3, 45.9, 126.9, 127.0, 129.7, 130.5, 132.9, 133.1, 133.7, 134.0, 134.4, 135.9, 136.0, 137.3, 138.0, 148.2, 148.3, 151.1, 153.6, 165.1, 166.2 ppm; ^{31}P NMR (200 MHz, [D$_7$]DMF): $\delta = -16.52$ ppm (^1J(Pt,P) = 3023 Hz); ESIMS: *m*/*z* (%): 1794 (10) $[M-$OTf$-$py-macrocycle$]^+$, 2833 (100) $[M-$OTf$]^+$; HRMS (ESI$^+$): *m*/*z* calcd for $C_{166}H_{176}F_3N_{10}O_{11}P_2PtS$: 2833.2365 $[M-$OTf$]^+$; found: 2833.2438.

Rotaxane 39: Under an argon atmosphere, P_1 base (0.24 mL, 1.02 mmol) was added to a suspension of **38** (176 mg, 0.66 mmol) in CH_2Cl_2 (300 mL). After the reaction mixture was stirred for 1 h at room temperature, macrocycle **3** (662 mg, 0.69 mmol) was added and stirring was continued for 15 min. Upon addition of triethylamine (0.18 mL), the reaction mixture was cooled down to 0–5°C, and a solution of triphenylacetyl chloride (405 mg, 1.32 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The reaction mixture was stirred for 3 d at room temperature, washed twice with saturated aqueous ammonium chloride solution and twice with deionized water. The organic layer was dried over magnesium sulfate, the solvents were then evaporated, and the residue was purified by column chromatography (silica gel, EtOAc) and again by column chromatography (silica gel, CH_2Cl_2/EtOAc/MeOH 14:2:1). The product was redissolved in diethyl ether, and after evaporation of solvents, rotaxane **39** was obtained as a white solid (165 mg, 0.09 mmol, 14%). $R_f = 0.41$ (CH_2Cl_2/EtOAc/MeOH 14:2:1); ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 1.46$ (s, 9H; C(CH_3)$_3$), 1.59 (s, 4H; CyCH_2), 1.69 (br, 8H; CyCH_2), 1.92–1.94 (br, 24H; ArCH_3), 2.21–2.24 (br, 8H; CyCH_2), 2.43 (br, 4H; NCH_2, station inside the wheel cavity), 3.52–3.63 (br, 4H; NCH_2, station outside the wheel cavity), 6.64 (br, 4H; N*H*), 6.81 (t, $J = 8.0$ Hz, 1H; Ar*H*), 6.97–7.22 (br, 40H; Ar*H*), 8.15 (br, 2H; N*H*), 8.19 (br, 2H; N*H*), 8.52 (br, 2H; Ar*H*), 8.62 (br, 1H; Ar*H*), 9.08 (br, 1H; Ar*H* (py)), 9.25 (d, $J = 1.0$ Hz, 2H; Ar*H* (py)), 15.54 ppm (s, 1H; O*H*); ^{13}C NMR (125 MHz, CD_2Cl_2): 18.6, 23.5, 26.7, 31.5, 35.6, 36.1, 37.0, 45.6, 119.4, 124.1, 126.7, 126.9, 127.1, 127.8, 128.4, 128.5, 129.9, 130.5, 131.5, 132.1, 134.1, 135.0, 135.6, 135.8, 149.2, 149.3, 152.3, 153.9, 161.7, 164.4, 166.4, 177.5 ppm; FTICR-MS (ESI$^-$, from MeOH): *m*/*z* (%): 1767 (100) $[M-H]^-$; HRMS (ESI$^-$): *m*/*z* calcd for $C_{115}H_{116}N_9O_9^-$: 1766.8901 $[M-H]^-$; found: 1766.8863.

MIA 40: Under an argon atmosphere, a solution of rotaxane **39** (20.4 mg, 0.012 mmol) in CH_2Cl_2 (2.5 mL) was slowly added to a solution of bis(benzonitrile)palladium(II)dichloride (2.15 mg, 0.006 mmol) in CH_2Cl_2 (1.5 mL). The reaction mixture was stirred at room temperature for 1 d and was then stored in the refrigerator. After a week, the pale precipitate obtained was filtered to obtain the product (5 mg, 11%). ^{1}H NMR

(500 MHz, $CDCl_3$): $\delta = 1.43$ (s, 9H; $C(CH_3)_3$), 1.57–1.62 (br, 12H; $CyCH_2$), 1.88–1.95 (br, 24H; $ArCH_3$), 2.15–2.21 (br, 8H; $CyCH_2$), 2.34–2.36 (br, 4H; NCH_2), 3.55–3.68 (br, 4H; NCH_2), 6.59 (br, 4H; NH), 6.85–7.24 (br, 40H; ArH), 8.02 (br, 2H; NH), 8.17 (br, 2H; NH), 8.51–8.59 (br, 3H; ArH), 9.19 (br, 1H; ArH(py)), 9.53 ppm (br; 2H; ArH(py)); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 18.5$, 23.1, 26.4, 31.5, 35.6, 36.1, 36.9, 45.3, 51.1, 119.5, 123.8, 127.1, 127.6, 127.9, 128.1, 128.4, 128.7, 130.2, 130.4, 130.5, 131.5, 131.6, 134.6, 135.0, 135.4, 135.8, 141.7, 142.7, 153.7, 155.6, 161.3, 161.4, 166.4 ppm; ESIMS: m/z (%): 3738 (100) $[M+Na]^+$; HRMS (ESI^+): m/z calcd for $C_{230}H_{234}Cl_2N_{18}NaO_{18}Pd^+$: 3738.6328 $[M+Na]^+$; found: 3738.6191.

Rotaxane 41: Dibenzo[18]crown-6 (13.0 mg, 0.036 mmol), **16** (150 mg, 0.144 mmol), potassium carbonate (198 mg, 1.44 mmol), α,α′-dibromoparaxylene (38.0 mg, 0.144 mmol), and tritylphenol (96.9 mg, 0.288 mmol) were stirred in dry CH_2Cl_2 (20 mL) for a week. The solvent was then evaporated and the residue was eluted on an alumina column with 2% methanol in CH_2Cl_2. The second band collected was the pure rotaxane (100 mg, 38%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.31$ (s, 9H; $C(CH_3)_3$), 1.50–1.70 (br, 12H; $CyCH_2$), 1.88 (s, 12H $PhCH_3$), 1.90 (s, 12H; $PhCH_3$), 2.33 (br, 8H; $CyCH_2$), 4.36 (s, 4H; OCH_2), 5.89 (s, 4H; PhH_{axle}), 6.40 (d, $J = 4.5$ Hz, 4H; $PhH_{stopper}$), 6.99 (d, $J = 4.5$ Hz, 4H; $PhH_{stopper}$), 7.02 (s, 8H; PhH), 7.09–7.25 (m, 30H; $PhH_{stopper}$), 7.31 (d, $J = 7.7$ Hz, 2H; 5,5″-tpyH), 7.54 (s, 1H; 2-isophthH), 7.75 (s, 1H; 2-isophthH), 7.76 (d, $J = 8.3$ Hz, 2H; PhH), 7.87 (t, $J = 7.7$ Hz, 2H; 4,4″-tpyH), 7.97 (d, $J = 8.3$ Hz, 2H; PhH), 8.14 (s, 2H; 4,6-isophthH), 8.42 (s, 2H 4,6-isophthH), 8.86 (d, $J = 7.7$ Hz, 2H; 3,3″-tpyH), 8.73 (d, $J = 7.7$ Hz, 2H; 6,6″-tpyH), 8.78 ppm (s, 2H; 3,5′-tpyH); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 18.7$, 23.1, 26.3, 31.2, 35.7, 45.4, 64.3, 70.9, 113.4, 118.8, 121.4, 121.7, 123.1, 123.8, 126.1, 126.9, 127.5, 127.8, 127.9, 129.2, 130.5, 130.9, 131.0, 131.2, 132.7, 134.6, 135.1, 135.4, 135.7, 136.9, 138.4, 139.5, 141.2, 142.9, 146.5, 149.1, 149.2, 149.2, 149.5, 154.2, 155.7, 156.1, 156.2, 165.2, 165.8 ppm; ESIMS: m/z (%): 2043.0 (100) $[M+H]^+$, 2144.1 (40) $[M+HNEt_3]^+$; HRMS (ESI^+): m/z calcd for $C_{149}H_{147}N_8O_6^+$: 2144.144 $[M+HNEt_3]^+$; found: 2144.144.

MIA $42^{2+}(ClO_4^-)_2$: Rotaxane **41** (12.0 mg, 5.87 μmol) in $CDCl_3$ was introduced into a metal solution containing half an equivalent of metal ion from a stock solution separately prepared from $Zn(ClO_4)_2{\cdot}6H_2O$ in CD_3CN. Two drops of CD_3OD (without which the NMR spectra seem to be overwhelmingly broad in this case) was added to the mixture. The resulting mixture was stirred for 1 d to yield the desired complex. ^1H NMR (500 MHz, $CDCl_3$ + 2 drops CD_3OD): $\delta = 1.27$ (s, 18H; $C(CH_3)_3$), 1.34–1.65 (br, 24H; $CyCH_2$), 1.84 (s, 48H; $ArCH_3$), 2.57 (br, 16, $CyCH_2$), 4.35 (s, 8H; OCH_2), 6.18 (s, 8H; PhH_{axle}), 6.43 (d, $J = 8.65$ Hz, 8H; $PhH_{stopper}$), 6.90 (d, $J = 8.65$ Hz, 8H; $PhH_{stopper}$), 6.99 (s, 8H; PhH), 6.85–6.92 (m, 8H; 6,6″; 3,3″-tpyH) 7.02–7.11 (m, 60H; $PhH_{stopper}$), 7.30 (s, 2H; 2-isophthH), 7.41 (s, 4H; 4,6-isophthH), 7.60 (t, $J = 7.15$ Hz, 4H; 5,5″-tpyH), 7.70 (s, 2H; 2-isophthH), 7.83 (t, $J = 7.15$ Hz, 4H; 4,4″-tpyH), 7.97 (s, 4H; 4,6-isophthH), 8.12 (d, $J = 7.05$ Hz, 4H; PhH), 8.38 (s, 4H; 3′,5′-tpyH), 8.61 (d, $J = 7.05$ Hz, 4H; Ph), 8.85 ppm (s, 4H; NH); ^{13}C NMR (125 MHz, $CDCl_3$ + 2 drops CD_3OD): $\delta = 18.1$, 22.5, 25.8, 29.1, 30.5, 34.7, 35.0, 44.8, 63.8, 69.4, 112.9, 116.4, 120.0, 121.0, 122.6, 125.5, 126.1, 127.1, 127.3, 127.5, 127.8, 128.1, 128.3, 129.6, 130.4, 130.9, 131.9, 133.8, 134.7, 134.7, 134.9, 135.5, 139.8, 141.0, 141.1, 146.3, 147.2, 147.3, 147.8, 148.2, 149.3, 153.3, 155.6, 165.5, 165.9.

X-ray crystallographic data for 3: Chemical formula: $C_{67.33}H_{82.33}Cl_{11.33}N_5O_4$, $M_w = 1427.48$; $T = 173.0(1)$ K; $Mo_{K\alpha}$ radiation (0.71073 Å); triclinic; $P\bar{1}$; $a = 14.105(3)$, $b = 18.436(4)$, $c = 22.291(5)$ Å; $\alpha = 70.38(3)$, $\beta = 88.36(3)$, $\gamma = 89.41(3)°$; $V = 5458(2)$ Å^3; $Z = 3$; $\rho_{calcd} = 1.303$ g cm^{-3}, $\mu = 0.480$ mm^{-1}; $F(000) = 2238$; colorless; $0.40 \times 0.12 \times 0.06$ mm^3 crystal; Bruker Nonius Kappa CCD diffractometer; 13974 Independent reflections; 11756 with $I > 2\sigma$; Gaussian absorption correction; min and max transmission: 0.8311 and 0.9718; 2121 restraints; 1220 parameters; $R1 = 0.1609$; $wR2 = 0.4740$ [$I > 2\sigma$]; $R1 = 0.1757$; $wR2 = 0.4863$ [all data]; GOF = 2.296; extinction coefficient = 0.038(6); largest diff. peak and hole: 2.57 and −1.04 e Å^{-3}.

X-ray crystallographic data for 34: Chemical formula: $C_{144.40}H_{164.40}Cl_3N_{10}O_{23.80}Pd$; $M_w = 2633.63$; $T = 173.0(1)$ K; $Cu_{K\alpha}$ radiation (1.54184 Å); triclinic; $P\bar{1}$; $a = 12.0618(8)$, $b = 16.091(2)$, $c = 24.424(2)$ Å; $\alpha = 72.443(4)$, $\beta = 82.028(4)$, $\gamma = 69.181(3)°$; $V = 4221.8(6)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.036$ g cm^{-3}, $\mu = 1.800$ mm^{-1}; $F(000) = 1388.2$; colorless; $0.10 \times 0.15 \times 0.20$ mm^3 crystal; Bruker Nonius APEX II diffractometer; 9747 independent reflections; 5581 with $I > 2\sigma$; multiscan absorption correction; min and max transmission: 0.7148 and 0.8405; 2121 restraints; 883 parameters; $R1 = 0.1457$; $wR2 = 0.3410$ [$I > 2\sigma$]; $R1 = 0.2167$, $wR2 = 0.3825$ (all data); GOF = 1.067, largest diff. peak and hole: 1.078 and −0.66 e Å^{-3}.

CCDC-687761 and -687762 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are grateful for funding from the Deutsche Forschungsgemeinschaft (SFB 765 "Multivalency"), the Fonds der Chemischen Industrie (FCI) and the Academy of Finland (K.R.: no. 122350 and 113437). C.A.S. thanks the FCI for a Dozentenstipendium. S.S.Z. thanks the Studienstiftung des deutschen Volkes for a PhD scholarship.

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Received: June 27, 2008
Published online: September 30, 2008

