Interlocked Porphyrin Switches

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Abstract: We describe the synthesis of a series of catenanes and molecular necklaces from porphyrin-glycoluril cage compounds and bis-olefin terminated viologens by an olefin metathesis protocol. The length of the chain connecting the olefin substituents with the viologen has a marked effect on the products of the ring closure reaction. Long chains yield [2]- and [3]-catenane structures, whereas short chains give a mixture of [3]-catenane and [4]- and [5]-molecular necklaces. For comparison also several [2]-rotaxane compounds were prepared. The interlocked catenane and rotaxane structures display switching behavior, which can be controlled by the addition of acid and base. The kinetic and thermodynamic parameters of the switching processes have been determined by NMR.

Keywords: Interlocked structures, porphyrins, switches, rotaxanes, catenanes

Introduction

The development and study of mechanically interlocked molecules such as rotaxanes, catenanes, molecular necklaces and Borromean rings remains a fascinating area of supramolecular chemistry. These interlocked architectures have shown to be potential candidates for incorporation in molecular memory devices due to their tunable switching (on/off) behaviour. The group of Stoddart, for example, has demonstrated that it is possible to immobilize switchable [2]catenanes onto a surface, while retaining their switching behaviour, resulting in prototypical molecular memories. The same group has more recently shown that certain [3]rotaxanes, when grafted onto a thin metal surface, are capable of bending the surface as a result of electrochemically induced contraction of the rotaxanes. These examples clearly demonstrate that interlocked molecules are promising building blocks, which can be applied as functional elements in nanotechnology. They have stimulated us to investigate interlocked structures that contain one or more functional components, viz. porphyrins, as part of a project aimed at developing a so-called molecular Turing machine. In 1937 Alan Turing described a theoretical machine that can manipulate symbols on a strip of tape according to a table of rules obtained from a tape head (see Figure 1a). A Turing machine is a simple device, but nevertheless can be adapted to simulate the logic of any computer algorithm. We have embarked on a program to construct a molecular Turing machine, i.e. a molecular device that can perform actions on a polymer tape according to instructions from a tape head. The blueprint is shown in Figure 1c. As a tape, polymers will be used containing sites that can be chemically transformed, e.g. alkene double bonds in polybutadiene that can be converted into epoxide functions. The tape head will be a glycoluril double cage compound of the type shown in Figure 1b. It contains two metal porphyrin cages that are held together by a ligand bond (1,4-diazabicyclo[2.2.2]octane) and by hydrogen bonding interactions. In a previous paper we have shown that in this compound information can be transferred from one porphyrin cage to the other by four positive allosteric interactions. One of the cages will contain a ring compound, i.e. a catenane, that can rotate and provide the instructions. The other cage will be threaded onto a polymer chain (see Figure 1).
The components in the ring have to be designed in such a way that information can be transferred to the polymer tape, e.g. by allosteric actions. One such component may be a pyridine group, which when positioned in the tape head will give the instruction to perform a catalytic reaction on an alkene double bond in the polymer tape. Another component could be a viologen group or a (protonated) amine function or a light switchable azobenzene group, which may give the instruction to the tape head to bind to a certain place on the polymeric tape. The ultimate goal would be to modify a polymer substrate with a repeating pattern, which is imparted by the catenane.

As a first step in the construction of such a molecular Turing machine we decided to study the synthesis of a porphyrin-glycoluril rotaxane architecture using olefin metathesis chemistry. We have already demonstrated that olefin metathesis in combination with the selective recognition of viologens by porphyrin-glycoluril host 1 (Scheme 1) is an excellent way to synthesize rotaxanes. This stimulated us to further explore this approach and use it for the synthesis of porphyrin-based catenanes, that might function as simple molecular switches. Here, the synthesis and (photo)physical properties of a variety of interlocked structures (catenanes, molecular necklaces and rotaxanes) based on porphyrin host 1 are described.

Scheme 1. Formation of a host-guest complex between the cavity-containing porphyrin 1 and a viologen guest.

Results and Discussion

Design. Our strategy to construct porphyrin-containing catenanes is based on an olefin model to construct metathesis, which was published previously by our group. In organic solvents porphyrin host 1 forms very stable complexes with viologen (N,N'-dialkyl-4,4'-bipyridinium) derivatives (Scheme 1). The strong binding of these guests relies on a combination of factors, viz. π-π stacking interactions between the aromatic surfaces of the viologen and of 1, electrostatic interactions between the positive charges on the guest and the crown ether moieties of 1, and C-H•••O hydrogen bonding between the α-bipyridinium protons and the crown ether and carbonyl oxygen atoms of 1. When viologens that contain terminal olefins as N-substituents are complexed in the cavity of 1, the resulting host-guest complexes can in principle be subjected to olefin metatheses reactions, so that interlocked porphyrin-containing species are generated. Similar olefin ring-closing and cross metathesis protocols have proven to be very effective for the high yield synthesis of a variety of interlocked molecules. In the research described in this paper we will make use of two olefin-containing viologens, 3 and 4 (see Scheme 2), that differ in the length of the bipyridine N-substituents.

Synthesis of olefin-containing viologens. The synthesis of viologen 3 started with the etherification of 1,10-dibromodecane with 9-decenol using NaH as a base in DMF, affording bromide derivative 2 in 44% yield after purification by column chromatography (Scheme 2). This compound was subsequently coupled to 4,4'-bipyridine in hot DMF, after which ion exchange with NH4PF6 in water gave 3 in 23% yield, after recrystallization from methanol. To obtain a viologen with a shorter substituent, 4,4'-bipyridine was reacted with an excess of 8-bromoctene in hot DMF, followed by ion-exchange with NH4PF6, to give viologen 4 in 61% yield.

Synthesis of catenanes and molecular necklaces. The mixing of porphyrin clip 1 with viologen 3 in CHCl3/acetonitrile (1:1, v/v), followed by precipitation of the product in n-hexane, quantitatively furnished [2]pseudorotaxane 5 (Scheme 3). Indicative for [2]pseudorotaxane formation are the large complexation-induced shifts observed in the 1H NMR spectrum (CDCl3) for the signals of the aromatic viologen protons H4 (Δδ = −2.65 ppm) and H6 (Δδ = −4.07 ppm), as a result of shielding by the porphyrin macrocycle and the aromatic side walls of 1. The complex was readily soluble in CH2Cl2, which set the stage for a ring-closing metathesis reaction (RCM) of the terminal alkene groups of the viologen using the first generation Grubbs’ catalyst RuCHPh(Cl)(PCy3)2 (Scheme 3). To minimize intermolecular crosslinking, the reaction was performed under high dilution conditions ([S] = ca. 0.0005 M). At these concentrations, more than 99% of 1 is complexed by 3 because of the high association constant (Ks ≈ 107 M−1). Subjecting a solution of 5 in CH2Cl2 to 20 mol% of Grubbs’ catalyst for 24 hours at room temperature resulted in a mixture of products, of which [2]catenane 6 could be isolated in 69% yield after column chromatography, as a mixture of E/Z isomers in a 4:1 ratio. [3]Catenane 7 was also isolated in 3% yield, as a mixture of E/E, E/Z, and Z/Z isomers (total E/Z ratio = 4:1). Both catenanes contain a very large macrocycle: a 48-membered ring in the case of 6 and a 96-membered one in the case of 7. The MALDI-TOF spectra of the [2]catenanes (Figure 2a-b) showed one peak for 6 at m/z = 2064 amu, corresponding to [M-2PF6]+ and four peaks for 7 at m/z = 4128, 4273, 4415, 4560 amu, corresponding to [M-nPF6]+ (n=1-4).

Scheme 2. Synthesis of olefin-terminated viologens.

Figure 2. MALDI-TOF spectra of (a) [2]catenane 6, (b) [3]catenane 7, (c) [4]molecular necklace 10 and (d) [5]molecular necklace 11.

The 2D-NOESY spectrum of 6 revealed nOe-contacts between the pyrrole NH protons of the porphyrin and the aromatic protons H_a and H_b (see Scheme 2) of the viologen, which indicates that the latter moiety is situated inside the cavity of 1. The resonances of the trans-alkene protons H_c (see Scheme 3) are shifted upfield to δ = 4.87 ppm, (Δδ ≈ –0.5 ppm compared to other internal alkenes), which is attributed to shielding effects by the porphyrin macrocycle and/or the aromatic side walls of 1. In the ^1H NMR spectrum of [3]catenane 7, the trans-alkene protons resonate at δ = 5.39 ppm, indicating that the alkene parts of the thread are in this case situated further away from the aromatic surfaces of the host.

To investigate the effect of spacer length on the outcome of the metathesis reaction, the same RCM reaction was repeated using viologen 4, which has shorter N-substituents. The desired [2]pseudorotaxane 8 was readily assembled according to the aforementioned procedure. Exposing a 0.001 M solution of 8 in CH_2Cl_2 to 20 mol% of Grubbs’ catalyst in refluxing CH_2Cl_2 for 24 hours gave a mixture of products, containing [3]catenane 9.


The synthesis of [2]rotaxanes 18-20 was based on our previously reported protocol.\cite{10} It started with the synthesis of bulky alkyl bromides 12-14 by reacting the appropriate dibromides (in the case of 12 and 13) with 3,5-di-tert-butylphenol under basic conditions in DMF. Compounds 12 and 13 were isolated in 70-80% yield.

[4]molecular necklace 10, [5]molecular necklace 11 and some higher cyclooligomers (Scheme 4).\cite{13} It appeared that refluxing the solution resulted in a much better conversion than performing the reaction at room temperature. The necklaces 10 and 11 could be isolated from the product mixture in 18% and 11% yield, respectively (~95% pure), using a combination of silica and size exclusion chromatography. To the best of our knowledge, these are the first examples of porphyrin-containing molecular necklaces.\cite{11} MALDI-TOF showed five peaks for necklace 10 at m/z = 5088, 5234, 5378, 5523 and 5668 amu, corresponding to [M–nPF6]⁺ (n=2-6) (Figure 2c). For necklace 11, MALDI-TOF showed six peaks at m/z = 7073, 7218, 7363, 7508, 7654 and 7798 amu, corresponding to [M–nPF6]⁺ (n=1-6) (Figure 2d). No formation of a [2]catenane was observed, even when the reaction was performed at higher dilution (0.0005 M), which indicates that the N-substituents of 4 are too short to be engaged in an intramolecular crosslink. Hence, by varying the spacer length it is possible to control, at least to some extent, the outcome of the metathesis reaction.

Synthesis of [2]rotaxanes. It was decided to also synthesize a series of [2]rotaxanes based on 1, containing threads of different lengths (Scheme 5), in order to be able to compare their physical properties with those of the aforementioned catenane structures.
Bromide 14 was synthesized by first coupling 11-bromoundecan-1-ol and 3,5-di-tert-butylphenol (yield: 77%), after which the alcohol was converted to a bromide by reacting it with PbCl₃ in CH₂Cl₂ to give 14 in 62% yield. This procedure was followed since it appeared impossible to purify the product mixture obtained after reaction of the bulky phenol with 1,1,1-dibromoundecane. The bulky bromides were reacted with an excess of 4,4'-bipyridine in MeCN to give mono-alkylated bipyridium derivatives 15-17 in yields up to 90%, after ion-exchange with aqueous NH₄PF₆. It was now possible to synthesize the corresponding rotaxanes 18-20 by simply heating a mixture of 1, five equivalents of respectively 15-17 and 40 equivalents of respectively 12-14 in DMF. After ion exchange with aqueous NH₄PF₆ and purification by column chromatography, the [2]rotaxanes were isolated in yields up to 60%.

Protonation-induced shuttling. With the novel interlocked porphyrins at hand, it was decided to investigate if these molecules could be used as molecular switches. We anticipated that protonation of the pyrrole nitrogen atoms of the porphyrin ring with trifluoroacetic acid (TFA) would result in an expulsion of the viologen moiety from the porphyrin cavity due to Coulombic repulsion, as was observed previously in a related system published by Gunter et al.⁵⁶ Indeed, the addition of 5 vol% of TFA to a CDCl₃ solution of the simplest [2]catenane, 6, resulting in dramatic downfield shifts for viologen resonances H₄₂ (Δδ = +2.78 ppm, see Scheme 2 for proton numbering) and H₃₆ (Δδ = +3.77 ppm), because of expulsion of the viologen from the cavity of 1 (Figure 3). In addition, a significant downfield shift was observed for the alkene resonance H₅₂ (Δδ = +0.53 ppm). Both observations indicate a rotation of the viologen-containing ring with respect to the porphyrin host. Notably, new resonances appear at high field (0 to ~4 ppm), most probably as a result of shielding effects exerted by the porphyrin ring current on protons present inside the cavity. Low temperature COSY experiments were used to assign some of these resonances, as is indicated for proton H₁ of 6 (Table 1). It is clear from these experiments that protonation induces a motion in the [2]catenane, involving a switching of the porphyrin moiety between two degenerate states (Scheme 6).

**Table 1** ¹H NMR data of [2]catenane 6 and protonated catenane [6·2H][⁺]

<table>
<thead>
<tr>
<th>Proton</th>
<th>6 (δ, ppm)</th>
<th>6·2H⁺ (δ, ppm)</th>
<th>Shift (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.18</td>
<td>8.96</td>
<td>+2.78</td>
</tr>
<tr>
<td>b</td>
<td>4.80</td>
<td>8.57</td>
<td>+3.77</td>
</tr>
<tr>
<td>c</td>
<td>4.87</td>
<td>5.40</td>
<td>+0.53</td>
</tr>
<tr>
<td>d</td>
<td>1.20</td>
<td>0.63</td>
<td>-0.57</td>
</tr>
<tr>
<td>e</td>
<td>1.50</td>
<td>0.20</td>
<td>-1.30</td>
</tr>
<tr>
<td>f</td>
<td>1.68</td>
<td>-0.60</td>
<td>-2.28</td>
</tr>
</tbody>
</table>

⁵⁶ 500 MHz, 298 K, CDCl₃, ca. 10⁻³ M. See Schemes 2 and 3 for proton numbering.

Figure 3 Part of the ¹H NMR spectra (300 MHz) of (a) unprotonated [2]catenane 6 and (b) protonated [2]catenane [6·2H][⁺]. See Schemes 2 and 3 for proton numbering.

Since the resonances of H₃₆, H₄₂, and H₅₂ appear at positions where they are expected in uncatenated compounds, it can be concluded that the porphyrin bead in [6·2H][⁺] does not reside on the viologen, whereas in 6 it exclusively resides on this moiety. Detailed investigations using COSY and 2D-NOESY spectroscopy revealed that the protonated porphyrin in [6·2H][⁺] is situated near one of the ether oxygen atoms of the thread, possibly because of the presence of NH₃⁺–O hydrogen bonds, since increasingly larger upfield shifts are observed for the signals of H₃₆, H₄₂, and H₅₂ (Table 1). The resonance for proton H₂ in [6·2H][⁺] could not be identified, as it was either obscured by other signals, or severely broadened.

The symmetry observed in the NMR spectrum of [6·2H][⁺] can be attributed to the porphyrin bead shuttling between two degenerate states in which the porphyrin is near the oxygen atoms in the viologen-containing ring. To investigate this dynamic behaviour further, variable temperature ¹H NMR (VT-NMR) spectroscopy was carried out on [6·2H][⁺]. As is shown in Figure 4, going down in temperature causes dramatic changes in the NMR spectrum.

Using the coalescence method, the rate and the corresponding activation Gibbs energy for this dynamic process were estimated to be k₂₇₈ = 7.0 × 10³ s⁻¹ and ΔG°₂₇₈ = 47 kJ mol⁻¹, respectively. It is however not known if in this dynamic behaviour the shuttling between the two degenerate states takes place via the double bond, via the viologen moiety or via both routes (Scheme 6). In order to obtain a better picture of the dynamic process, it was decided to investigate in more detail how a viologen can create a barrier for a shuttling process of the type shown above. To this end, the dynamic behaviour of the series of [2]rotaxanes 18-20 as result of their protonation with TFA was investigated. In this type of interlocked molecule, similar dynamic behavior as observed for the [2]catenane is only possible when the porphyrin overcomes the
electrostatic barrier posed by the viologen. Protonating [2]rotaxane 18, to give [18-2H]2+, again led to dramatic changes in the 1H NMR spectra. Most strikingly, the signals of the aromatic viologen protons H$_b$ and H$_a$ shifted downfield: by +1.69 ppm and +2.71 ppm, respectively. These resonances are, however, at higher field (H$_a$ at 7.81 ppm and H$_b$ at 7.67 ppm) than expected in an uncomplexed viologen. This is explained by assuming that the short C5-spacer and the blocking group prevent the viologen from completely leaving the porphyrin host, whereas the viologen can completely slide away from the porphyrin moiety in [2]catenane [6-2H]2+. Also in the case of [18-2H]2+, a symmetrical NMR spectrum was observed, indicative of a movement of the porphyrin clip over the viologen moiety between the two blocking groups, which is fast on the NMR timescale at room temperature. This dynamic behavior was confirmed by VT-NMR experiments (Figure 5), in which the temperature dependence of the resonances H$_b$ of the side-wall of the porphyrin host, and both resonances H$_a$ and H$_i$ of the blocking group are displayed.

As is shown in Figure 5, the signals H$_a$ and H$_i$ of the blocking group split up into a downfield and upfield-shifted signal, which is a consequence of shielding effects of the porphyrin on the protons that are nearest to it. We propose that the porphyrin also reduces the conformational freedom of these protons, since the upfield signals are somewhat broadened. Similar to what was observed in the VT-NMR study of the [2]catenane [6-2H]2+, new resonances appeared below 0 ppm, which are assigned to the aliphatic spacer protons that are situated inside the cavity (vide infra). It is therefore proposed that protonated [2]rotaxane [18-2H]2+ shuttles between the two degenerate states that are created due to the unfavourable electrostatic interactions between the doubly charged viologen moiety and the protonated porphyrin (Scheme 7).

![Scheme 7](image)

Table 2: Thermodynamic and kinetic data for the shuttling process in protonated [2]rotaxanes [18-20 2H]2+

<table>
<thead>
<tr>
<th>Rotaxane</th>
<th>Probe proton</th>
<th>$T_c$ (K)</th>
<th>$k_c$ (s$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[18-2H]2+</td>
<td>i</td>
<td>258</td>
<td>970</td>
<td>48</td>
</tr>
<tr>
<td>[19-2H]2+</td>
<td>a</td>
<td>244</td>
<td>62</td>
<td>51</td>
</tr>
<tr>
<td>[20-2H]2+</td>
<td>g</td>
<td>302</td>
<td>71</td>
<td>63</td>
</tr>
</tbody>
</table>

$\Delta G^\ddagger$: Coalescence temperature. $\ddagger$: Estimated error 10%. For proton numbering see Schemes 2 and 5.
It should be noted that these values are not determined at the same temperature, so a detailed comparison between the $\Delta G^\circ$ values is not really allowed. Unfortunately, the activation parameters $\Delta H^\circ$ and $\Delta S^\circ$ could not be determined, as the quality of the spectra was not good enough for a line shape analysis. However, we tentatively conclude that the energy barrier associated with the shuttling process increases as the spacer length increases. This can be explained by assuming that in the case of a longer spacer, the doubly charged porphyrin host can slide away further from the doubly charged viologen moiety, thereby lowering the energies of the two degenerate states associated with the shuttling process, because the electrostatic repulsion is reduced. Based on these observations we propose that the porphyrin in [2]catenane [6-2H]$^{2+}$ shuttles between the two oxygen atoms and moves predominantly over the alkene part and not over the viologen, due to unfavourable electrostatic interactions. This behaviour is in marked contrast with the circumrotational movement of a similar [2]catenane, observed by Gunter et al.\cite{15} It is thus possible to induce a shuttling motion of the porphyrin host across the circular thread in [2]catenane 6 by simply protonating the porphyrin pyrrole nitrogen atoms. We also made attempts to investigate the dynamic behaviour of the large molecular necklaces 10 and 11. Unfortunately, complicated NMR spectra were observed in which the proton signals could not be assigned.

In a final series of experiments we studied the photophysical properties of the interlocked complexes. We first studied [2]catenane [6-2H]$^{2+}$ by means of UV/Vis and fluorescence spectroscopy. Addition of an excess of TFA (5 vol%) to a CHCl$_3$ solution of [2]catenane 6 ([6] = $10^{-6}$ M) revealed a red shift of the Soret band from $\lambda_{\text{max}}$ = 421 nm to $\lambda_{\text{max}}$ = 437 nm, accompanied with significant broadening, which is a spectral change that is generally observed for protonation of simple porphyrins (Figure 7a). The fluorescence spectrum of 6 in CHCl$_3$ changed dramatically upon protonation of the porphyrin. Whereas in 6 no detectable fluorescence emission could be observed upon excitation at $\lambda_{\text{max}}$ = 421 nm, due to efficient fluorescence quenching by the viologen inside the cavity, a large fluorescence emission peak at $\lambda_{\text{em}}$ = 643 nm emerged upon addition of TFA and excitation at $\lambda_{\text{max}}$ = 437 nm (Figure 7b).

Figure 7. UV/Vis (a) and fluorescence (b) spectra of [2]catenanes 6 and [6-2H]$^{2+}$.

Since upon protonation of the porphyrin the viologen moiety is expelled from the cavity, it can no longer act as a quencher, resulting in a dramatic increase in porphyrin fluorescence. The addition of pyridine to the solution resulted in deprotonation of [6-2H]$^{2+}$, regenerating 6, as well as the previously observed UV/Vis and fluorescence spectra, indicating the reversible nature of the switching process. This result clearly demonstrates that [2]catenane 6 can be switched between a non-fluorescent and a fluorescent state, using simple acid-base chemistry.\cite{18} Rotaxanes 18-20 were also protonated and their fluorescence spectra recorded. Figure 8a shows the UV/Vis spectra of protonated catenane [6-2H]$^{2+}$ and protonated rotaxanes [18-20 2H]$^{2+}$.

The protonated rotaxanes exhibit a broader Soret band than the one observed for the protonated catenane. This effect may be related to the different geometries of the two types of structures and the different types of interactions between the porphyrin and viologen moieties resulting from this. The fluorescence spectra display some interesting features (Figure 8b). Although [18-20 2H]$^{2+}$ display fluorescence emission upon excitation, the observed fluorescence intensities are much lower than the emission intensity originating from catenane [6 2H]$^{2+}$. Moreover, a clear spacer length effect on the fluorescence intensity is observed: if the length of the rotaxane thread increases, the fluorescence emission also increases. This can be explained by assuming that when the distance between the viologen moiety and the porphyrin clip is larger, the viologen moiety is less efficient in quenching the porphyrin’s fluorescence.

Conclusion

We have demonstrated that catenanes and molecular necklaces based on porphyrin 1 and bis-olefin-terminated viologens can be easily synthesized in high yields using an olefin metathesis protocol. The size of the olefin substituents of the viologens has a marked effect on the products of the ring-closing reaction. Whereas a viologen with long substituents (21 atoms) yields a [2]catenane and a [3]catenane, the viologen with shorter substituents (8 atoms) gives a mixture of a [3]catenane, a [4]molecular necklace, a [5]molecular necklace and higher oligomers, from which the [4]molecular necklace and [5]molecular necklace could be isolated. In addition, several [2]rotaxanes with threads of different lengths were successfully synthesized by SN$_2$-type reactions. The interlocked [2]catenane and [2]rotaxane structures show interesting switching behaviour: a shuttling motion of the porphyrin in the described catenane and rotaxanes can be turned on and off using acid and base stimuli. The protonated porphyrin host in the [2]catenane shuttles between two oxygen atoms predominantly by a route via the carbon-carbon double bond in the aliphatic ring, because the cationically charged viologen moiety poses a severe electrostatic barrier. In the case of the protonated [2]rotaxanes, the energy barrier associated with the shuttling is length-dependent: when the spacer length between the viologen moiety and the blocking group of the thread is increased, the energy barrier also increases. The induction of motion of the porphyrin moiety in the [2]catenane and [2]rotaxanes is also accompanied by interesting photophysical changes. Upon protonation of the [2]catenane, the viologen that quenches the porphyrin fluorescence is expelled from the cavity, resulting in a dramatic increase in the fluorescence emission. Similar effects were observed for the [2]rotaxanes, but not as dramatic as in the case of the [2]catenane, and a clear dependency of the fluorescence properties on the length of the spaced between the viologen and the blocking group was observed.

Following the protocols described in this paper we are currently planning the synthesis of functional catenane structures derived from metal-porphyrin (metal is Zn or Mn) containing glycoluril compounds. These will be allowed to form double cage compounds with other glycoluril derivatives as schematically shown in Figure 1.
The study of the properties of these systems as a first step towards a molecular Turing machine is envisaged.

Experimental Section

Materials and methods. Tetrahydrofuran was distilled under nitrogen from sodium and benzophenone. Acetonitrile was distilled under nitrogen from calcium hydride. Dichloromethane was distilled from calcium chloride. n-Hexane was distilled under nitrogen from sodium. Dimethyloformamide was dried over BaO for one week and then vacuum distilled. The first 30% of the distillate was discarded. All other solvents and chemicals were either commercially available and used without further purification.

Compounds 12 and 15 were synthesized as described previously.4 BioRad Biobeads (100 mg) were used for size exclusion chromatography (silica 60 mmol) and 6 (Menof) was used for column chromatography. Fluorescence experiments were performed on a Perkin Elmer LS50 luminance spectrometer equipped with a thermostated cuvette holder. UV/VIS spectra were recorded on a Varian Cary 50 Conc spectrometer. 1H NMR spectra were recorded on a Bruker DPX-200, AM-300 or Bruker DRX-500 spectrometers. Chromatography was performed either on silica gel plates with an aqueous saffron solution (1.0%) or on silica gel plates with a sodium silicate solution (1:10, v/v). 1H NMR spectra were recorded on a Bruker Biflex III spectrometer using dithranol as a matrix. H NMR (CDCl3) 6.50-7.50 ppm were recorded using 3-(trimethylsilyl)propionic-2,2,3,3-d4 acid as an internal standard.

Syntheses

10-(Bromocycloxy)dec-1-en-2-one. Under an argon atmosphere, dec-9-en-1-ol (1.4 g, 9 mmole) was added to a mixture of NaH (384 mg, 9.6 mmole) and 10% methanol (15 ml). After an equimolar amount of hydrogen gas had ceased, 1,10-dibromodecane (16.1 g, 53.6 mmol) was added and the resulting mixture was stirred for 5 days. The solvent was removed by rotary evaporation, after which the resulting crude product was dissolved in Et2O. This solution was washed with water, dried (MgSO4) and filtered to dryness. The residue was subjected to column chromatography (silica, CHCl3/C6H6, 9:1, v/v) to yield 4 as a white solid in a yield of 260 mg (80%).

A mixture of 4,4''-biphenyldine (102 mg, 0.65 mmole) and 6 (Menof) (23 mg, 33 mmole) in DMF (1 ml) was stirred overnight under a N2 atmosphere at 100°C. After cooling, Et2O was added and the resulting precipitate was filtered and washed with Et2O and MeCN to give 3 as white solid (153 mg, 23%). 1H NMR (CDCl3/CDC1D, 1:1, v/v) 8.00-8.40 (m, 28H, CH=CH), 7.05 (m, 72H, CH=C), 5.05-4.86 (m, 4H, H6=CH2), 4.25-3.65 (m, 8H, CH2), 3.38 (m, 4H, CH2), 2.95-2.40 (m, 8H, CH3), 2.08 (m, 8H, CH2), 1.39 (bs, 12H, CH2) ppm. MALDI-TOF MS: m/z 746 (M+PF2)+.

10-(4,4'-Bipyrinidin-4'-yldiene)dehydrophosphoranylidene. (4). A mixture of 4,4'-bipyrindine (102 mg, 0.65 mmole) and 2 (123 mg, 3.3 mmole) in DMF (1 ml) was stirred overnight under a N2 atmosphere at 100°C. After cooling, Et2O was added and the resulting precipitate was filtered and washed with Et2O and MeCN. The solid was dissolved in MeCN/H2O (1:1, v/v) after which the addition of a saturated solution of NileRed in H2O was added. The resulting mixture was immersed in an argon atmosphere. After 5 days, the resulting clear yellowish sauce was filtered and washed with MeCN to yield 3 as a yellow solid (123 mg, 20% yield). 1H NMR (CDCl3/CDC1D, 1:1, v/v) 8.40-6.90 (m, 102H, CH=CH), 5.93-7.00 (m, 20H, CH=C), 5.05-4.86 (m, 4H, H6=CH2), 4.25-3.65 (m, 8H, CH2), 3.38 (m, 4H, CH2), 2.95-2.40 (m, 8H, CH3), 2.08 (m, 8H, CH2), 1.39 (bs, 12H, CH2) ppm. MALDI-TOF MS: m/z 746 (M+PF2)+.

10-(2-(Oct-7-enyl)-4,4'-bipyrinidin-4'-yldiene)dehydrophosphoranylidene (4). A mixture of 4,4'-bipyridine (100 mg, 0.64 mmole) and 8-bromo-octene (1.2 g, 6.3 mmole) in DMF (1 ml) was stirred overnight under a N2 atmosphere at 100°C. After cooling, Et2O was added and the resulting precipitate was filtered and washed with Et2O and MeCN. The solid was dissolved in MeCN/H2O (1:1, v/v) and a saturated solution of NileRed in H2O was added, which resulted in the precipitation of 4 as a white solid in a yield of 260 mg (61%). 1H NMR (CDCl3, 200 MHz) δ 8.91 (d, 4H, pyrBpy, J = 6.9 Hz), 8.39 (d, 4H, pyrBpy, J = 6.9 Hz), 5.95-5.73 (m, 2H, Hc=CH2), 5.14-4.89 (m, 4H, H6=CH2), 4.61 (t, 4H, CH2), 3.75 (m, 2H, CH2), 3.17 (m, 4H, CH2), 2.08 (m, 8H, CH3), 1.39 (bs, 12H, CH2) ppm. MALDI-TOF MS: m/z 787 (M+PF2)+.

[2]Catenate 6 and [3]catenate. A solution of 4 (40 mg, 0.03 mmole) in a minimal amount of CHCl3 and precipitated in n-hexane. After drying in vacuo, the thus obtained [2]pseudoxoratane 5 was dissolved in CHCl3 (60 ml), and the first generation Graubs’ catalyst (5 mg, 0.1 mmole) was added under an argon atmosphere. The resulting mixture was stirred overnight at room temperature, after which the solvent was removed by rotary evaporation. The crude mixture was subjected to column chromatography (silica, CHCl3/MeCN, 9:1, 4:1, 3:1, v/v) yielding a mixture of 1, 10 and 11. 1H NMR (CDCl3, 500 MHz) δ 6.50-6.90 ppm (20H, CH=c), 4.50-4.80 ppm (4H, CH2=CH), 3.50-3.80 ppm (8H, CH3), 2.80-2.40 ppm (8H, CH2), 1.27-1.00 ppm (18H, CH2) ppm. MALDI-TOF MS: m/z 7073, 7218, 7363, 7508, 7654, 7798 [M+NPBF]+ (n=2-6).

1-(8-Bromocyloxy)-3,5-di-tert-butylenzylene (13). A mixture of 3,5-di-tert-butylenzylene (3 g, 14.5 mmole), 1,8-dibromooctane (0.73 g, 33.5 mmole) and K2CO3 (10 g, 72.4 mmole) in DMF (30 ml) was stirred overnight under an argon atmosphere, after which the solvent and the remaining 1,8-dibromoazomethin was distilled off. The resulting crude product was subjected to column chromatography (silica, n-hexane/EtOAc/n-hexane (1:1:1 v/v) to yield 13 as a colourless oil (4.5 g, 78%). 1H NMR (CDCl3, 200 MHz) δ 7.01 (t, 1H, para-ArH, J = 1.7 Hz), 6.75 (d, 2H, ortho-ArH, J = 1.7 Hz), 3.96 (t, 2H, OCH3), 3.64 (d, 4H, 2 CH2), 6.95 (s, 4H, 2CH4), 1.95-1.74 (m, 12H, CH2), 1.57-1.23 (m, 8H, CH2), 1.31 (s, 18H, CH2) ppm.

1-(3,5-Di-tert-butyl-phenoxo)-undecane-1,3-di. 3,5-Di-tert-butylenzylene (300 mg, 1.46 mmole) and 11-bromoundecanol (350 mg, 1.39 mmole) were suspended in argon-flushed DMF (10 ml). K2CO3 (750 mg, 5.43 mmole) was added and the mixture was heated overnight at 100°C under an argon atmosphere. After cooling, the solvent was evaporated and the residue dissolved in CHCl3. The organic layer was washed first with aqueous 1N HCl and then with an aqueous saturated NaHCO3 solution. After evaporation of the solvent, the crude product was purified by column chromatography (silica 60% ETOAc/n-hexane, 1:1) to give the desired product as a white solid (420 mg, 77%). 1H NMR (CDCl3, 300 MHz) δ 6.95 (s, 4H, ArH J = 1.8 Hz), 6.73 (d, 2H, ArH J = 1.8 Hz), 3.94 (s, 2H, OCH3), 3.64 (d, 4H, 2CH2), 1.66 (s, 6H, 2CH3), 1.95-1.74 (m, 12H, CH2), 1.57-1.23 (m, 8H, CH2), 1.31 (s, 18H, CH2) ppm.

1-(1-Bromoundecyl)-3,5-di-tert-butylenzylene (14). 1-(3,5-Di-tert-butyl-phenoxo)-undecan-1-ol (420 mg, 1.12 mmole) was dissolved in freshly distilled CHCl3 (15 ml) under argon and this solution was cooled to 0°C. PB (0.5 g, 1.85 mmole) was added and the mixture was allowed to warm to room temperature and stirred
overnight. Water was added dropwise to quench the reaction, and the mixture was extracted with aqueous 0.5% NaOH. The organic layer was evaporated to dryness, and the residue was purified by column chromatography (silica 60H, CHC{l}l) to give 14 (305 mg, 62%) as a white solid. 1H NMR (CDCl{3}, 300 MHz) δ 6.09 (t, 1 H, ArH, J = 1.8 Hz), 6.72 (2 H, ArH, J = 1.8 Hz), 1.34 (36 H, CH{3}), 0.94 (48 H, CH{2})), 4.39-4.30 (m, 4 H, H{4}, 4.28 (d, 4 H, H{4}, J = 15.9 Hz), 4.10-4.00 (m, 4 H, H{4}), 4.03 (t, 4 H, OCH{3}, J = 6.0 Hz), 3.74 (4 H, H{4}, J = 15.8 Hz), 3.58-3.54 (m, 4 H, H{4}), 3.32 (4 H, BipyCH{2}), 2.92 (7.5 Hz, 4 H, H{4}), 1.87-0.8 (36 H, CH{2})), 2.81 (s, 2 H, H{4}) ppm. MALDI-TOF: m/z 2220 (M+2P){sup 2}.

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