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A Double-Leg Donor–Acceptor Molecular Elevator: New Insight into Controlling the Distance of Two Platforms

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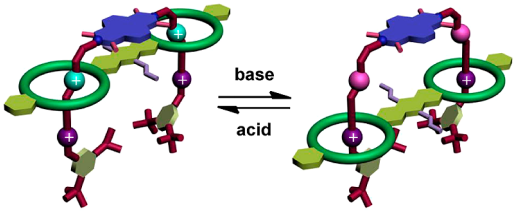
ABSTRACT



A double-leg elevator with an electron-rich anthracene moiety at the platformlike component and an electron-deficient naphthalenediimide unit in the middle of a double-leg riglike component was prepared through "click chemistry", in which the reversible elevator movement between different levels could be controlled upon the addition of base and acid.

To learn from the natural world and mimic the functions of biological molecular machines, chemists have been fabricating various artificial molecular machines.[1] In the past few years, several different kinds of artificial molecular machines have been designed and constructed, such as molecular rotary motors,[2] molecular shuttles,[3] molecular muscles,[4] nanocars,[5] and so on. Until now, the two-station shuttling mode based on the complexation of 24-crown-8 (24C8) with the relative cationic guests has been used in many artificial molecular machines[6,4b] with specific functions.[7,3b] Stoddart, Credi, and co-workers reported the first molecular elevator[8] which consisted of a trifurcated riglike component and a trimacrocycle platformlike component. Such an interlocked system was constructed based on a triply threaded two-component complex, which was stabilized by the multivalent associations between the

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tritopic host and guest. The elevator movement was realized by the shuttling of the crown ether macrocycles between the two different stations on the legs of the rig upon the addition of base and acid. It should be a good choice to use the elevator mode for accurately controlling the distance between two platforms. However, the synthetic difficulty of a three-leg elevator limits its application. Therefore, offering a more precise and simple way to control the distance between two units in the elevator-type system is necessary.

Herein, we report a switchable double-leg molecular elevator containing one acceptor and one donor on its top and bottom, respectively. Based on our previous research,[9] we chose a bis-24C8 macrocycle fused to an electron-rich anthracene moiety in the middle for the platformlike component **1**, and a bis-secondary dialkylammonium bearing electron-deficient naphthalenediimide (NDI) unit as the spacer for the double-leg riglike component **6**-2H·2PF_6. When the precursor **2**-2H·2PF_6 is mixed with host **1**, a stable divalent complex can be formed which is stabilized by the charge transfer (CT) interaction of complementary rigid spacers (anthracene vs NDI) and the complexation between two pairs of 24C8 and secondary dialkylammonium sites.[10] By using the "threading followed by stoppering" protocol, the ends of legs are connected with bulky 3,5-di-*tert*-butylbenzyl feet to generate the mechanically interlocked molecule **3**-2H·2PF_6 and further methylation reaction affords the molecule **4**-2H·4PF_6 (Scheme 1).

The past few years have witnessed a surge in the use of the copper(I)-catalyzed Huisgen alkyne−azide 1,3-dipolar cycloaddition (CuAAC "click" reaction), which has often been used in the synthesis of mechanically interlocked compounds.[11] For our system, the "click chemistry" approach is an attractive one not only due to its high efficiency and mild condition, but also its generated triazole group which can be easily converted to the methyl triazolium, a second binding site for 24C8 after the deprotonation of the NH_2 site.[11a] In the two-station molecular elevator **4**-2H·4PF_6, the platform is situated on the upper level at the original state. The bis-24C8 platform moves to the lower level upon addition of the base and backs to the upper level through addition of the suitable acid.

The host **1** and divalent guest **2**-2H·2PF_6 were prepared based on our previous report.[9,6c] To confirm the formation of a stable complex between **1** and **2**-2H·2PF_6 in solution, ^{1}H NMR experiments were performed on the equimolar mixture of the two substrates. As shown in Figure S11 in the Supporting Information, the ^{1}H NMR spectrum of the 1:1 mixture of **1** and **2**-2H·2PF_6 is well resolved, and free host or guest species can hardly be detected. The signals of hydrogen atoms H_j on the NDI, H_k adjacent to the NDI, H_f on the anthracene moiety and protons on the propyl group (H_g, H_h and H_i) all exhibit large upfield shifts, which should result from the mutual shielding effects between the anthracene and NDI. Moreover, H_m and H_n adjacent to the ammonium site are shifted downfield, the ethylidene protons of the crown ether ring are split and show upfield shifts. These shifts should be attributed to the complexation between the 24C8 ring and the secondary dialkylammonium group. The above observations suggest that the 1:1 complex [**1**·**2**-2H]·2PF_6 in which anthracene and NDI are located directly over each other dominates in the equimolar mixture of **1** and **2**-2H·2PF_6. The binding constant for the complex was calculated to be 5.4×10^4 M^{-1} by the single-point method based on the NMR spectra (Figure S12, Supporting Information).The formation of [**1**·**2**-2H]·2PF_6 is further evidenced by ESI-MS. The mass spectrum of a 1:1 mixture of **1** and **2**-2H·2PF_6 shows a signal at m/z 837, which corresponds to $[\mathbf{1}\cdot\mathbf{2}\text{-2H}]^{2+}$ (Figure S6, Supporting Information).

The formation of [**1**·**2**-2H]·2PF_6 is also supported by UV/vis and fluorescence spectroscopies (Figure 1 and Figure S13, Supporting Information). Upon mixing equivalent bis-crown ether **1** and guest **2**-2H·2PF_6, the color of the solution changed from pale yellow of both host and guest to dark green with a characteristic CT band centered around 640 nm in the UV/vis spectrum. Upon the complexation, the fluorescence of anthracene on the host **1** undergoes a dramatic decrease. These observations suggest the close proximity of the anthracene and NDI as a donor−acceptor pair in [**1**·**2**-2H]·2PF_6. The CT interactions between the complementary rigid spacers and the multivalent association between the binding motifs cooperate to contribute to the stability of [**1**·**2**-2H]·2PF_6.

The CuAAC "click" reaction was performed through mixing bis-crown ether **1**, guest **2**-2H·2PF_6, stopper 3,5-di-*tert*-butylbenzyl azide, and catalyst Cu(MeCN)$_4$$PF_6$ in a mixed solvent (CH_3CN/CH_2Cl_2 = 3:1) and then stirring for 24 h at room temperature. The rotaxane **3**-2H·2PF_6 was isolated in 53% yield after purification by column chromatography. Finally, the methylation of two triazole groups in **3**-2H·2PF_6 and the subsequent salt exchange gave **4**-2H·4PF_6 in 72% yield.

The structure of **3**-2H·2PF_6 was confirmed through the comparison of the ^{1}H NMR spectra of **3**-2H·2PF_6, uncomplexed dumbbell-shaped component **5**-2H·2PF_6, and host **1** (Figure 2). It can be found that H_j on the NDI, H_k adjacent to the NDI, H_f on the anthracene moiety and the propyl group (H_g, H_h and H_i) are all shifted upfield, which indicates the close proximity of the anthracene and NDI moiety. The downfield shifts of H_m and H_n adjacent to the

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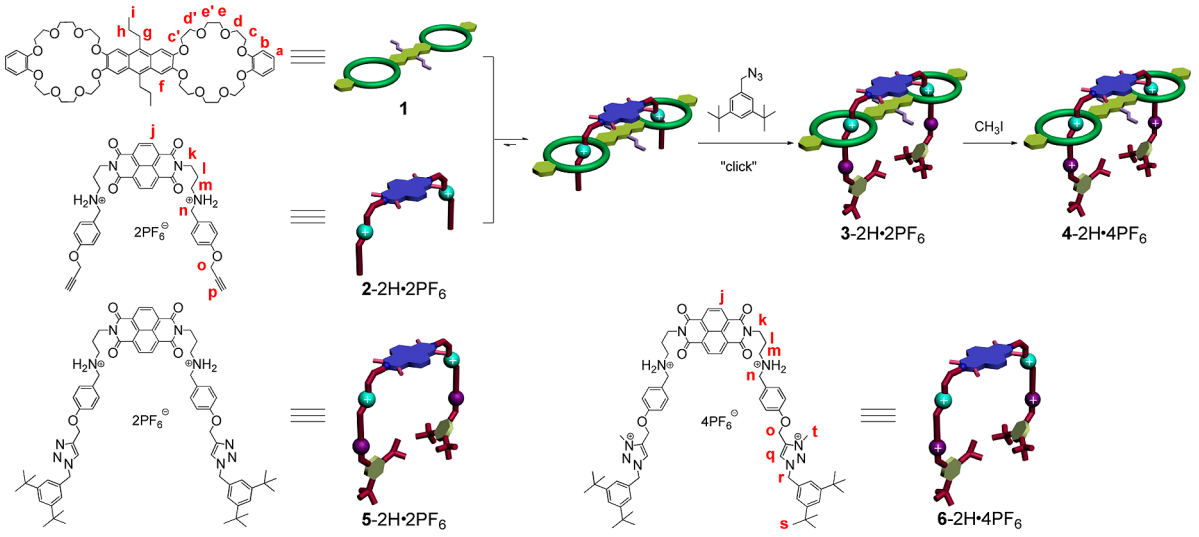
Scheme 1. Structures of Compounds **1**, **2**-2H·2PF$_6$, **5**-2H·2PF$_6$, and **6**-2H·4PF$_6$ and the Synthesis of the Rotaxanes **3**-2H·2PF$_6$ and **4**-2H·4PF$_6$



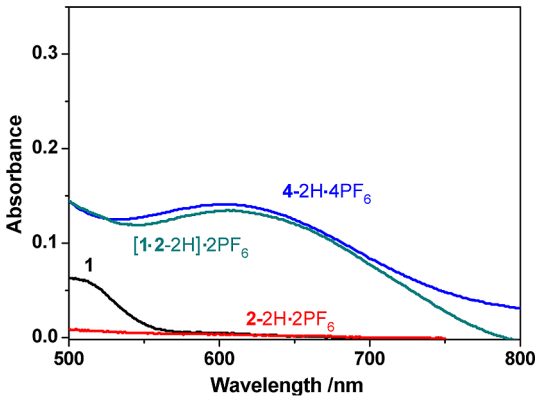


Figure 1. Absorption spectra of (a) **1**, (b) **2**-2H·2PF$_6$, (c) [**1**·**2**-2H]·2PF$_6$, and (d) **4**-2H·4PF$_6$ ($CHCl_3/CH_3CN$ = 1:1, 1.5 mM).

ammonium site and the split and the upfield shifts of the ethylidene protons on the crown ether ring confirm the threading of the secondary dialkylammonium group into the 24C8 ring. Moreover, the appearance of H_q on the triazole group and H_s on the tertiary butyl group further confirms the success of the stoppering reaction.

From the comparison of the ^{1}H NMR spectra of **4**-2H·4PF$_6$, uncomplexed riglike component **6**-2H·4PF$_6$, and host **1** (Figure S14, Supporting Information), we can find a similar change on the chemical shifts similar to that for rotaxane **3**-2H·2PF$_6$. Moreover, the methylation of the triazole can be confirmed by the appearance of H_t on the methyl group and the downfield shift (~0.4 ppm) for the proton H_q on the triazolium ring, which can be attributed to the decrease of the density of electron cloud on the triazolium ring. These observations on the chemical shifts further confirm the formation of **4**-2H·4PF$_6$ with dialkylammonium and methyl triazolium stations on its legs. A CT band for **4**-2H·4PF$_6$ can be observed in the UV/vis spectrum, and the fluorescence of **4**-2H·4PF$_6$ (Figure 1 and Figure S13, Supporting Information) is quenched, indicating the existence of CT interaction between the anthracene and NDI moieties in **4**-2H·4PF$_6$.

Then we used ^{1}H NMR to investigate the base-acid controlled movement of the two-station elevator **4**-2H·4PF$_6$ (Figure 3). At the original state, the platform prefers the ammonium stations on the rig and stays at the upper level. We first tried to use the Bu_3N to deprotonate the ammonium centers. However, the basicity of Bu_3N is not strong enough to realize the neutralization. Then we chose a stronger phosphazene base *N*-*t*-butyl-*N*′,*N*′,*N*″,*N*″,*N*‴,*N*‴-hexamethyl-phosphorimidic triamide (P_1-tBu). After the addition of P_1-tBu, H_q on the triazolium moiety experience a large downfield shift, and H_t on the methyl group and H_o adjacent to the triazolium moiety are shifted upfield, which suggest that the complexation occurs between the 24C8 ring and the triazolium unit. H_f on the anthracene moiety and the propyl group (H_g, H_h, and H_i) are all shifted downfield. These observations indicate that the 24C8 ring moves from the ammonium station to the triazolium station and the platform moves to the lower level. It is noteworthy that H_j on the NDI moiety are shifted downfield, but not back to their original uncomplexed positions, which may be attributed to the intermolecular CT interaction between the NDI and anthracene of different molecules at a high concentration, and the weak CT interaction between the base and the NDI unit. Upon the addition of trifluoroacetic acid (TFA) to the sample treated by the base, the original NMR spectrum can be regenerated, which suggests that the elevator goes back completely to the upper level. The energy-minimized structures of **4**-2H·4PF$_6$ (before and after the addition of base) obtained by molecular modeling are also consistent

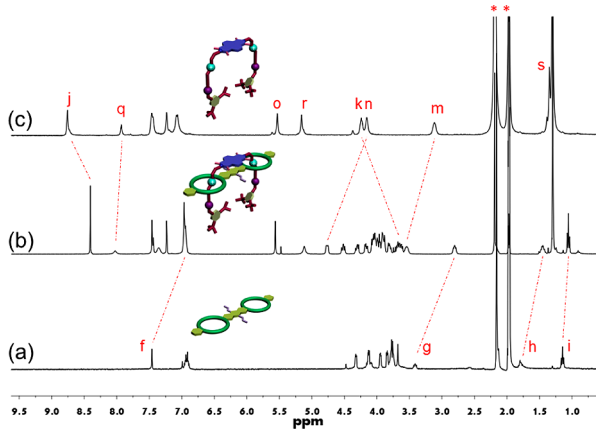


Figure 2. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 5 mM, 298 K) of (a) the uncomplexed host **1**, (b) the [3]rotaxane **3**-2H·2PF_6, and (c) the uncomplexed dumbbell-shaped thread **5**-2H·2PF_6. * = peaks of solvent and H_2O. See Scheme 1 for atom labels.

with the proposed structures (Figure S15, Supporting Information).

We can also find the changes of the UV/vis spectra upon the addition of base to the dilute solution of **4**-2H·4PF_6 (0.01 mM), which was consistent with the spectral change of the divalent pseudorotaxane after addition of base Bu_3N.[9] Through monitoring the spectral change at 377 nm, it can be confirmed that the acid/base controlled process can be repeated for several times (Figure S16, Supporting Information). However, the weakening of CT band of **4**-2H·4PF_6 after being treated by base could not be observed directly by the UV/vis spectroscopy because the intermolecular CT interaction between the NDI and anthracene of different molecules occurs at a high concentration and phosphazene base P_1-tBu was found to form a CT complex with the NDI unit as an electron donor (Figures S17 and S18, Supporting Information). The acid/base-controlled process was further investigated by fluorescence spectroscopy, which also showed a reversible switching behavior (Figure S19, Supporting Information).

In conclusion, the molecular elevator **4**-2H·4PF_6 was constructed based on a stable CT complex containing a divalent host and a guest through the "click chemistry" approach. This stoppering reaction generated two triazole groups which can be easily methylated to become the second binding station for the bis-24C8 platform. Through the base/acid switchable 2-fold host–guest interaction, the distance between the two different platforms can be adjusted precisely.

Besides the anthracene and NDI, various functional units can be easily connected with the divalent host and guest. The double-leg elevator mode should be suitable because (1) reducing the leg numbers can not realize the accurate position control; and (2) increasing the leg numbers will increase the synthetic difficulty and make it difficult to integrate with functional units. Moreover, by separating the two platforms, a switchable cavity can be opened up which can be used to accommodate some specific guests under the assistance of its "floor" and "roof". Research is ongoing in our laboratory. In short, the result presented here allows precise control of the distance between two platforms in a complex system and will benefit the development of molecular devices and machines accompanied by more advanced and integrated functions.

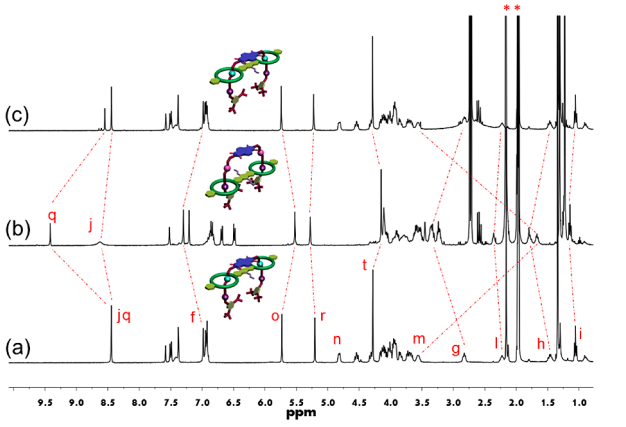


Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 5 mM, 298 K) of **4**-2H·4PF_6 (a) the original spectrum, (b) after addition of 3.0 equiv P_1-tBu; and (c) further addition of 2.0 equiv of TFA. * = peaks of solvent and H_2O.

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Supporting Information Available. Synthesis and characterization of compounds, ESI-MS, NMR, UV–vis, and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.