Interlocked Molecules

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An Acid–Base-Controllable [c2]Daisy Chain**

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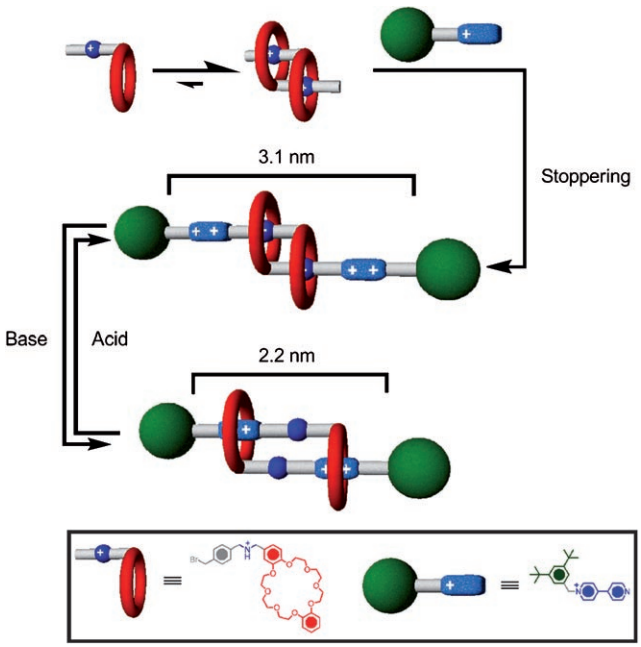
Artificial molecular-based muscles, which can convert chemical, electrochemical, or photochemical energy into mechanical motion, have attracted attention as a result of their potential for spawning nanoelectromechanical systems (NEMS).[1] Several materials, such as conducting polymers,[2] single-walled carbon nanotubes,[3] and dielectric elastomers,[4] have been developed which exhibit muscle-like behavior at the nanoscale level. However, all these systems rely upon the response of a bulk substance, rather than on the behavior of individual molecules. Recently, artificial muscles have been designed on a molecular scale by taking advantage of conformational changes exerted by electrochemical stimuli.[5–8] For example, oligothiophene-calix[4]arene copolymers[5] and thiophene-fused annulenes[6] exhibit molecular actuating behavior under redox control while crown-ether-annelated oligothiophenes[7] and polyheterocyclic strands[8] have ion-triggered muscle-like properties. Nanoscale molecular motions, based on artificial molecular machines,[9] offer alternative opportunities to design artificial muscle-like materials.

Bistable rotaxanes are a promising component for such materials, because relative linear mechanical translocation of the ring and dumbbell components can be achieved upon activation by chemical,[10] electrical,[11] or light irradiation[12] stimuli. Converting such internal molecular motions into practical actuating materials requires relocating these internal motions into components, which, when taken together, exhibit linear expansion and contraction. Sauvage et al.[13] have reported a linear molecular muscle, based on a transition-metal templated, doubly threaded rotaxane, which can undergo the required expansion and contraction motions on the addition or removal of metal ions. On the other hand, we have reported a switchable, palindromically constituted, doubly bistable [3]rotaxane[14] which can be self-assembled onto gold-coated microcantilevers with disulfide-terminated tethers emanating from its two rings in such a manner that they can be moved towards and away from each other under redox control. Controllable and reversible deflection of the microcantilevers can be achieved when the integrated system is exposed to the addition of oxidants or reductants (or subjected to oxidizing or reducing electrochemical potentials).

Acid–base controllable, bistable, rotaxane-based molecular shuttles have been reported[10b,c] in which a dibenzo[24]-crown-8 (DB24C8) ring switches under acid–base control between two different recognition sites on a dumbbell component, where one of the sites is a secondary dialkylammonium ($R_2NH_2^+$) center and the other site, an *N*,*N*′-dialkylated-4,4′-bipyridinium ($Bpym^{2+}$) unit. Although this switching has subsequently been employed[10d,e] in the design of more complex machines, such as nanoscale elevators, the mechanical motions are still only relative internal movements, that is to say, there is no contraction/expansion in their overall molecular dimensions. Herein, a bistable molecular architecture incorporating a two-component [c2]daisy chain topology[15] is designed and synthesized (Scheme 1), wherein two mechanically interlocked filaments glide along one another through the terminal crown ether rings and in which the end of each filament is attached to bulky stoppers to prevent



Scheme 1. Schematic representation of the anticipated mechanical motions within an acid–base-controlled molecular muscle system based on a [c2]daisy chain.

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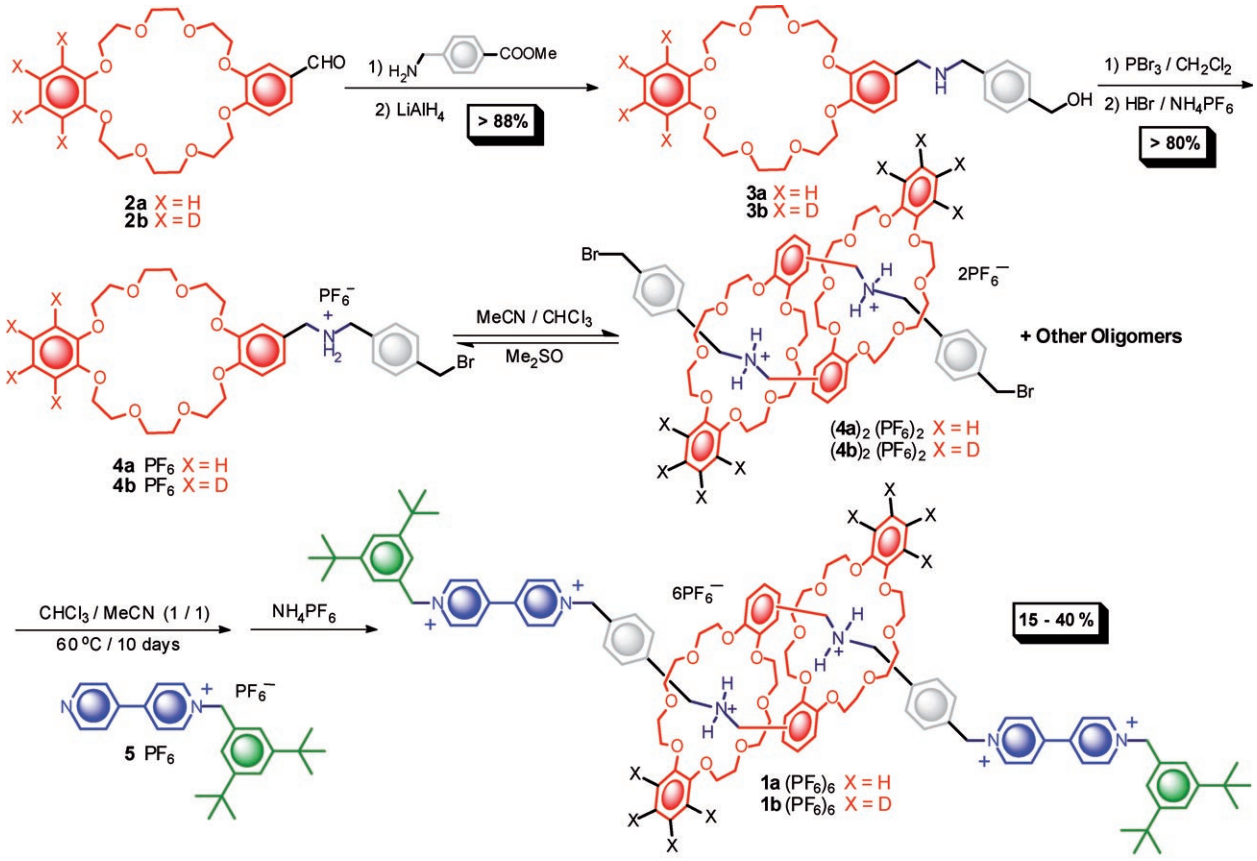
dethreading of the rings. In this Janus-type molecule, the two DB24C8 rings move between the two different recognition sites—$R_2NH_2^+$ and $Bpym^{2+}$—under acid–base control, conferring upon the molecule contraction and expansion, reminiscent of the action of a muscle.

The template-directed synthesis[15b,c] of this kind of [c2]daisy chain relies on the self-assembly of two benzylammonium-terminated DB24C8 rings to give a thermodynamically stable, dimeric pseudorotaxane,[16] in solvents such as MeCN. The incorporation of the second recognition site ($Bpym^{2+}$) equipped with a bulky stopper affords a kinetically stable, [c2]daisy chain. Employing this synthetic strategy, both **1a**$(PF_6)_6$ and **1b**$(PF_6)_6$ have been prepared (Scheme 2) in which the latter compound (**1b**$(PF_6)_6$) contains tetradeuterated catechol rings.

The intermediate compounds **4a**PF_6 and **4b**PF_6 with benzylic bromide groups self-assemble (Scheme 2) into the dimeric superstructures (**4a**$)_2(PF_6)_2$ and (**4b**$)_2(PF_6)_2$, respectively. Prior to this self-assembly step, the synthesis involves the condensation of the formyl-substituted DB24C8 derivatives **2a** and **2b**[15b] with methyl 4-(aminomethyl)benzoate to give the corresponding imines. Simultaneous reduction ($LiAlH_4$) of the imine bonds and the ester functions gave compounds **3a** and **3b**, respectively, with overall yields in excess of 88%. The hydroxymethyl groups in **3a** and **3b** were then brominated by reaction with PBr_3 in CH_2Cl_2, followed by protonation of the amino groups with HBr and counterion exchange with NH_4PF_6 to afford the compounds **4a**PF_6 and **4b**PF_6 in overall yields exceeding 80%. The ^{1}H NMR spectra of **4a**PF_6 and **4b**PF_6 revealed that the molecules exist as monomers in polar solvents, such as Me_2SO. In less polar solvents, such as $CHCl_3$ and MeCN, the self-assembled dimers (**4a**$)_2(PF_6)_2$ and (**4b**$)_2(PF_6)_2$ and higher oligomers constitute the major components. The solvent-dependent aggregation was further confirmed by electrospray ionization mass spectrometry (ESI-MS) measurements of **4a**PF_6 in protic and aprotic solvents. A peak at m/z 660.22, corresponding to the single positively charged ion $[M-PF_6]^+$, was detected when a protic solvent, such as methanol, was used as the solvent. On the contrary, a peak at m/z 660.40, corresponding to the doubly positively charged ion $[M_2-2PF_6]^{2+}$ (differentiated by the isotopic mass profile), was observed when using a less polar and aprotic solvent, such as MeCN, indicating the formation of dimeric species (see Figure S1 in the Supporting Information).[15b,16] Finally, solutions of (**4a**$)_2$-$(PF_6)_2$ and (**4b**$)_2(PF_6)_2$ were treated with **5**PF_6[10] in MeCN/$CHCl_3$ (1:1 v/v) at 60 °C for 10 days, after which the products were purified by column chromatography on silica, using MeOH/2 M aqueous NH_4Cl/$MeNO_2$ (7:2:1 v/v/v) as the eluent before being subjected to counterion exchange with NH_4PF_6, yielding **1a**$(PF_6)_6$ and **1b**$(PF_6)_6$ in 15–40% yields. The low yields can be attributed to the propensity of the dimeric superstructures, (**4a**$)_2(PF_6)_2$ and (**4b**$)_2(PF_6)_2$, to disassemble during the stoppering reaction at elevated temperatures. High resolution ESI mass spectra of **1a**$(PF_6)_6$ and **1b**$(PF_6)_6$ showed major peaks at m/z 1230.996 and 1234.986, respectively, which



Scheme 2. The template-directed syntheses of the molecular muscles **1a**$(PF_6)_6$ and **1b**$(PF_6)_6$.

can be assigned to doubly threaded species after the loss of two PF_6^- counterions (see Supporting Information). ^{1}H NMR and COSY-NMR spectroscopies were also used to characterize these doubly interlocked structures. Although compound **1a**$(PF_6)_6$ shows well-resolved peaks in its ^{1}H NMR spectrum in CD_3CN, the resonances originating from the aromatic protons of both the simple and substituted rings overlap (see Supporting Information). This drawback can be overcome by recording the ^{1}H NMR spectrum of the deuterated analogue **1b**$(PF_6)_6$.

The ^{1}H NMR spectrum of **1b**$(PF_6)_6$ in CD_3CN revealed well-resolved peaks, all of which could be assigned (Figure 1a) with the help of COSY-NMR spectroscopic measurements. The spectrum indicates that the DB24C8 rings exhibit an overwhelming selectivity for the encirclement of the $R_2NH_2^+$ recognition sites. The peaks arising from the -OCH_2CH_2O- repeating unit appear in the region $\delta = 3.2$–4.5 ppm and are not individually resolved on account of the association of the DB24C8 rings with the -NH_2^+- centers. The resonance signal for the NH_2^+ protons was observed at $\delta =$ 7.21 ppm. The protons on the uncomplexed $Bypm^{2+}$ units appear as clearly resolved peaks, resonating downfield in the region $\delta = 8.3$–9.0 ppm. As a result of the diamagnetic ring currents of the DB24C8 and the π–π interaction the catechol rings, the signals (box in Figure 1) for H_a, H_b, and H_c are shifted upfield. In addition, two sets of signals (see Figure 1, red for the major isomer and pink for the minor isomer) for the undeuterated catechol rings were indentified in the region $\delta = 6.1$–7.0 ppm, indicating that there are two diastereoisomers present in the solution. This phenomenon was also detected in a previously reported[15b] self-assembling [c2]daisy chain involving DB24C8 rings and -NH_2^+- center. On account of the unsymmetrical substitution of the DB24C8 ring, dimerization gives two C_2-symmetrical (chiral) enantiomers and a C_i symmetrical (meso) diastereoisomer (see Supporting Information). The two sets of signals for the catechol ring protons in the ^{1}H NMR spectrum of **1b**$(PF_6)_6$ can be assigned to the racemic modification and the meso isomer.

To initiate muscle-like behavior at the molecular level, 2.1 equivalents of phosphazene base P_1–*t*Bu[17] were added to a solution of **1b**$(PF_6)_6$ in CD_3CN. The ^{1}H NMR spectrum of the resulting mixture revealed that the deprotonation of the -NH_2^+- centers brought about the migration of the DB24C8 rings to the $Bypm^{2+}$ recognition sites (Figure 1b). This interpretation was supported by the following: 1) the peaks for the $Bypm^{2+}$ protons are shifted downfield on association with the DB24C8 rings; 2) the peaks for the protons (H_f and H_g) on the phenylene spacers are shifted upfield because of the mutually π-overlapping nature of the para-phenylene ring systems in the contracted geometry; 3) the separate peaks for H_a, H_b, and H_c in the diastereoisomers are less anisochronous and give only one set of accidentally equivalent signals because of the lack of π–π interactions of the catechol ring; 4) the signal for proton H_h is shifted upfield when the DB24C8 rings migrate to the $Bypm^{2+}$ sites. Reprotonation of the -NH_2^+- centers following the addition of 2.1 equivalents of CF_3CO_2H resulted in the return of the DB24C8 rings to the -NH_2^+- centers as evidenced by the regeneration of the original ^{1}H NMR spectrum (Figure 1c). Thus, ^{1}H NMR spectroscopic measurements demonstrate that molecules **1a**$^{6+}$ and **1b**$^{6+}$ perform reversible muscle-like contraction and expan-

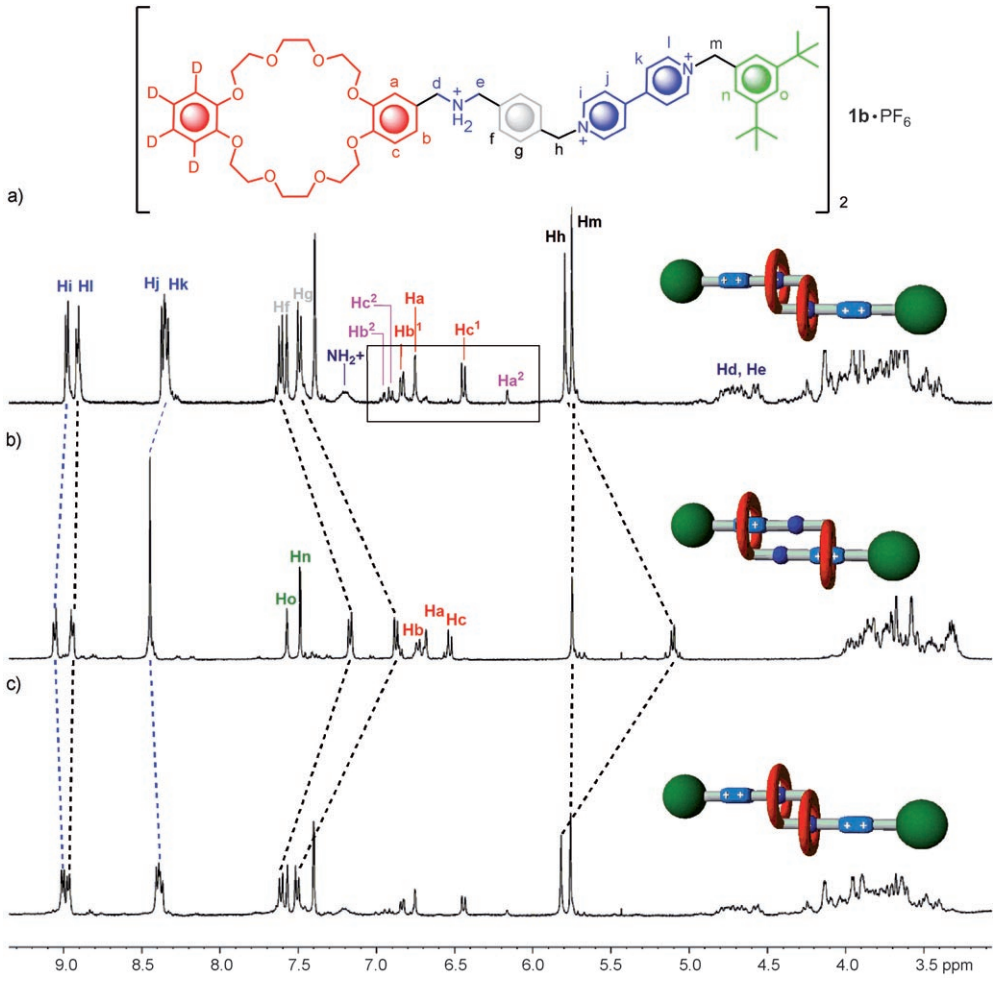


Figure 1. ^{1}H NMR spectra of compound **1b**$(PF_6)_6$ in CD_3CN: a) the original spectrum; b) after addition of 2.1 equivalents P_1–*t*Bu base; and c) further addition of 2.1 equivalents CF_3CO_2H.

sion under acid–base control. AMBER[18] molecular modeling also suggested that, after deprotonation, the longitudinal molecular size became approximately 29% (0.9 nm) shorter than the original extended length (Scheme 1).

Acid–base switching was monitored by UV/Vis absorption spectroscopy in a 0.39 mM solution of **1a**$(PF_6)_6$ in MeCN (Figure 2). Upon addition of 2.1 equivalents of phosphazene base P_1–*t*Bu, the colorless solution turned yellow and a new maximum appeared at approximately 400 nm in the spectrum. This band[16] corresponds to the charge-transfer interaction between the $Bypm^{2+}$ and DB24C8 rings. Upon addition of 2.5 equivalents of CF_3CO_2H to the yellow solution the color was expelled and the original UV/Vis spectrum was reinstated.[19]

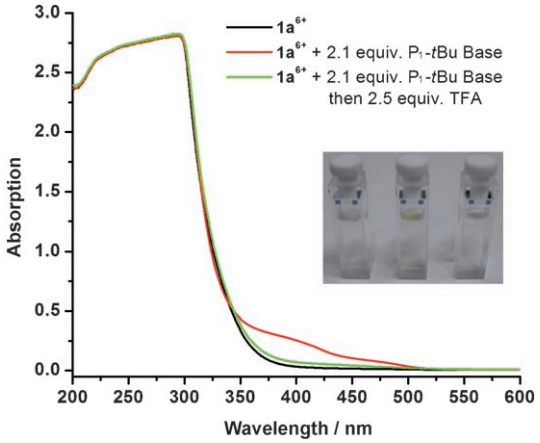


Figure 2. Change in UV/Vis absorption spectra of compound **1a**$(PF_6)_6$ in CD_3CN (0.39 mM) before deprotonation (black), after deprotonation with 2.1 equiv of P_1–*t*Bu base[17] (red) and after reprotonation with 2.5 equivalents of trifluoroacetic acid (TFA, green). Inset, from left to right side, shows the color change during this process.

The versatile synthetic strategy we have employed to make this acid–base controllable [c2]daisy chain is readily amenable to modification with carefully chosen functional groups, leading to the production of functionalized muscle molecules, which could, for example, be incorporated into liquid crystalline[21] or polymeric[22] systems. The material properties of these much larger supramolecular and molecular systems should then be responsive to changes in pH at the monomeric level within their superstructures and structures, respectively.

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[17] Full name: *N-tert*-butyl-*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-hexamethylphosphorimidic triamide.

[18] http://amber.scripps.edu

[19] It should be pointed out that, after the deprotonation/reprotonation cycle, waste salts are produced in solution. Moreover, some PF_6^- counterions are partially replaced by $CF_3CO_2^-$. Therefore, there are slight shifts in the NMR spectrum with respect to the original spectrum. A similar phenomenon is seen in the UV/Vis absorption spectra for the same reasons.

[20] Two communications, submitted around the same time as this communication, also describe [c2]daisy chain structures that are acid–base- and light-switchable, respectively: F. Coutrot, C. Romuald, E. Busseron, *Org. Lett.* **2008**, DOI: 10.1021/ol801390h; R. E. Dawson, S. F. Lincoln, C. J. Easton, *Chem. Commun.* **2008**, DOI: 10.1039/b809014a.

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