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Disabling Molecular Recognition through Reversible Mechanical Stoppering

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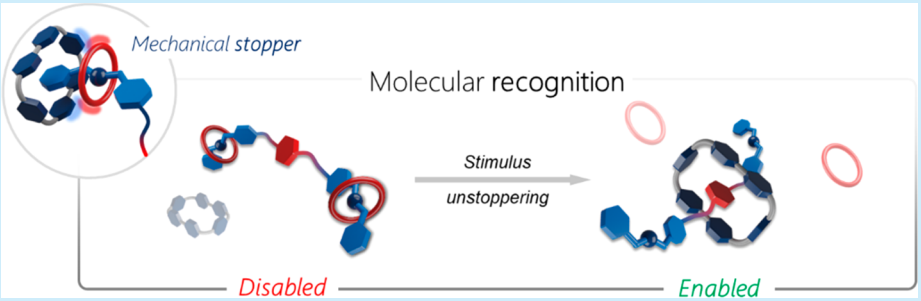
Supporting Information



ABSTRACT: Mechanical stoppering of a guest molecule prevents its self-assembly with a macrocycle unit, so that both species coexist in a medium but do not recognize each other. The application of a chemical or physical stimulus reverses mechanical stoppering and subsequently enables molecular recognition. This process, which occurs without cross-reactivity and is perceptible at the macroscopic scale, could facilitate programming on/off states in supramolecular materials and molecular devices.

Rotaxanes, catenanes, and molecular knots are part of the vast array of mechanically interlocked molecules[1] (MIMs) that have been important in supramolecular chemistry for developing sensors,[2−4] actuators,[5,6] molecular machines,[7,8] and other intriguing structures.[9−11] These systems are equally relevant for emerging concepts such as supramolecular catalysis[12−14] and molecular protection,[15,16] where the mechanical bond plays a critical role to prevent chemical degradation and efficiency loss.

The mechanical bond has recently been involved in creating ever more sophisticated MIMs, including hetero[*n*]-rotaxanes,[17] *i.e.*, species composed of a dumbbell-shaped molecule and at least two different macrocycles. Figure 1a illustrates a hetero[4]rotaxane containing two identical outer macrocycles and a larger one in the center, all of them threaded onto a dumbbell-shaped axle. The interlocked nature of this assembly is preserved through an artful design; the dumbbell end-caps are bulky enough to prevent the outer macrocycles from escaping, and these rings are bigger than the cavity of the central macrocycle, so it cannot escape if the outer macrocycles are present. This stoppering effect emerges in a cascade-like manner, as previously introduced by Schalley in a self-sorting system.[18] The outer rings and dumbbell end-caps synergistically operate as a physical barrier: a *mechanical stopper*.

This class of stoppering has been used to prevent the disassembly of a few hetero[*n*]rotaxane structures,[19,20] but not attempted to prevent other phenomena to occur such as chemical reactivity or self-assembly. We envisaged that blocking/unblocking a functional species via reversible

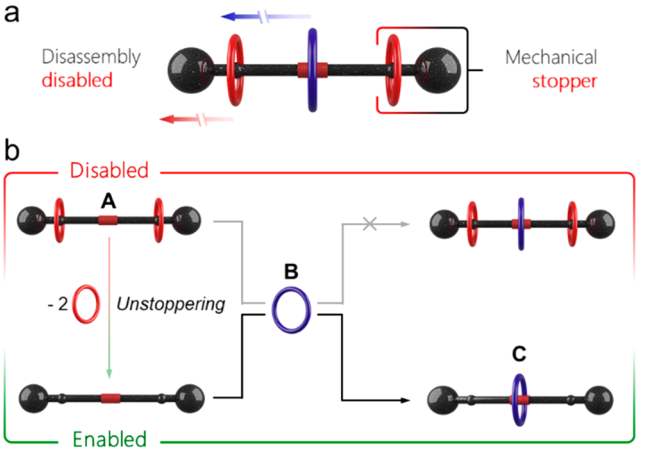


Figure 1. Schematics of (a) a hetero[4]rotaxane and (b) a disabled/enabled recognition process by mechanical stoppering.

mechanical stoppering might be a powerful tool to program on/off stages for distinct processes, including chemical transformations, reconfiguration of mechanically bonded molecules, and the hierarchical assembly of supramolecular materials.

Here, we present as a proof-of-concept the use of mechanical stoppering to disable a molecular recognition process between

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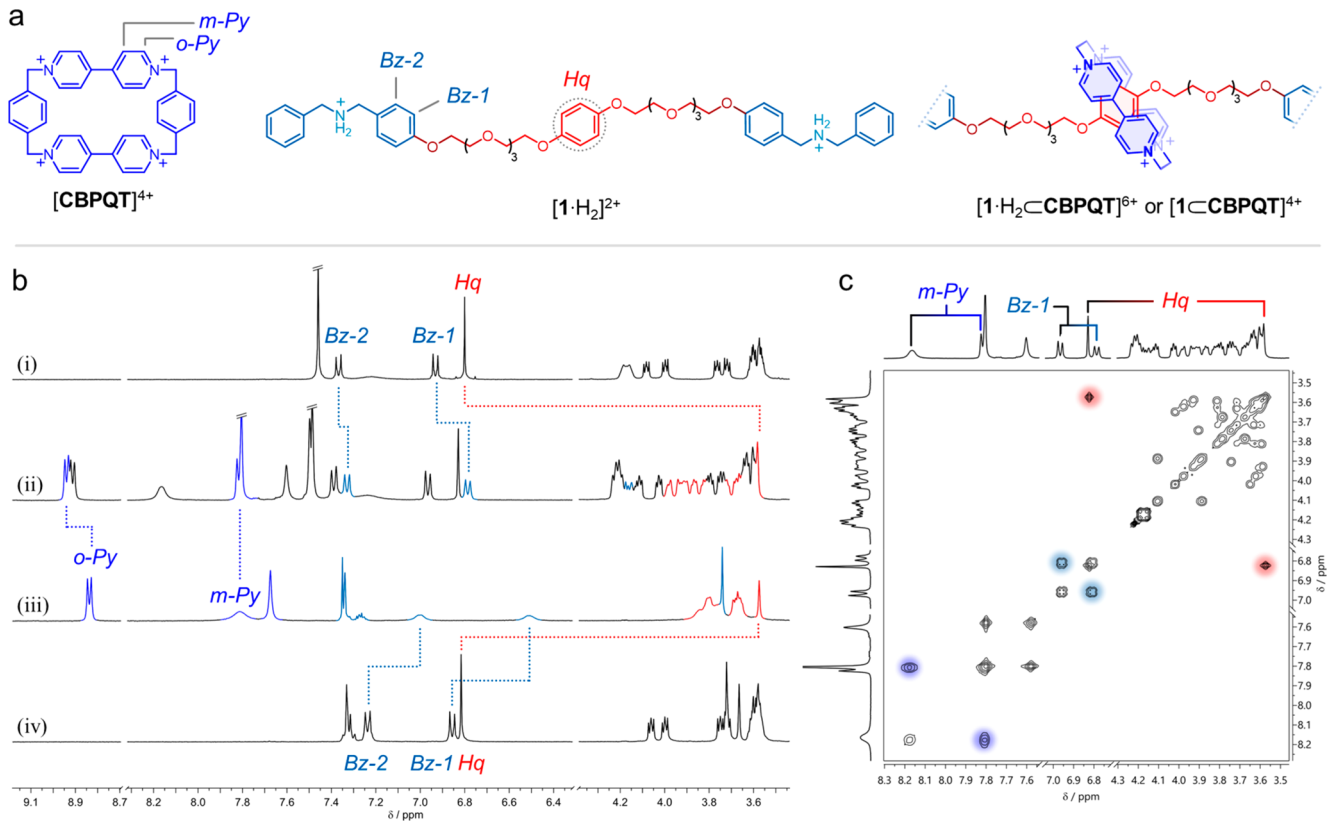

Figure 2. (a) Chemical structure and proton assignment for thread, macrocycle, and [2]pseudorotaxane species. (b) ^{1}H NMR spectra (CD_3CN, 400 MHz, 25 °C) of (i) thread $[\mathbf{1}\cdot H_2]^{2+}$, (ii) a 1:1 mixture of $[\mathbf{1}\cdot H_2][PF_6]_2$ and $[\mathbf{CBPQT}][PF_6]_4$ (5×10^{-3} M), (iii) thread **1**, and (iv) an equimolar solution of $[\mathbf{1}\cdot H_2][PF_6]_2$ and $[\mathbf{CBPQT}][PF_6]_4$ (5×10^{-3} M). (c) Partial EXSY NMR (CD_3CN, 400 MHz) collected from (ii).

a thread-like molecule and a macrocycle, a process that would otherwise occur extremely rapidly. Figure 1b illustrates our concept: structure **A**, which does not contain a central macrocycle, comprises two mechanical stoppers along with a central station suitable for macrocycle **B**. When **A** and **B** are mixed, mechanical stoppering prevents the molecular recognition between the thread and **B**. If the mechanical stoppers in **A** are removed by a stimulus-controlled dissociation, macrocycle **B** can bind the thread to give **C**, a pseudorotaxane complex; this may be accompanied by a change in color or other properties.

To demonstrate our approach, we first focused on molecular design and screened for species functioning as reversible stoppers. Metastable rotaxanes, also referred to in the literature as size-complementary rotaxanes, seem ideal.[21−23] These systems remain assembled under specific environments but disassemble under others to deposit the dumbbell and macrocycle components in solution. We identified a minimalist system reported by Dasgupta and Wu, composed of a dibenzylammonium cation (**DBA**$^+$) and a [22]-membered crown ether (**22C6**), i.e. a [2]rotaxane, [**DBA⊂22C6**]$^+$.[24] This molecule undergoes full disassembly in just a few minutes when exposed to two combined stimuli, polarity and temperature (DMSO, 100 °C), and cannot regenerate. Because of its structural simplicity and stimuli-responsiveness, we chose this species as a potential stopper. On the other hand, we selected a hydroquinone-based guest and the cyclobis(paraquat-*p*-phenylene) macrocycle (Figure 2a), [**CBPQT**]$^{4+}$, as the target pair for molecular recognition. This selection was made based on the following judgments: (i) these species are easily accessible, (ii) both components assemble in solution quickly and with moderate affinity in noncompetitive solvents, (iii) their self-assembly leads to a detectable color change, and (iv) the similar size of both selected macrocycles, [**CBPQT**]$^{4+}$ vs **22C6** (Figure S1), ensures effective stoppering.

With these choices in mind, we designed and synthesized the dicationic structure $[\mathbf{1}\cdot H_2]^{2+}$ incorporating two independent dibenzylammonium moieties, an electron-rich phenylene core, and two tetraethylene glycol bridging chains (Figure 2a). The end-groups of this molecule were designed as scaffolds for the synthesis of two mechanical stoppers, whereas the central component was intended as a recognition site for macrocycle [**CBPQT**]$^{4+}$. In addition, we expected the bridging chains to reinforce the interaction of the central core with [**CBPQT**]$^{4+}$, as previously reported by Stoddart.[25] Compound $[\mathbf{1}\cdot H_2][PF_6]_2$ was synthesized in four steps in 36% overall yield and characterized by NMR spectroscopy and mass spectrometry (see Supporting Information (SI)).

Following synthesis, we first analyzed the molecular recognition process of [**CBPQT**]$^{4+}$ with the thread molecule in its protonated $[\mathbf{1}\cdot H_2]^{2+}$ and neutral **1** form. When CD_3CN solutions of $[\mathbf{CBPQT}][PF_6]_4$ and $[\mathbf{1}\cdot H_2][PF_6]_2$ were combined in a 1:1 ratio, the solution immediately changed from colorless to orange. An absorption band at 450 nm in the UV−visible spectrum (see Figure S25) confirms the formation of a charge-transfer complex between the electron-rich phenylene core on $[\mathbf{1}\cdot H_2]^{2+}$ and the electron-poor macrocycle [**CBPQT**]$^{4+}$, in good agreement with other similar pseudorotaxane complexes.[26]

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On the other hand, the recorded ^{1}H NMR spectrum exhibits distinct sets of signals corresponding to the complexed and uncomplexed (free) components (Figure 2b, i–ii). Resonances for the tetraethylene glycol portions and the phenylene core (H_{Hq}) are the most dramatically affected by the presence of $[\mathbf{CBPQT}]^{4+}$. The resonance for H_{Hq} moves upfield by 3.1 ppm, which is ascribed to a $\pi-\pi$ stacking between the host and guest components. The position of this pair of signals was unequivocally assigned using 2D exchange NMR spectroscopy (EXSY), where cross peaks for the complexed and uncomplexed species are evident (Figure 2c). Both EXSY and ^{1}H NMR spectra also revealed a slight effect on the dibenzylammonium resonances, e.g. the inner benzyl proton $H_{Bz\text{-}1}$ ($\Delta\delta_{HBz\text{-}1}$ = −0.2 ppm), implying that host $[\mathbf{CBPQT}]^{4+}$ sits on the central recognition site of $[\mathbf{1}\cdot H_2]^{2+}$ to yield pseudorotaxane $[\mathbf{1}\cdot H_2\subset\mathbf{CBPQT}]^{6+}$. Moreover, signals corresponding to the macrocycle show moderate shifts, for instance, $H_{m\text{-}Py}$ moves from 8.2 to 7.8 ppm.

Similarly, we confirmed the assembly of the pseudorotaxane $[\mathbf{1}\subset\mathbf{CBPQT}]^{4+}$ through three spectroscopic observations: upfield shift for the H_{Hq} ($\Delta\delta_{HHq}$ = −3.2 ppm), $H_{Bz\text{-}1/2}$ ($\Delta\delta_{HBz\text{-}1/2} \approx -0.3$ ppm), and $H_{m\text{-}Py}$ ($\Delta\delta_{Hm\text{-}Py}$ = −0.4 ppm) resonances in the ^{1}H NMR spectrum (Figure 2b, iii–iv); through-space coupling between H_{Hq} and $H_{o/m\text{-}Py}$ protons, observed by NOESY NMR spectroscopy (which implies that both the phenylene and bipyridinium planes are in close proximity); and an absorbance band centered at 465 nm in the UV–vis experiment. These results together corroborate the expected $\pi-\pi$ stacked structure for pseudorotaxane $[\mathbf{1}\subset\mathbf{CBPQT}]^{4+}$ (Figures S28–S29).

Interestingly, the charge difference between $[\mathbf{1}\cdot H_2]^{2+}$ and **1** has two main consequences in the association process with $[\mathbf{CBPQT}]^{4+}$. First, the exchange in solution between the complexed and uncomplexed species operates on different time scales: slow for $[\mathbf{1}\cdot H_2\subset\mathbf{CBPQT}]^{6+}$ (as confirmed by EXSY NMR, Figure 2c) and fast for $[\mathbf{1}\subset\mathbf{CBPQT}]^{4+}$. Second, the stability of the complexes (ΔG_{asso}, measured in CD_3CN at 25 °C) drops by 5.7 ± 0.2 kJ/mol for the hexacationic complex $[\mathbf{1}\cdot H_2\subset\mathbf{CBPQT}]^{6+}$ [K_{asso} = (8.1 ± 0.1) × 10^2 M^{-1}] with respect to the tetracationic species $[\mathbf{1}\subset\mathbf{CBPQT}]^{4+}$ [K_{asso} = (7.9 ± 0.2) × 10^3 M^{-1}]. This behavior may be explained by the cation–cation repulsion between host $[\mathbf{CBPQT}]^{4+}$ and guest $[\mathbf{1}\cdot H_2]^{2+}$, which would not occur for the **1**-based system. Similar effects have been identified for other cation-gated pseudorotaxane complexes containing $[\mathbf{CBPQT}]^{4+}$ as a host.[27]

Despite these differences, the linear species in both states, $[\mathbf{1}\cdot H_2]^{2+}$ and **1**, quickly assemble with $[\mathbf{CBPQT}]^{4+}$, enabling the recognition process as revealed by a color change. Therefore, we employed $[\mathbf{1}\cdot H_2]^{2+}$ to synthesize the stoppered molecule, a [3]rotaxane (Figure 3a), aiming to disable molecular recognition.

Ring-closing metathesis of pentaethylene glycol dibut-4-enyl ether in the presence of $[\mathbf{1}\cdot H_2][PF_6]_2$, followed by hydrogenation, generated $[\mathbf{1}\cdot H_2\subset(\mathbf{22C6})_2][PF_6]_2$ in 40% overall yield (see SI). Figure 3b shows the partial ^{1}H NMR spectrum of the isolated product, where three principal regions are distinguished: (i) glycol resonances from 2.9 to 4.1 ppm (from both the crown ether units and the thread); (ii) dibenzylammonium moieties observed at 4.5 (H_{CH_2}), 7.0–7.6 (H_{Bz}), and 7.9 ppm ($H^{+}_{NH_2}$); and (iii) the central core (H_{Hq}) at 6.8 ppm. The relative integrals on the spectrum confirm the stoichiometry of the structure, corresponding to one linear

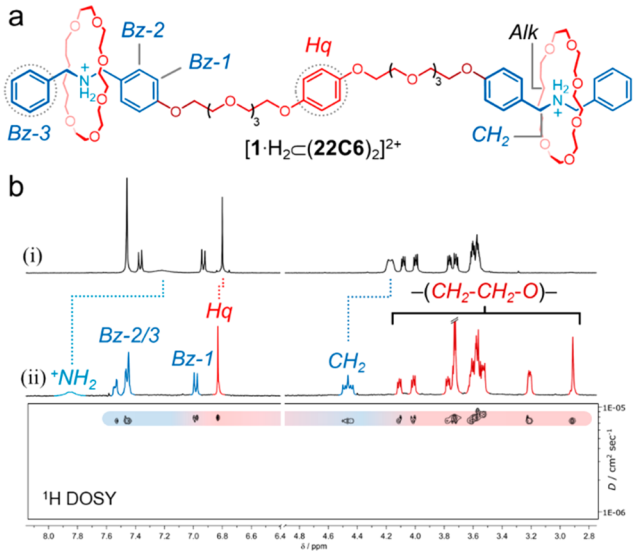

Figure 3. (a) Chemical structure and proton assignment for the obtained stoppered system. ^{1}H NMR spectra (CD_3CN, 400 MHz) of (i) $[\mathbf{1}\cdot H_2][PF_6]_2$ and (ii) $[\mathbf{1}\cdot H_2\subset(22C6)_2][PF_6]_2$; DOSY NMR is shown in the bottom section.

molecule per two **22C6** units, which was supported by HRMS where the parent ion $[\mathbf{1} + 2 \times (\mathbf{22C6}) + 2H]^{2+}$ was detected at m/z = 747.4554.

By comparing the collected ^{1}H spectrum with a pure sample of $[\mathbf{1}\cdot H_2][PF_6]_2$, we verified that the most affected regions are those corresponding to the dibenzylammonium units, consistent with the **22C6** rings wrapping exclusively around the ammonium stations. Indeed, protons $H^{+}_{NH_2}$ and H_{CH_2} register a downfield shift of 0.6 and 0.3 ppm, respectively, which is ascribed to the intercomponent $[^+N-H\cdots O]$ hydrogen bonding. This was further supported by NOESY NMR (see Figure S21), where cross peaks between the dibenzylammonium signals and the **22C6** glycolic protons were noticed. We additionally proved, by diffusion-ordered NMR spectroscopy (DOSY), that the identified ^{1}H resonances correspond to a single species, which diffuses in solution (CD_3CN, 25 °C) at ca. 8.0 × 10^{-6} $cm^2\cdot s^{-1}$.

The obtained molecule is soluble in a range of solvents such as MeCN, Me_2CO, CH_2Cl_2, and THF and remains assembled when stored in solution. In principle, it could disassemble as its parent [2]rotaxane $[\mathbf{DBA}\subset\mathbf{22C6}]^{+}$, reported by Dasgupta and Wu, in DMSO-d_6 at 100 °C. Nonetheless, DMSO may interfere in the recognition process between the thread molecule and $[\mathbf{CBPQT}]^{4+}$, so we targeted and evaluated two stimuli (base and heat), using MeCN as solvent. Treating a CD_3CN solution of $[\mathbf{1}\cdot H_2\subset(\mathbf{22C6})_2][PF_6]_2$ with 2 equiv of base ($NaOH_{(aq)}$) leads to fast deprotonation of the thread component followed by dissociation; **1** and two **22C6** units were detected in solution as free components (Figure S33). This process was too fast to quantitatively analyze by NMR spectroscopy.

On the other hand, the use of temperature as a trigger also causes disassembly, although the process is clearly slowed down compared to the effect of proton transfer. Heating a sample containing $[\mathbf{1}\cdot H_2\subset(\mathbf{22C6})_2]^{2+}$ (70 °C, CD_3CN) triggers gradual disassembly in a stepwise fashion, generating first the one-ring-containing molecule $[\mathbf{1}\cdot H_2\subset\mathbf{22C6}]^{2+}$, which ultimately disassembles to release $[\mathbf{1}\cdot H_2]^{2+}$. The presence of

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these species along the dissociation process was verified by NMR spectroscopy and HRMS (Figures S34–S35). From the obtained kinetic data, the half-life ($t_{1/2}$) to reach full dissociation is 63 ± 3 h [k_{off} = (3.1 ± 0.2) × 10^{-6} s^{-1}], ca. twice the value we measured for rotaxane [**DBA⊂22C6**]$^{+}$ ($t_{1/2}$ = 33 ± 3 h), which has only one ring (see Table S2).

With both the dissociation of [**1**·H_2⊂(**22C6**)$_2$]$^{+}$ and the [2]pseudorotaxane formation between [**1**·H_2]$^{2+}$ (or **1**) and [**CBPQT**]$^{4+}$ confirmed, we interrogated our system toward molecular recognition. Initially, a CD_3CN solution of [**1**·H_2⊂(**22C6**)$_2$][PF_6]$_2$ was probed by ^{1}H NMR spectroscopy before and after the addition of 2 equiv of [**CBPQT**][PF_6]$_4$. The ^{1}H NMR spectrum is unaffected by the presence of [**CBPQT**]$^{4+}$ (see H_{Hq} resonance in Figure 4a), and no changes

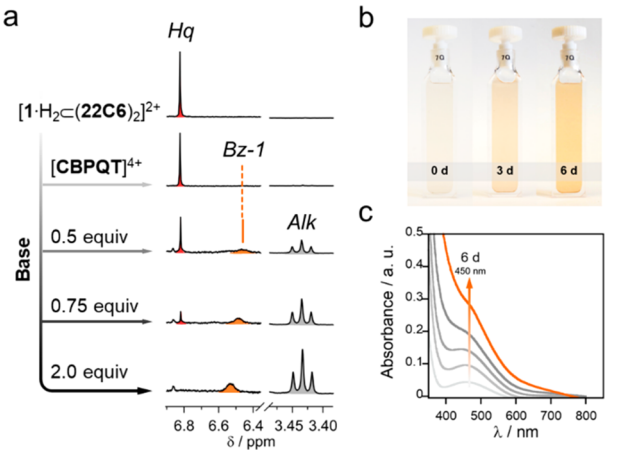

Figure 4. (a) ^{1}H NMR spectrum (400 MHz, CD_3CN) for the process driven by proton transfer using 1 M $NaOH_{(aq)}$ as base. (b,c) Photographs and absorption spectra of the unstoppering/recognition sequence triggered by heat.

were noticed after several days at 25 °C, suggesting an effective stoppering process that prevents the threading of [**CBPQT**]$^{4+}$ onto the linear component. A faint yellow color for the solution may be attributed to a weak intercomponent interaction, possibly due to the external stacking of [**CBPQT**]$^{4+}$ with the electron-rich core of [**1**·H_2⊂(**22C6**)$_2$]$^{2+}$.

The mixture of both components, [**1**·H_2⊂(**22C6**)$_2$]$^{2+}$ and free macrocycle [**CBPQT**]$^{4+}$, was then treated with an alkaline solution to control the unstoppering process. Upon addition of 0.5 equiv of base [$NaOH_{(aq)}$], the solution immediately changed color, from pale to deep yellow, which we ascribe to the formation of a charge-transfer complex between the released thread **1** and [**CBPQT**]$^{4+}$. By ^{1}H NMR spectroscopy, we saw a drop in the relative intensity of the rotaxane signals, including H_{Hq} (6.8 ppm). Moreover, two new sets of resonances were identified, one for free **22C6** (H_{Alk}, 3.4 ppm), and another set for pseudorotaxane [**1⊂CBPQT**]$^{4+}$ (*e.g.*, $H_{Bz\text{-}1}$ at 6.5 ppm); see Figure 4a. After addition of an excess of base, all resonances for the stoppered species were no longer observed, while $H_{Bz\text{-}1}$ and H_{Alk} attained maximum intensity. This corroborates that base addition triggers unstoppering to rapidly enable molecular recognition, allowing for the assembly of a pseudorotaxane.

Heating the system at 70 °C generates comparable results, although the process is significantly slowed down, as confirmed by ^{1}H NMR and UV–vis spectroscopy (Figure S37). In the NMR spectrum, we identified the dissociation of [**1**·H_2⊂(**22C6**)$_2$]$^{2+}$ and [**1**·H_2⊂**22C6**]$^{2+}$, the release of **22C6** units, and the self-assembly of pseudorotaxane [**1**·H_2⊂**CBPQT**]$^{6+}$, although we do not discard the presence of complex [**CBPQT**⊃**1**·H_2⊂**22C6**]$^{6+}$ along the process. The relative concentration of these species varies over time, reaching completion in about 6 days. Interestingly, the unstoppering/recognition sequence was also detected at the macroscopic scale. The initial pale-yellow mixture gradually transforms into an orange solution (Figure 4b). This phenomenon is attributed to the presence of pseudorotaxane [**1**·H_2⊂**CBPQT**]$^{6+}$, evidenced by an absorbance band at 450 nm in the UV–vis spectrum. Indeed, this band gradually increases in intensity in parallel to the heating time and reaches a maximum in 6 days (Figure 4c), after the unstoppering process has been completed.

In summary, we have installed mechanical stoppers on a guest molecule to disable its molecular recognition with a macrocycle. By applying a specific stimulus (heat or base), we directed the controlled disassembly of the mechanical stoppers to subsequently enable molecular recognition and yield a pseudorotaxane complex with a readout: a macroscopic change of color. We anticipate that this method may serve for the development of new supramolecular materials, those constructed by the controlled disassembly of mechanically stoppered species. This concept is now under investigation in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00310.

Full experimental description, spectroscopic characterization (NMR, UV–vis and HRMS), and kinetic analyses for the unstoppering processes (PDF)

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Notes

The authors declare no competing financial interest.

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