Molecular Switches

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A Light-Stimulated Molecular Switch Driven by Radical–Radical Interactions in Water**

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One of the unique properties of planet earth is its ability to maintain a large amount of liquid water on its surface. Although water in its liquid state is a relatively rare occurrence in our solar system,[1] nature has taken advantage of this aqueous medium to generate and support life, creating biological molecular machines such as ATP synthase,[2] kinesin,[3] myosin,[4] and bacterial flagella,[5] all of which accomplish their important tasks in aqueous environments. Inexorably, one of the challenges nowadays for the scientific community is understanding conceptually how nature presents itself at the molecular level through the medium of biology.

Synthetic analogues[6,7] of the biological molecular motors—that is, artificially designed molecular switches[6] and machines[7]—have undergone extensive development during the past few decades. On account of their inherent ability to exercise controllable intramolecular motion, involving their mechanically bonded components residing between their different low energy states, mechanically interlocked molecules[8] (MIMs), in the form of multi- and bistable rotaxanes[9] and catenanes,[10] have attracted the attention of many researchers as potential candidates for prototypical artificial molecular machines. These MIMs have been shown to participate in a wide range of applications in molecular nanotechnology, including mechanical actuators,[11] molecular memory,[12] and drug delivery vehicles.[13] Although MIMs have been shown[14] to be capable of switching upon exposure to light and so possess unique advantages in terms of their addressability, most of this research has been conducted in organic solvents. In our quest to better understand the functions of biological molecular motors as well as to orchestrate biocompatible applications, molecular switches and machines that are soluble and operational in aqueous media must be developed.[7b,14c,15] Only a few examples, however, have been reported.[15–17] In particular, molecular switches based on tetrathiafulvalene (TTF) units can be switched[16] between two states by means of chemical or electrochemical oxidation. On account of the poor reversibility[17] of the redox processes of TTF in water, however, the practical applications of these artificial systems are limited. Our ability to fabricate artificial molecular machines, capable of reversible switching, which can be stimulated by light in aqueous environments as opposed to in organic solvents, presents opportunities to develop nanobiomechanical systems for applications, in particular, molecular prosthetics.[7i,18] Herein, we present a light-stimulated molecular switch in the form of a bistable [2]rotaxane, which can undergo relative mechanical movements of its components in water.

Ruthenium(II)tris(2,2′-bipyridine) ([Ru(bpy)$_3$]$^{2+}$) is an important inert metal complex well known[19] for its photocatalytic electron-transfer properties. In particular, its ability to reduce 4,4′-dialkylbipyridinium (BIPY^{2+}) units, upon exposure to light in the presence of a sacrificial reducing agent, has been exploited by us recently[20] in the templation of mechanical bond formation by making use of radical-pairing interactions between BIPY$^{(\bullet+)}$ radical cations that occur following photocatalytic reduction of the BIPY^{2+} units. These BIPY$^{(\bullet+)}$ radical cations can form[20] strong inclusion complexes with cyclobis(paraquat-*p*-phenylene)[21] (CBPQT^{4+}) in its diradical dicationic redox state (CBPQT$^{2(\bullet+)}$) as a result of a radical-pairing interaction under redox control. We now demonstrate that the [Ru(bpy)$_3$]$^{2+}$ complex can be used as a photosensitizer to reduce the BIPY^{2+} units to their radical cations and hence induce switching in appropriate bistable [2]rotaxanes. To this end, we

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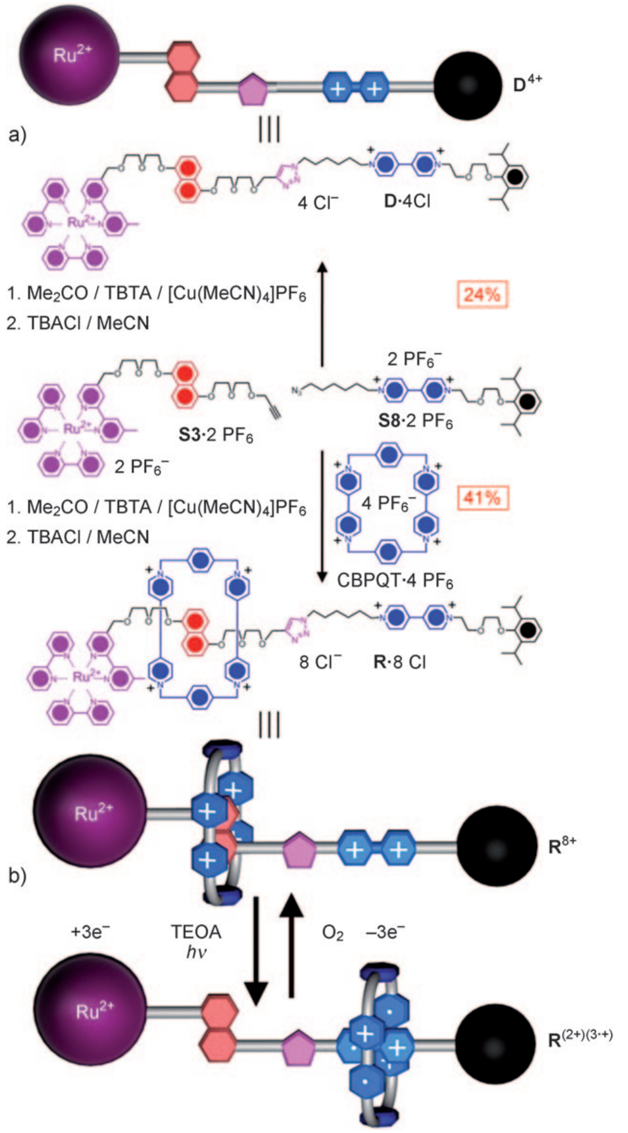
have designed, synthesized, and characterized the [2]rotaxane **R**·8Cl, as well as its organic soluble counterpart **R**·8PF$_6$ (Scheme 1). The [2]rotaxane **R**·8Cl contains a CBPQT^{4+} ring and a dumbbell bearing the π-electron-rich 1,5-dioxynaphthalene (DNP) recognition site, and a π-electron-deficient BIPY^{2+} unit, which serves as a binding site for the CBPQT^{4+} ring when the [2]rotaxane is reduced to its pentacationic trisradical state. In order to be able to activate switching of the ring between the DNP and BIPY$^{\bullet+}$ sites using light, the dumbbell component was designed to have a [Ru(bpy)$_3$]$^{2+}$ complex as one of its two stoppers. Upon irradiation with visible light in the presence of the sacrificial electron donor,[22] triethanolamine (TEOA), all three of the BIPY^{2+} units, two in the CBPQT^{4+} ring and one in the dumbbell, are reduced to BIPY$^{\bullet+}$ units by the [Ru(bpy)$_3$]$^{2+}$ in its excited state, after which the Ru^{III} state of the metal is reduced back to Ru^{II} by an electron from TEOA. The resulting diradical dicationic CBPQT$^{2(\bullet+)}$ ring undergoes translation in order to encircle the BIPY$^{\bullet+}$ unit in the dumbbell, on account of stabilizing radical-pairing interactions,[20] in addition to the loss of recognition of the donor–acceptor interactions between the DNP site and the reduced CBPQT$^{2(\bullet+)}$ ring. As soon as the BIPY$^{\bullet+}$ units are oxidized by oxygen, the donor–acceptor interactions[8e,23] are reinstated while the Coulombic repulsion between the CBPQT^{4+} ring and the BIPY^{2+} unit in the dumbbell induces the ring to shuttle back and encircle the DNP unit.



Scheme 1. a) The template-directed synthesis of the [2]rotaxane **R**·8Cl relying upon a threading-followed-by-stoppering approach based on click chemistry, as does the synthesis of its corresponding dumbbell **D**·4Cl. b) The graphical representation of **R**$^{8+}$ and the process of light-stimulated switching. Upon exposure to light, the ruthenium stopper transfers a total of three electrons photocatalytically, to all three BIPY^{2+} units situated in the ring and dumbbell components, generating the reduced trisradical species of **R**$^{8+}$, wherein the CBPQT$^{2(\bullet+)}$ ring encircles the BIPY$^{\bullet+}$ unit in the dumbbell component. Exposure to O$_2$ reoxidizes **R**$^{(2+)(3\bullet+)}$ and leads to the ground-state co-conformation, wherein the CBPQT^{4+} ring encircles the DNP unit.

The template-directed strategy, which was employed in the synthesis of **R**·8Cl, is outlined in Scheme 1 and described in detail in the Supporting Information. The bipyridinium derivative **S8**·2PF$_6$ bearing an azide terminal function, and the [Ru(bpy)$_3$]$^{2+}$ derivative **S3**·2PF$_6$, incorporating a DNP unit and a terminal alkyne function were obtained in relatively high yields in four and three steps, respectively. The [2]rotaxane **R**·8PF$_6$ was isolated in 41 % yield, following the reaction of **S3**·2PF$_6$ with **S8**·2PF$_6$ in Me$_2$CO using a copper(I)-catalyzed azide–alkyne cycloaddition[24] (CuAAC) in the presence of **CBPQT**·4PF$_6$ while relying upon a threading-followed-by-stoppering approach to form the [2]rotaxane. The water-soluble [2]rotaxane **R**·8Cl is obtained in quantitative yield from **R**·8PF$_6$ after counterion exchange with a saturated solution of tetrabutylammonium chloride (TBACl) in MeCN. The resulting [2]rotaxane was fully characterized by NMR spectroscopy and mass spectrometry (see the Supporting Information). The 1D and 2D ^{1}H NMR spectra of **R**·8Cl in D$_2$O revealed (Figure S2) that the CBPQT^{4+} ring encircles the DNP unit in the ground-state co-conformation (GSCC) of the [2]rotaxane.

The light-induced switching of **R**·8Cl (for similar investigations carried out on **R**·8PF$_6$ in MeCN, see the Supporting Information) has been monitored using UV/Vis spectroscopy. The absorption spectrum of **R**·8Cl was recorded (Figure 1 a) at room temperature in degassed H$_2$O. The [Ru(bpy)$_3$]$^{2+}$ unit in **R**$^{8+}$ has a characteristic absorption band with a maximum at $\lambda_{max} = 456$ nm. Irradiation of the aqueous solution (in the presence of TEOA) with a household, visible-light lamp gave rise to another characteristic absorption ($\lambda_{max} = 534$ nm) band, accompanied by the appearance of a broad band centered on 1083 nm and consistent with the absorption spectra of the BIPY$^{\bullet+}$ radical cations in their pimerized forms.[20] On exposing the **R**·8Cl solution to air, the absorption band at 534 nm and that centered on 1080 nm were no longer observed, indicating that the CBPQT^{4+} ring is once again encircling the DNP unit.[25] We have also investigated (Figure 1 b) how the photoinduced reduction takes place over time and discovered that the photosensitized electron transfer takes aproximately 270 min to reach completion. Control experiments were also carried out on the dumbbell **D**·4Cl (inset in Figure 1 a & Figure S8 in the Supporting Informa-

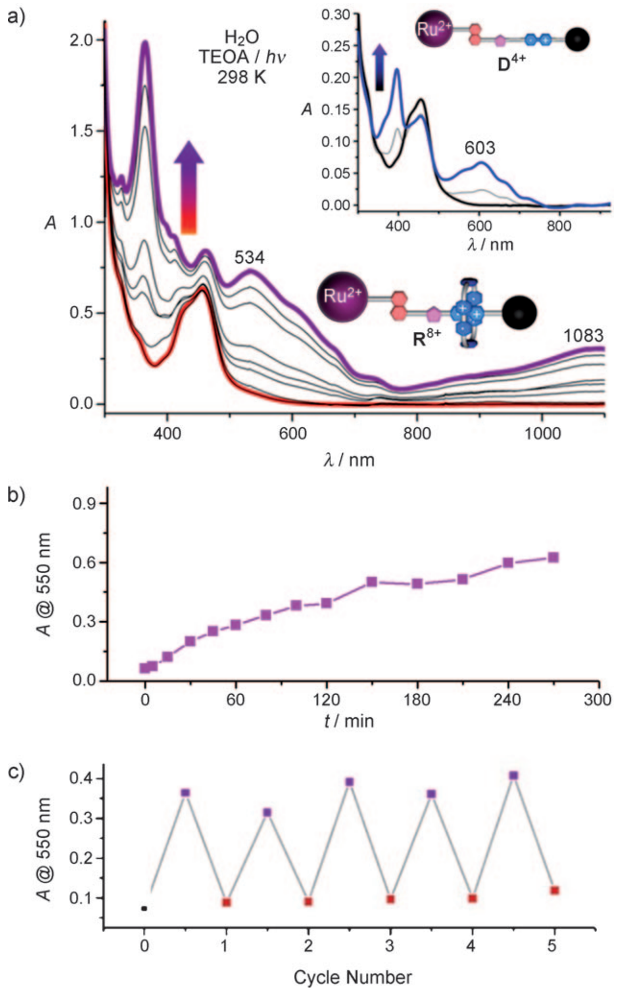


Figure 1. a) The UV/Vis absorption spectra of the [2]rotaxane **R**·8Cl (0.2 mM) in the presence of TEOA with no exposure to visible light (red trace), and after irradiation with visible light for 240 min (purple trace). Shown in the inset is the UV/Vis absorption spectra of the dumbbell **D**·4Cl (0.03 mM) in the presence of TEOA with no exposure to visible light (black trace), and after irradiation with visible light for 240 min (blue trace). All UV/Vis spectra were recorded in a quartz cell with a 2 mm cell path length under the same conditions of temperature (298 K) and solvent (argon-purged H_2O). b) A plot of absorbance at 550 nm versus irradiation time for an aqeous solution of **R**·8Cl (0.2 mM) in the presence of TEOA. All UV/Vis spectra were recorded in a quartz cell with a 2 mm cell path length under the same conditions of temperature (298 K). c) A plot of the absorbance at 550 nm versus the number of cycles as an aqueous solution of **R**·8Cl is cycled through photocatalytic reduction upon exposure to light in the presence of TEOA (purple dots) and subsequent oxidation with aerial oxygen (red dots). All UV/Vis spectra were recorded in a quartz cell with a 10 mm cell path length under the same conditions of temperature (298 K), solvent (argon-purged H_2O), and concentration (0.03 mM).

tion), which provides additional evidence for the hypothesis that the absorption bands (Figure 1) of **R**·8Cl centered on 534 nm and on 1083 nm can be attributed to the mechanical movement of the CBPQT$^{2(\bullet+)}$ ring to the BIPY$^{\bullet+}$ unit of the dumbbell component in $\mathbf{R}^{8+}$ in an aqueous environment.

In order to evaluate the ability of this integrated molecular system to serve as a prototypical artificial molecular machine, a solution of **R**·8Cl in degassed H_2O was irradiated for 30 min[26] per cycle, followed by flushing with oxygen for 1 min. No evidence of significant decomposition was observed[27] over five consecutive cycles while monitoring by UV/Vis spectroscopy.

Cyclic voltammetry (CV) of **R**·8Cl in degassed H_2O (0.1 M TBACl) reveals (Figure 2 a) a single reduction process occurring[28] at a voltage of −0.45 V (redox potential) versus the Ag/AgCl reference electrode. A combination of chronocoulometry (Figure 2 b) and ^{1}H NMR diffusion-ordered spectroscopy (DOSY) experiments (see the Supporting Information) indicate the occurrence of a three-electron process at this potential. This observation confirms our hypothesis that, upon irradiation with visible light, $\mathbf{R}^{8+}$ undergoes a three-

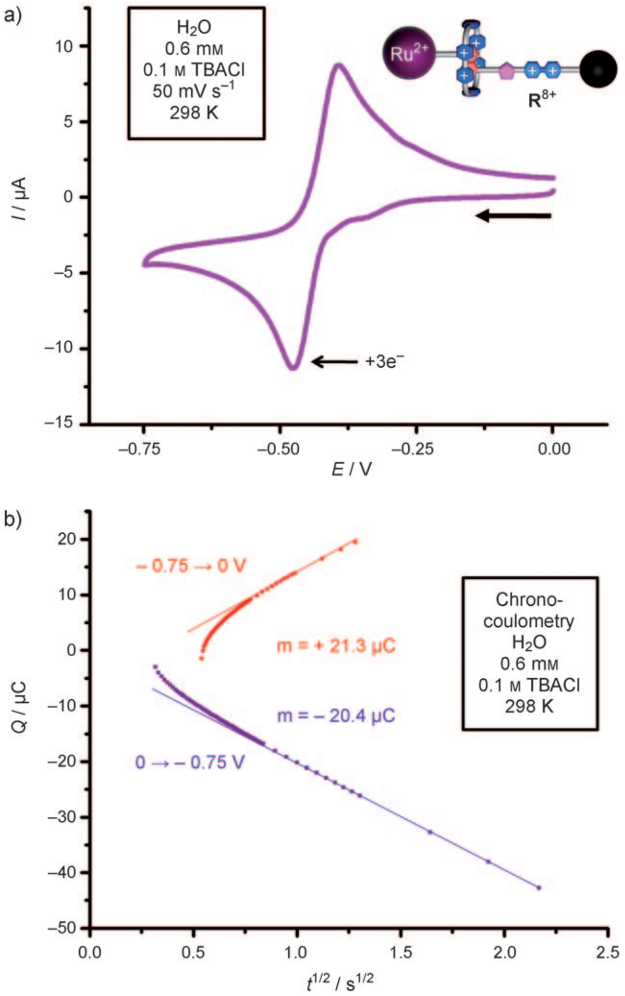


Figure 2. a) A cyclic voltammogram (CV) of **R**·8Cl which shows a single three-electron process that occurs at approximately −0.4 V vs. Ag/AgCl. The CV was recorded at 298 K in argon-purged H_2O; concentration: 0.6 mM and electrolyte: 0.1 M (TBACl). The scan rate was set at 50 mV s^{-1}. b) Integrated Cottrell chronocoulometry plot of the rotaxane **R**·8Cl. Application of the Anson equation, using a value for the diffusion coefficient obtained (see the Supporting Information) from ^{1}H DOSY NMR allowed us to determine that the reduction peak shown above is a three-electron process.

electron reduction process, resulting in the formation of the $BIPY^{\bullet+}\subset CBPQT^{2(\bullet+)}$ co-conformation.

Square-wave differential pulse voltammetry (SQWDPV) experiments have been performed (Figure 3) in aqueous solutions[29] on the supramolecular components and the results compared to those obtained for the rotaxane. The first reduction potential of the $BIPY^{2+}$ derivative V^{2+}, leading to its radical cation form, was found to come at −0.64 V, while the $CBPQT^{4+}$ ring alone in solution is much easier to reduce, its first reduction potential at −0.46 V, generating the diradical dicationic, $CBPQT^{2(\bullet+)}$. SQWDPV of an equimolar mixture of V^{2+} and $CBPQT^{4+}$ reveals that only one redox process is observed, at −0.44 V and is similar to that of $CBPQT^{4+}$ alone in aqueous solution. The fact that the reduction of V^{2+} alone in water is not detected in this case is an observation which is consistent with the formation of the trisradical complex $V^{\bullet+}\subset CBPQT^{2(\bullet+)}$. (See the Supporting Information for a CV titration study.) The large thermodynamic driving force for the formation of the trisradical complex acts to shift the reduction of V^{2+} to a more positive potential, such that it occurs at the same potential as does the first reduction of the $CBPQT^{4+}$ ring. These results are consistent with what we have observed[20a] previously for the formation of a trisradical complex in MeCN. SQWDPV of the rotaxane $\mathbf{R}^{8+}$ in water shows that the first reduction occurs at a potential −0.45 V, which is nearly identical to that of the 1:1 mixture of $CBPQT^{4+}$ and V^{2+}, both of which can be assigned to a three-electron reduction of each of the $BIPY^{2+}$ units—two involving the $CBPQT^{4+}$ ring and one involving the thread or dumbbell components.

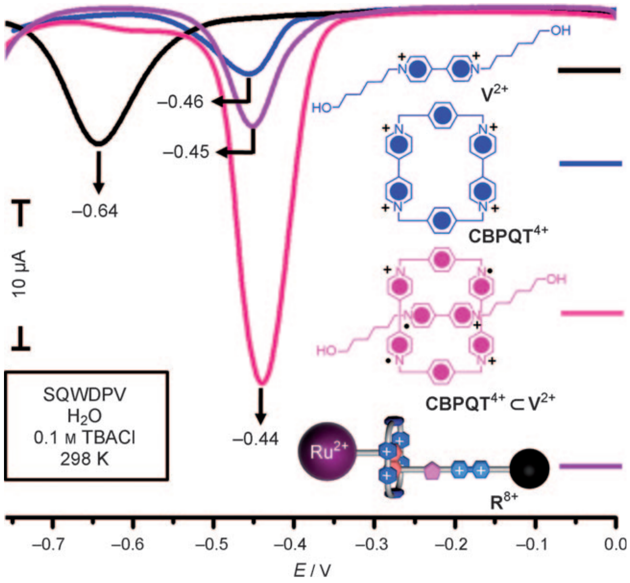


Figure 3. Square-wave differential pulse voltammograms (SQWDPV) of the viologen derivative V^{2+} (0.5 mM, black trace), the $CBPQT^{4+}$ ring (0.06 mM, blue trace), a 1:1 mixture of V^{2+} and $CBPQT^{4+}$ (0.5 mM, pink trace), which leads to formation of the trisradical complex upon reduction, and the [2]rotaxane $\mathbf{R}^{8+}$ (0.6 mM, purple trace). All voltammograms were recorded in H_2O at 298 K, with 0.1 M TBACl supporting electrolyte. Ref.: Ag/AgCl.

In order to demonstrate that, in its fully oxidized ground state, the $CBPQT^{4+}$ ring component of $\mathbf{R}^{8+}$ resides around the DNP unit, and that the ring returns after oxidation of the trisradical form of $\mathbf{R}^{8+}$, ^1H NMR spectroscopy was carried out on $\mathbf{R}\cdot 8Cl$ at 298 K. The light-induced switching of $\mathbf{R}^{8+}$, after exposure to light, (for investigations of $\mathbf{R}\cdot 8PF_6$ in MeCN, see the Supporting Information) was monitored by ^1H NMR spectroscopy at 298 K in degassed D_2O. The ^1H NMR spectroscopic data (Figure 4) support the hypothesis that $\mathbf{R}^{8+}$ has the $CBPQT^{4+}$ ring encircling the DNP unit in the ground state prior to undergoing light-stimulated switching in the presence of TEOA. The resonances associated with the $H_{2/6}$ and $H_{3/7}$ protons of the DNP unit, the upfield shifts of which compared to those in the dumbbell (see the Supporting Information), provide direct evidence for the encirclement of the $CBPQT^{4+}$ ring around the DNP unit ($DNP\subset CBPQT^{4+}$) in the GSCC. On irradiation with visible light for 240 min[26] in the presence of excess of TEOA (Figure 4), the resonances associated with the protons of the encircled DNP unit are observed to broaden out gradually into the baseline,[30] on account of the formation of the single unpaired $BIPY^{\bullet+}$ and $CBPQT^{2(\bullet+)}$ radicals, as suggested by UV/Vis spectroscopy. After aeration of the sample for only 1 min, the $H_{2/6}$ and $H_{3/7}$ resonances associated with the protons of the encircled DNP are restored, indicating that the radicals become fully oxidized back to the $CBPQT^{4+}$ ring and $BIPY^{2+}$ unit. When the switching sequence was repeated a second time in D_2O, the process was found to be reproducible. This repeatable reversible switching of $\mathbf{R}^{8+}$ points to its potential to serve as a molecular machine that can be powered over and over again in an aqueous environment by light and oxygen in an alternating sequence.

The fact that the [2]rotaxane $\mathbf{R}^{8+}$ can have its components driven back and forth relative to each other through many

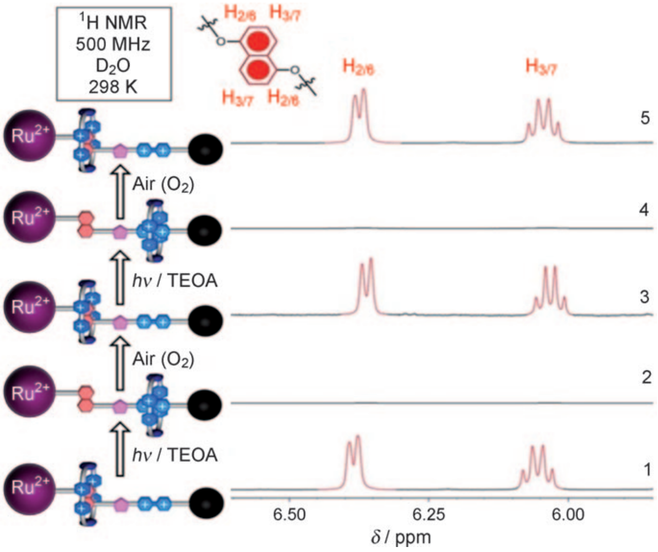


Figure 4. Partial 500 MHz ^1H NMR spectra recorded in D_2O at 298 K of 1) $\mathbf{R}\cdot 8Cl$, 2) after 240 min irradiation with visible light in the presence of TEOA (20 equiv), 3) after opening the NMR tube for 1 min to the air, 4) after another 240 min irradiation with visible light in the presence of TEOA (20 equiv), and 5) after opening the NMR tube for 1 min yet again to the air.

cycles without decomposition in aqueous solution represents a step forward in the design and operation of an artificial molecular machine that can function in water. This demonstration opens up opportunities for developing integrated nanobiomechanical systems in the direction of applications such as molecular prosthetics.[18]

Experimental Section

R·8PF$_6$: A solution of **S3**·2PF$_6$ (77 mg, 0.061 mmol), **S8**·2PF$_6$ (50 mg, 0.061 mmol), **CBPQT**·4PF$_6$ (67 mg, 0.061 mmol), TBTA (9 mg, 0.017 mmol), and $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$ (6 mg, 0.017 mmol) in anhydrous $\mathrm{Me_2CO}$ (5 mL) was stirred for 24 h at room temperature. The solvent was then evaporated off and the resulting orange solid was purified by column chromatography ($\mathrm{SiO_2}$: 2 M $\mathrm{NH_4Cl/MeOH/MeNO_2}$ 12:7:1), then MeOH, $\mathrm{Me_2CO}$, and 2% $\mathrm{NH_4PF_6/Me_2CO}$, respectively. The dark orange fraction in $\mathrm{Me_2CO}$ was collected, and concentrated to a minimum volume, before the crude product was precipitated by the addition of $\mathrm{H_2O}$. The resulting solid was collected by filtration to afford the [2]rotaxane **R**·8PF$_6$ (80 mg, 41%) as an orange powder. ^{1}H NMR (500 MHz, $\mathrm{CD_3CN}$, 233 K): $\delta = 9.02$–9.00 (m, 4H),8.93 (d, $J = 6.0$ Hz, 2H), 8.83 (d, $J = 6.0$ Hz, 2H), 8.62–8.60 (m, 4H), 8.50 (d, $J = 7.0$ Hz, 2H), 8.47 (d, $J = 7.0$ Hz, 2H), 8.41 (s, 1H), 8.37 (d, $J = 5.5$ Hz, 2H), 8.35 (d, $J = 5.5$ Hz, 2H), 8.30 (s, 1H), 8.10 (s, 1H), 8.05–8.03 (m, 4H), 7.95 (br, 2H), 7.89 (br, 2H), 7.87 (br, 2H), 7.71 (s, 1H), 7.70–7.68 (m, 4H), 7.59 (d, $J = 5.0$ Hz, 1H), 7.53 (d, $J = 5.0$ Hz, 1H), 7.41–7.34 (m, 8H), 7.30 (d, $J = 4.5$ Hz, 1H), 7.23 (d, $J = 5.0$ Hz, 1H), 7.18 (br, 2H), 7.14–708 (m, 5H), 6.23 (d, $J = 6.5$ Hz, 1H), 6.20 (d, $J = 7.0$ Hz, 1H), 5.95–5.91 (m, 2H), 5.63–5.52 (m, 8H), 4.84 (br, 4H), 4.61(s, 2H), 4.51 (t, $J = 6.5$ Hz, 2H), 4.28–3.78 (m, 24H), 3.27 (septet, $J = 7.0$ Hz, 2H), 2.47 (s, 3H), 2.29 (d, $J = 7.0$ Hz, 1H), 2.27 (d, $J = 7.0$ Hz, 1H), 1.87–1.15 (m, 8H), 1.15 ppm (d, $J = 7.0$ Hz, 12H). ^{13}C NMR (125 MHz, $\mathrm{CD_3CN}$): $\delta = 156.7$, 156.6, 155.8, 152.4, 151.3, 151.3, 151.1, 151.0, 150.7, 150.6, 150.5, 150.2, 149.8, 149.4, 145.8, 145.2, 144.9, 144.3, 143.6, 143.2, 141.4, 137.4, 136.2, 131.0, 128.1, 127.7, 127.2, 126.8, 126.4, 125.9, 124.9, 124.7, 124.5, 124.0, 123.9, 123.8, 123.8, 123.5, 121.6, 107.9, 107.8, 104.0, 103.9, 98.4, 73.2, 70.5, 70.2, 70.2, 70.1, 69.8, 69.4, 69.3, 68.7, 68.3, 68.0, 68.0, 67.0, 64.7, 63.2, 61.5, 61.4, 54.0, 53.8, 49.2, 31.2, 30.9, 30.3, 30.0, 29.6, 29.2, 28.4, 25.7, 25.0, 24.6, 23.0, 19.9, 18.9 ppm. ESI-HRMS calcd for $m/z = 915.5811$ $[M-3\mathrm{PF_6}]^{3+}$, found $m/z = 915.5855$. Counterion exchange from **R**·8PF$_6$ to **R**·8Cl: Excess of tetrabutylammonium chloride (TBACl) was added to a solution of **R**·8PF$_6$ in MeCN. Some orange solid was precipitated, which was collected by filtration and washed by MeCN to afford **R**·8Cl in quantitative yield as an orange powder.

D·4PF$_6$: A solution of **S3**·2PF$_6$ (77 mg, 0.061 mmol), **S8**·2PF$_6$ (50 mg, 0.061 mmol), TBTA (9 mg, 0.017 mmol), and $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$ (6 mg, 0.017 mmol) in anhydrous $\mathrm{Me_2CO}$ (5 mL) were stirred for 24 h at room temperature. The solvent was then evaporated off and the resulting orange solid was purified by column chromatography ($\mathrm{SiO_2}$: 2 M $\mathrm{NH_4Cl/MeOH/MeNO_2}$ 12:7:1), then MeOH, $\mathrm{Me_2CO}$, and 2% $\mathrm{NH_4PF_6}$ in $\mathrm{Me_2CO}$, respectively. The orange fractions were collected, and concentrated to a minimum volume, before being precipitated by the addition of $\mathrm{H_2O}$. The resulting solid was collected by filtration to afford **D**·4PF$_6$ (30 mg, 24%) as an orange powder. ^{1}H NMR (500 MHz, $\mathrm{CD_3CN}$): $\delta = 8.96$ (d, $J = 7.0$ Hz, 2H), 8.84 (d, $J = 6.5$ Hz, 2H), 8.51(d, J=8.0 Hz, 2H), 8.49 (d, $J = 3.5$ Hz, 1H), 8.47 (d, $J = 3.0$ Hz, 1H), 8.43 (s, 1H), 8.39 (d, $J = 7.0$ Hz, 2H), 8.34 (d, $J = 6.5$ Hz, 2H), 8.32 (s, 1H), 8.08–8.03 (m, 4H), 7.75–7.71 (m, 7H), 7.61 (d, $J = 5.5$ Hz, 1H), 7.54 (d, $J = 6.0$ Hz, 1H), 7.41–7.37 (m, 4H), 7.35–7.32 (m, 2H), 7.26–87.23 (m, 2H), 7.16–7.09 (m, 3H), 6.94 (d, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 7.5$ Hz, 1H), 4.87 (t, $J = 5.0$ Hz, 2H), 4.77 (s, 2H), 4.58 (s, 2H), 4.57 (t, $J = 7.5$ Hz, 2H), 4.32 (t, $J = 7.0$ Hz, 2H), 4.29 (t, $J = 4.5$ Hz, 2H), 4.32–4.22 (m, 2H), 4.11 (t, $J = 4.5$ Hz, 2H), 3.98–3.69 (m, 16H), 3.32 (septet, $J = 7.0$ Hz, 2H), 2.49 (s, 3H), 1.88–1.83 (m, 2H), 1.37–1.31 (m, 4H), 1.19 ppm (d, $J = 7.0$ Hz, 12H). ^{13}C NMR (125 MHz, $\mathrm{CD_3CN}$): $\delta = 156.6$, 156.5, 156.0, 153.9, 152.5, 151.3, 151.3, 151.1, 151.1, 150.8, 150.7, 150.4, 150.1, 149.8, 149.2, 145.8, 145.1, 144.1, 141.4, 137.3, 128.0, 127.1, 126.8, 126.4, 126.1, 126.0, 125.1, 125.0, 124.7, 124.7, 124.6, 124.4, 123.8, 123.8, 122.9, 121.2, 113.7, 113.6, 105.6, 105.4, 73.2, 70.1, 69.7, 69.1, 69.0, 69.0, 68.4, 67.7, 63.5, 61.5, 61.4, 49.2, 30.2, 29.1, 25.7, 25.0, 24.4, 23.0, 19.9 ppm. ESI-HRMS calcd for $m/z = 1936.5490$ $[M-\mathrm{PF_6}]^{+}$, found $m/z = 1936.5540$. Counterion exchange from **D**·4PF$_6$ to **D**·4Cl: Excess of tetrabutylammonium chloride (TBACl) was added to a solution of **D**·4PF$_6$ in MeCN. Some orange solid was precipitated, which was collected by filtration and washed by MeCN to afford **R**·8Cl in quantitative yield as an orange powder.

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[25] The absorption spectrum of **R**·8PF$_6$, as well as that of its dumbbell **D**·4PF$_6$ (see Figure S7 and Figure S8 respectively), recorded in MeCN show that this light-driven mechanical movement can also take place in organic solvents.

[26] The timescale of the sacrificial-assisted light-stimulated reduction reaction and the consequent mechanical movement of the ring component is relatively long as shown by both UV/Vis and ^{1}H NMR spectroscopies. This observation can be attributed to the trace amount of oxygen that oxidizes most of the radicals generated by the reduction of the Ru^{II} stopper in its excited state. For an example that demonstrates that a trace amount of oxygen slows down the BIPY$^{\bullet+}$ generation by the reduction of excited [Ru(bpy)$_3$]$^{2+}$, see: D. Zon, S. Andersson, R. Zhang, S. Sun, B. Åkermark, L. Sun, *J. Org. Chem.* **2008**, *73*, 3775–3783.

[27] For comparison, we have performed a similar experiment but instead of using light, we employed the reducing agent $Na_2S_2O_4$. After five cycles, almost no sign of the formation of a radical cation could be observed in the absorption spectrum, an observation which could possibly be explained by the decomposition of **R**·8Cl.

[28] The first reduction potential of the rotaxane **R**$^{8+}$ in MeCN is −0.3 V, while in water it is −0.44 V. In a similar fashion, the first reduction potentials of both V^{2+} and CBPQT^{4+} as well as the 1:1 mixture are all shifted to more negative voltages in water compared to those observed in MeCN. We hypothesize that these observations are a result of the poorer ability of water to

solvate less charged species (specifically the radical cationic and neutral forms of the components) and, as a consequence, shift the redox potentials consistently to more negative potentials in the case of all the species.

[29] At 1 mM concentration, the rotaxane $\mathbf{R}^{8+}$ was observed to precipitate on the electrode after the first three-electron reduction process. This observation relates to our hypothesis that water is not as able to support less charged species compared to the situation in MeCN, causing precipitation to occur at 1 mM in H_2O, but not in the case of MeCN, a solvent in which no precipitation is observed at that concentration. At the slightly lower concentration of 0.6 mM in H_2O, however, the rotaxane remains soluble enough such that precipitation on the electrode can be avoided.

[30] The trisradical complex BIPY$^{\bullet+}$$\subset$CBPQT$^{2(\bullet+)}$ has a single unpaired radical, which renders it EPR active. The single unpaired radical broadens all the NMR signals. For details, see Ref. [20a].