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Metal Actuated Ring Translocation Switches in Water

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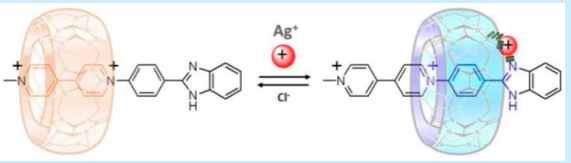
Supporting Information

ABSTRACT: Among a series of metal ions in water, silver is the only one to remotely and reversibly switch cucurbit[7]uril (CB[7]) movements (translocation or uptake) on a rigid and linear three-station viologen−phenylene−imidazole (***V−P−I***) derivative, avoiding undesired pH actuation. ^{1}H NMR, UV−vis spectroscopy, mass spectrometry, ITC, and modeling were combined to show that ring translocation or uptake along a molecular thread is possible in water by Ag^+ as a metal stimulus.



Molecular switches are increasingly investigated because of their high potential as elementary building blocks for the next generation of molecular machines.[1] Remarkable examples have been reported by several groups, with designs comprising flexible axle and ring molecules.[2] Even if water is attractive due to its lack of toxicity, possible enhanced affinity by hydrophobic effects,[3] and ability to make molecular switches more amenable for biological applications,[4] most molecular switches proceed in organic solvents.[5] Yet, water-soluble molecular switches are much less investigated and, even if pH[6] is an essential stimulus to trigger ring translocation, nature also uses metal ions or ATP hydrolysis, for instance to trigger reversible protein ring contraction in ion channels or to drive ring-shaped motor proteins over DNA strands to achieve essential functions in cells.[7] To make efficient molecular switches work in water in various contexts, one would ideally be able to choose the best stimulus to actuate ring translocation. Expanding the palette of available stimuli working in water, beyond pH, is thus desirable. For example, when buffers are undesired and H^+ unusable due to fragile motifs on hosts or guests, metal ions could be valuable stimuli.[8] However, there are, to the best of our knowledge, only a handful of examples of metal actuated ring translocation switches and none work in water.[9] Reasons for that may be because of difficulties in combining functions recognizable by a metal ion, in both the host and guest, or because most metal ions can behave as Brønsted acids in water and thus affect the pH,[10] rendering unbiased analyses more complicated.

Cucurbit[7]uril (CB[7])[11] is a ring shape receptor presenting several advantages to test metal ions as triggers of ring translocation because it is water-soluble and possesses (i) a versatile hydrophobic cavity and (ii) two carbonyl-laced portals amenable for metal ion binding. In line with our continuous work on CB[*n*],[12] we tested a series of commonly used water-soluble metal salts and found that Ag^+ selectively translocates CB[7] over a simple, rigid molecular axle containing a viologen (***V***), a phenylene (***P***), and an imidazole (***I***) station (***V−P−I***, Figure 1) or pull a second CB[7], without affecting the pH deleteriously.

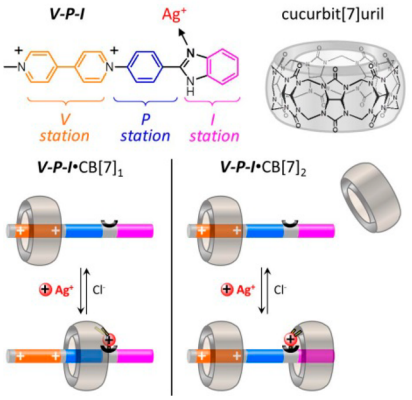


Figure 1. Molecular structures of ***V−P−I*** and of CB[7] and representation of the silver actuated molecular switches.

Imidazole ***V−P−I***[Cl_2] (2 Cl^- counterions) was prepared in a three-step sequence, and details are given in the Supporting Information (SI). Imidazole ***V−P−I***[Cl_2] is water-soluble and possesses two pK_a values, as the imidazole station can be either protonated (pK_{a1} = 4.0) or deprotonated (pK_{a2} = 10.4, Figure S6). Therefore, working at near-neutral pH was essential without buffers to (i) warrant having benzimidazole structures (Figures 1 and 2; i.e., not the protonated or deprotonated forms) and (ii) avoid complications due to cations that are

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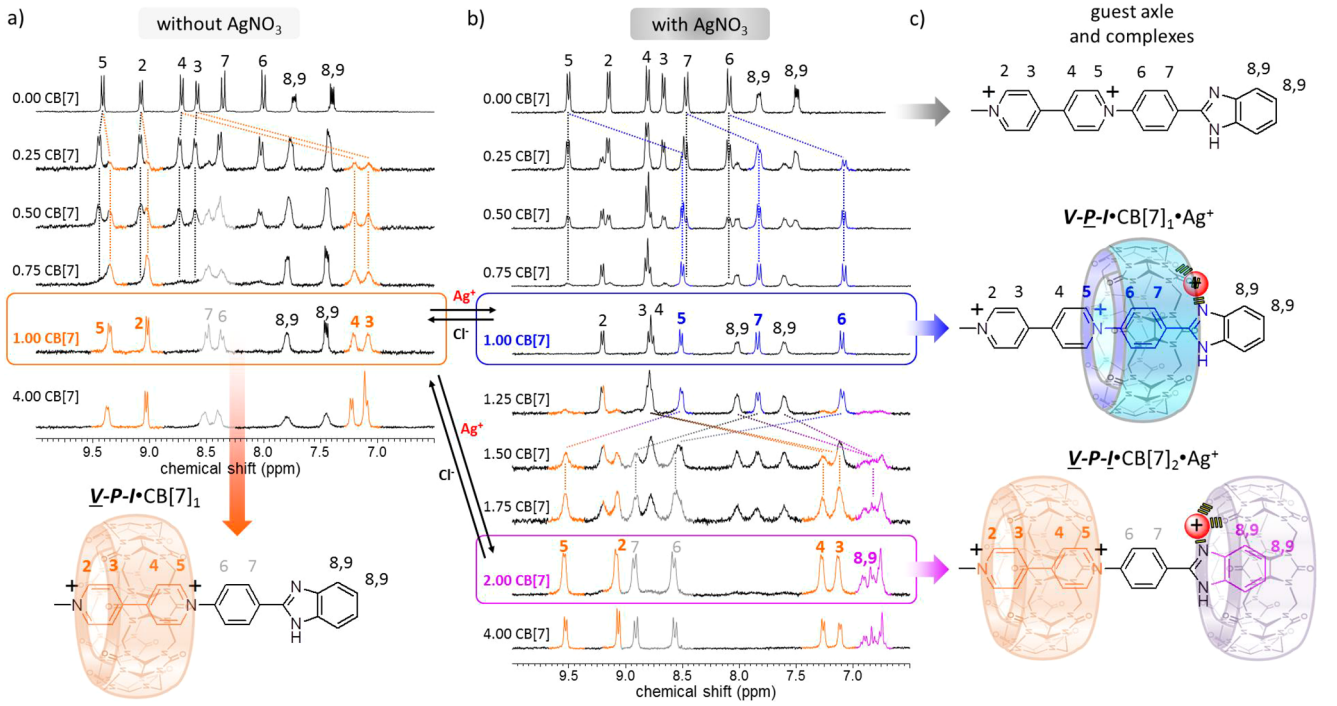

Figure 2. Excerpts of the aromatic region of ^{1}H NMR spectra for the CB[7] titration of ***V*–*P*–*I***[Cl_2] (1 mM, a) and ***V*–*P*–*I***[Cl_2] (1 mM) with $AgNO_3$ (8 equiv, b) in D_2O with (c) proposed structures of the complexes (Ag^+ ions: red spheres).

known to interact significantly with CB[7] carbonyl rims.[13] First, CB[7] complexation on the ***V*** station was easily monitored by ^{1}H NMR in D_2O (Figure 2a). Assignment of the ^{1}H NMR signals was without ambiguity, except for protons 8 and 9 despite the record of several Heteronuclear correlation spectroscopy experiments, probably because of the presence of the nearby imidazole function and the associated H/D exchange in D_2O. Then, NaCl, CsF, $AgNO_3$, $CaCl_2$, $MgCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $CuSO_4$, $MnCl_2$, $FeCl_2$, $FeSO_4$, $FeCl_3$, $GdCl_3$, $Cr(NO_3)_3$, and $AlCl_3$ were assessed for CB[7] translocation. Na^I, Cs^I, Ca^{II}, Mg^{II}, Co^{II}, Ni^{II}, Zn^{II}, Mn^{II}, and Gd^{III} had essentially no effect on ^{1}H NMR spectra, even after addition of several equivalents in water (up to 10 equiv Figure S7, pH reduced to 6.10 in the worst case). Conversely, Cr, Al, and Fe salts changed the spectrum of ***V*–*P*–*I***·CB[7] to assignable resonances, while Cu showed broad signals. The obtained spectra for Cr^{III}, Al^{III}, and Fe^{III} are very similar to that of ***V*–*P*–*I***–H^+·CB[7] (Figure S7) and are probably the result of metal-induced acidification as reflected by the measured pH values of the solutions (Figure S7). The addition of these metallic salts thus resulted in undesired pH triggered CB[7] translocation. Buffering the solutions to limit pH changes triggered by Fe, Cu, Al, or Cr would result in precipitates of hydroxides complexes.[14] pH Actuation of the present system is also interesting, but will be reported elsewhere since it exceeds the scope of this study. However, Ag^I resulted in new NMR spectra without altering too much of the pH. Without Ag^+, as expected, CB[7] quantitatively binds ***V*–*P*–*I*** on station ***V*** while a further increase in the CB[7] concentration does not change this 1:1 binding mode (Figure 2a). Split chemical resonances for free and complexed ***V*–*P*–*I*** suggest slow exchange on the NMR time scale. The signals of protons 3 and 4 are shifted upfield by ∼1.5 ppm in line with the CB[7] location on station ***V***, with one carbonyl rim downfield-shifting the signals of protons 6 and 7 by 0.37 and 0.13 ppm respectively ($\langle\Delta\delta\rangle \approx$ 0.25 ppm, carbonyl rims symmetry broken, Figures S9 and S11, 1 equiv, right). $AgNO_3$ had a weak, but significant effect on the spectrum of ***V*–*P*–*I*** alone (Figure S12), affecting H_7, H_8, and H_9 that are located nearby the imidazole function and thus reflecting weak binding on the imidazole function (significant effects were also observed by UV–vis spectroscopy, Figure S14). CB[7] Titration of ***V*–*P*–*I***[Cl_2] with $AgNO_3$ instead showed CB[7] binding on station ***P*** (slow exchange on the ^{1}H NMR time scale, Figure 2b). Silver ions have previously been shown to behave as soft Lewis acids,[15] and imidazoles[16] or the carbonyl rims of cucurbiturils[17] have been reported to be possible ligands for Ag^+. We postulate a silver-induced host translocation by multiple binding on the guest-imidazole function and by the oxygen carbonyl rims. Addition of 2 equiv of $AgNO_3$ was necessary to neutralize the effect of the two chloride ions present in ***V*–*P*–*I***[Cl_2]. Exchanging chlorides to nitrates could have been relevant to probe anion effects, but anion exchange adding $AgNO_3$ (AgCl precipitation) to isolate ***V*–*P*–*I***[$(NO_3)_2$] could lead to a product containing a slight excess or default of salts potentially biasing further analyses. However, ^{1}H NMR spectra in the presence of 2 equiv of $AgNO_3$ lead to ***V*–*P*–*I*** with two nitrates in water (precipitation of 2 equiv of AgCl) and no significant difference was observed compared to the spectrum of ***V*–*P*–*I***[Cl_2] (see Figure S18), showing no detectable anion effect in these conditions. This is further supported by the reversibility experiments where large excesses of NaCl and $AgNO_3$ were alternatively added (see below, and Figures S25 and S26). ^{1}H NMR titrations of $AgNO_3$ for a 1:1 ***V*–*P*–*I***[Cl_2]:CB[7] mixture showed large chemical shift changes up to ∼10 equiv of Ag^+ for species rapidly exchanging on the ^{1}H NMR time scale (Figure S18). This fast-exchange regime was presumably due to the lability of the silver–nitrogen bond upon Ag^+ binding on the imidazole function of ***V*–*P*–*I*** accompanied by the gradual translocation of CB[7] from station ***V*** to station ***P***. This allowed the indirect

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Org. Lett. XXXX, XXX, XXX–XXX

determination of the binding constant for Ag^+ (K_a = 3470 ± 550 M^{-1}, fit of experimental points using a 1:1 binding model) toward the ***V*–*P*–*I***·CB[7]$_1$ complex and suggested a 1:1:1 stoichiometry for the ***V*–*P*–*I***·CB[7]$_1$·Ag^+ complex (Figures S18 and S27). When ***V*–*P*–*I***[Cl_2] was titrated against CB[7] with enough Ag^+ (8 equiv of $AgNO_3$ kept constant, Figure 2b), signals of protons 5, 6, and 7 upfield shifted by 1.00, 0.99, and 0.60 ppm respectively up to 1 equiv of CB[7] (ring on station ***P***). While the threaded CB[7] seems to exchange fast on the binding sites with respect to the NMR time scale, the host prefers remaining on station ***P***. However, excess CB[7] completely changed the NMR spectra with large upfield shifts for both sets of protons, 3,4 (1.51 ppm) from station ***V*** and 8,9 ($\langle\Delta\delta\rangle \approx 0.80$ ppm) from station ***I*** while the signals of protons 6 and 7 are shifted downfield by approximately double the value as for the 1:1 binding on ***V*–*P*–*I*** ($\langle\Delta\delta\rangle \approx 0.50$ ppm, Figure 2b bottom). This agrees with a CB[7] binding on the ***V*** station and a second CB[7] located on the ***I*** station. The ***P*** station protons experienced significant deshielding effects from two carbonyl rims (one rim from each of the two CB[7]), while no further changes were observed for more than 2.0 equiv of CB[7]. Thus, Ag^+ ions were observed to (i) translocate CB[7] from the ***V*** to the ***P*** station at 1:1 guest/host ratio and (ii) pull a second CB[7] onto the ***I*** station at a 1:2 guest/host stoichiometry. Simultaneous binding of two CB[7] on two vicinal stations (***V*** and ***P*** or ***P*** and ***I***) was not observed. Mass spectrometry (MS) showed peaks assigned to ***V*–*P*–*I***, and ***V*–*P*–*I***·CB[7]$_1$ together with the corresponding H^+ adduct. With $AgNO_3$, ion mobility separation prior to analyses allowed us to observe additional peaks at m/z 545.1390 (theo. 545.1390) and m/z 848.7045 (theo. 848.7027) respectively corresponding to the formulas $C_{66}H_{62}N_{32}O_{14}Ag_1^{3+}$ and $C_{66}H_{62}N_{33}O_{17}Ag_1^{2+}$ in line with complexes ***V*–*P*–*I***·CB[7]$_1$·Ag^+ and ***V*–*P*–*I***·CB[7]$_1$·Ag^+·NO_3^- (Figure S19).

DFT minimized structures of ***V*–*P*–*I***·CB[7]$_1$ complexes[18] with CB[7] positioned on the ***V***, ***P***, or ***I*** stations (frequency checked and corrected for BSSE; see SI) showed a marked preference for the complex with CB[7] on station ***V*** (Figure 3a), which is in good agreement with ^{1}H NMR. With a silver ion (1 Ag^+ considered as suggested by NMR and mass spectrometry), the complex with CB[7] on station ***P*** is the most stable (Figure 3b, SI), also consistent with the ^{1}H NMR of ***V*–*P*–*I***·CB[7]$_1$·Ag^+, ***V*–*P*–*I***·Ag^+ and the UV–vis spectra of ***V*–*P*–*I***·Ag^+ which suggested an interaction between Ag^+ and *N*-imidazole. In this binding geometry, there are several hydrogen bonds between CB[7] and the guest, and the silver ion is 2.20 Å distant from the imidazole nitrogen atom (Ag^+···N); there are two additional Ag^+···O coordinating bonds (2.32 and 2.45 Å) with one CB[7] carbonyl rim (Figure 3b). The combination of these two kinds of interactions seems to be responsible for driving CB[7] from the ***V*** to the ***P*** station. The situation is similar for the 1:2 complex, except that one CB[7] is on station ***V*** and the second CB[7] is instead on station ***I*** (Figure 3c).

In this case, the silver ion interacts (i) with the imidazole nitrogen atom (2.20 Å) and (ii) with two carbonyl oxygen atoms of the CB[7] of the ***I*** station (2.33 and 2.46 Å). Thus, the imidazole function behaves as a pivot for Ag^+ which in turn attracts CB[7] providing an oxygen-rich environment to further stabilize Ag^+. Of course, other positions for Ag^+ near a carbonyl rim and around the imidazole station cannot completely be ruled out, but such other positions lead to less stable 1:1:1 complexes by DFT and Ag^+ also significantly affected the ^{1}H

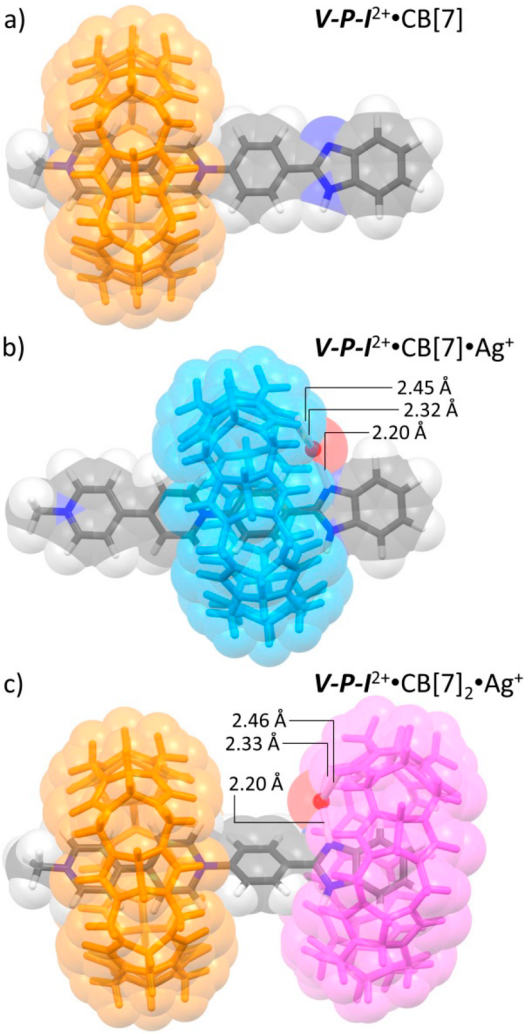

Figure 3. Proposed structures (DFT minimized) in line with ^{1}H NMR for the complexes (a) ***V*–*P*–*I***·CB[7], (b) ***V*–*P*–*I***·CB[7]$_1$·Ag^+, and (c) ***V*–*P*–*I***·CB[7]$_2$·Ag^+.

NMR signals of ***V*–*P*–*I*** near the imidazole function and maximum absorbance in the UV–vis spectra of ***V*–*P*–*I*** was also significantly shifted (Figures S12 and S14 respectively). The observed silver selectivity for ring translocation could be explained by (i) the charge of the metal ion (a monocationic metal ion is more likely to be bound by a CB[7] carbonyl rim for an overall 2+ charged complex), (ii) the soft lewis acid nature of silver capable of coordinating both an imidazole function and carbonyl groups of CB[*n*],[15–17] and (iii) because Ag^I cations do not generate insoluble metal oxides at neutral pH.[14]

The present system was also investigated by ITC (Figure 4). Without silver ions, the binding affinity between CB[7] and ***V*–*P*–*I*** was determined to be 7.25 × 10^5 M^{-1} (Figure 4a). The binding stoichiometry is 1:1, consistent with NMR, DFT, and MS. In the presence of Ag^+, results of ITC titration of ***V*–*P*–*I*** with CB[7] are consistent with a sequential complexation, with apparent binding constant values of K_{a1} = 6.45 × 10^6 M^{-1} and K_{a2} = 3.75 × 10^5 M^{-1}.

Below 1 equiv of CB[7], corresponding heat changes can tentatively be assigned to one Ag^+-assisted CB[7] binding on ***V*–*P*–*I*** (K_{a1}). The larger binding of CB[7] toward station ***P*** in the presence of Ag^+ is well consistent with NMR. The heat

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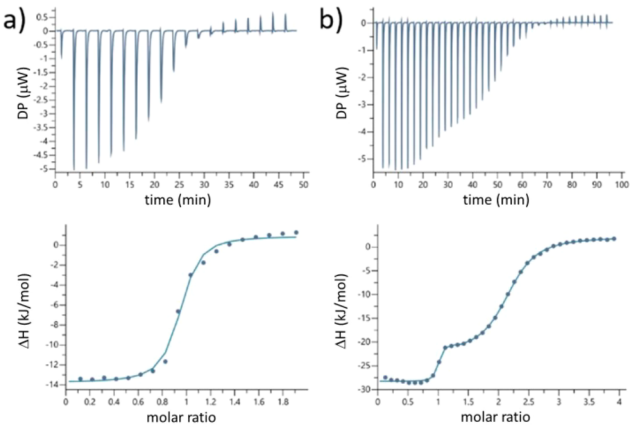

Figure 4. Microcalorimetric titration of ***V*–*P*–*I*** with CB[7] in aqueous solution, in the absence (a) and in the presence (b) of Ag^+. Top: thermograms of CB[7] injected into ***V*–*P*–*I*** solutions. Bottom: dependence of ΔH for each injection of CB[7] against the molar ratio between CB[7] and ***V*–*P*–*I*** (the solid line represents the best fit using "one set of binding sites" and "two separate one set of binding sites" models, respectively.

changes above 1 equiv of CB[7] are hard to interpret because of the suspected entanglement of two effects: (i) CB[7] translocation back to station ***V*** and (ii) binding of a second CB[7]. However, ITC confirmed the proposed stoichiometry and the process is both enthalpically and entropically driven (SI). Interestingly, the switching processes were simply reversed by addition of NaCl (Figure 2) precipitating Ag^+ in the form of AgCl. The reversibility of the molecular switches (1:1 and 1:2 guest/host ratios) was examined over two cycles by repetitive alternation of the position of CB[7] on stations ***V*** and ***P*** (Figure S25), or repetitive catch-and-release of a second CB[7] (Figure S26). Finally, the role of the anion should not be left unconsidered with a potentially binding imidazole function on the axle and cations ubiquitous in this system, but the carbonyl rims of CB[7] are rather expected to behave as anion repellants.

In summary, we report silver-triggered, reversible molecular switches in water based on CB[7] and a simple, rigid Viologen–Phenylene–Imidazole (***V*–*P*–*I***) guest axle. Ag^+ is unique for this system since it selectively and remotely controls (i) CB[7] sliding from station ***V*** to station ***P*** of the guest or (ii) a second CB[7] uptake and release on guest station ***I***. To the best of our knowledge, there is no previous example of a ring molecule reversibly guided (translocated) or pulled (caught) on a rigid axle by a metallic cation in water, but there is still room for improvement (excess Ag^+ needed) with appropriate design. We anticipate that other guests and hosts will also exhibit ring movements triggered by metal ions in water. The water solubility of the present system could broaden the perspective of biological applications of molecular switches[4] (i.e., acid-responsive imidazole function). We think that this ternary approach (Ag^+/imidazole/CB[7]) is also well suited to open the way to a new family of silver templated interlocked structures[19] and silver actuated molecular switches and machines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01019.

Preparation and characterization of ***V*–*P*–*I***[Cl_2], 1D-NMR and 2D-NMR spectra, details for mass spectrometry measurements, additional NMR titrations, ITC data, pK_a measurements and details of DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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