

Coordination-assembly for quantitative construction of bis-branched molecular shuttles†

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The development and utilization of a new way to build molecular devices is of importance. To build a novel topology of interlocked molecular systems with a controllable mechanical motion, an axle-like compound comprising azobenzene and alkoxy isophthalate moieties was synthesized first. It would form a switchable hemi-rotaxane structure with α -cyclodextrin (α -CD) ring encapsulated in aqueous solution. Next, the hemi-rotaxane was reacted with ethylene diamine palladium nitrate ($\text{Pd}(\text{en})(\text{NO}_3)_2$) and ethylene diamine platinum nitrate ($\text{Pt}(\text{en})(\text{NO}_3)_2$), respectively, to quantitatively form two bis-branched molecular shuttles *in situ*. The bis-coordinated Pd(II) complex was formed quickly at room temperature, whereas the bis-coordinated Pt(II) one was effectively treated at 333 K but more stable than the former. In this case, transformation of ring shuttling direction could take place in the stable bis-branched Pt(II) complex. The steric effect of the co-stopper, namely the Pt(II) metal center, made the α -CD ring dynamically shuttle inwards to the alkoxy isophthalate station with the azobenzene's photoisomerization, rather than dethreading from the axle.

Introduction

The design and construction of novel supramolecular devices can be categorized in one of the currently interesting fields of modern chemistry.¹ As a primary prototype of synthetic molecular machines, rotaxane analogue based interlocked molecular systems have been unfolding a developing course from simple to complicated, and from single-mode to multi-mode in the last two decades.² An intriguing challenge for developing this kind of system next is to enlarge their mechanical motion-mode, such as the controllable shuttling of the subcomponents,³ to achieve an integral device function. One practical approach is to incorporate switchable monomers to advanced topological systems for loading the functional performances. Recently, a class of Janus-type architectures bearing a two-component [c2]daisy chain topology⁴ was prepared. It was more advanced than a conventional molecular shuttle, and could mimic artificial muscle-like materials. Inspired by such innovative chemical systems that bring in reformative conceptions, chemists are developing more topologies with high yield for building advanced molecular machinery systems.

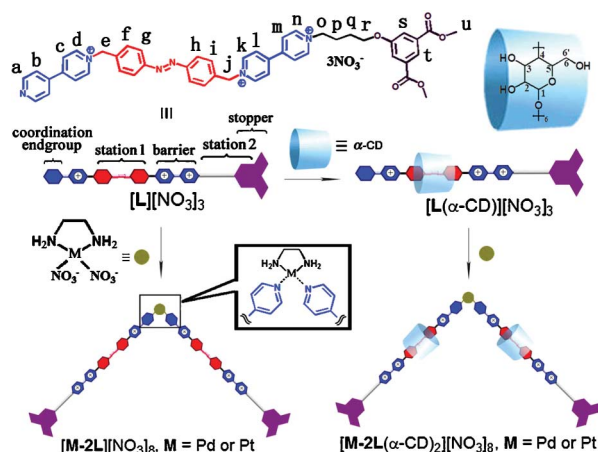
Coordination-assembly is a well-established methodology in supramolecular chemistry, because it allows for the spontaneous, selective formation of highly stable and specific supramolecular frameworks for materials and biological applications.⁵ Thus far, coordination-driven or -assembly has been utilized for construction of supramolecular ensembles capable of controllable transformations.⁶ However, the report about employing coordination-assembly to establish switchable molecular shuttles is still rare.⁷ Furthermore, there is also a need to realize the modulation or change of the components' shuttling motion with coordination-assembly as a cooperatively controlled manner.

We have focused on designing and preparing light-powered interlocked molecular shuttles for years, as photochemical response has the advantage of remote operations without generating any chemical waste.⁸ Azobenzene is an essential skeleton in building cyclodextrin-based light-driven⁹ molecular devices. To create a novel topology with light-controllable shuttling motion *via* coordination-assembly, an axle-like ligand ($[\text{L}][\text{NO}_3]_3$) was synthesized in this work (shown in Scheme 1). It comprises a light-active azobenzene unit as a strong binding station for α -cyclodextrin (α -CD), and this moiety can be encircled by one α -CD ring to form a stable hemi-rotaxane structure ($[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$). An alkoxy isophthalate unit was also introduced as a potential second binding station for the host. The two stations were harnessed to be covalently linked by a hydrophilic viologen unit, and only the pyridine nitrogen of the end group in the axle can participate in the coordination-assembly.

Herein, we choose ethylene diamine palladium nitrate and ethylene diamine platinum nitrate as the metal center, because both of the metals are prone to have a strong and quantitative

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† Electronic supplementary information (ESI) available: ESI-MS spectra of $[\text{Pt-2L}][\text{NO}_3]_8$ and $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$; Absorption spectra of $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$, $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ and their photostationary states; Fundamental characteristics (¹H NMR, ¹³C NMR, and MS spectra) of the precursors, the ligand and the bis-coordinated complexes. See DOI: 10.1039/c0ob01124j



Scheme 1 Illustration of the construction of the bis-branched molecular shuttles.

chelation with two eq. of the ligands *via* the pyridine nitrogen atom, to form stable bis-branched complexes with high yield *in situ*. A natural angle¹⁰ settled by the two ligands linked with Pd(II) or Pt(II) could form a co-stopper to well avoid the ring over-encircling.¹¹ Moreover, it is supposed that the strong steric effect generated by a high-stable coordination could effectively prevent the ring departing from the axle even under the photo-irradiation, thus resulting in the ring dynamically moving to the alkoxy isophthalate station across the viologen barrier.¹² In this way, transformation of ring shuttling direction would be realized *via* coordination-assembly as a cooperative control. This type of the bis-branched molecular shuttles could be regarded as a new topology with two of the switchable hemi-rotaxanes linked together by a metal center as the spacer ($[M-2L(\alpha-CD)_2][NO_3]_8$, $M = Pd$ or Pt) (Scheme 1). The demonstration of constructing such interlocked molecular system *via* coordination-assembly might be an important step towards the ultimate goal of building nano-machinery combination system.

Results and Discussion

Coordination-assembly for quantitative construction of bis-branched molecular shuttles

The synthetic details of the precursors and the ligand $[L][NO_3]_3$ are arranged in Experimental Section. All the anions were exchanged to NO_3^- because the nitrate ion is hydrophilic and can hardly compete with the pyridine ligand for the coordinations. $[L][NO_3]_3$ was fully characterized by 1H NMR, ^{13}C NMR, MS and elemental analysis. $[L][NO_3]_3$ can be quickly reacted with $Pd(en)(NO_3)_2$ at room temperature. Fig. 1 shows the 1H -NMR spectra of mixtures of $Pd(en)(NO_3)_2$ and $[L][NO_3]_3$ in D_2O at different molar ratios. We found the yield of the bis-branched complex was chiefly ratio-dependent. When the ratio reached 2 : 1 (0.5 eq. of $Pd(en)(NO_3)_2$ addition), almost all of the $[L][NO_3]_3$ was converted to the complex.¹³

The assignment of the proton signals in this system is to some extent assisted by the NOEs in 2D 1H NOESY spectroscopy. As shown in Fig. 1D, it clearly reveals well-assigned proton signals of the coordinated Pd(II) complex structure ($[Pd-2L][NO_3]_8$), which is totally different from that of $[L][NO_3]_3$ (Fig. 1A). It is suggested that such coordination brings in extremely high complexation

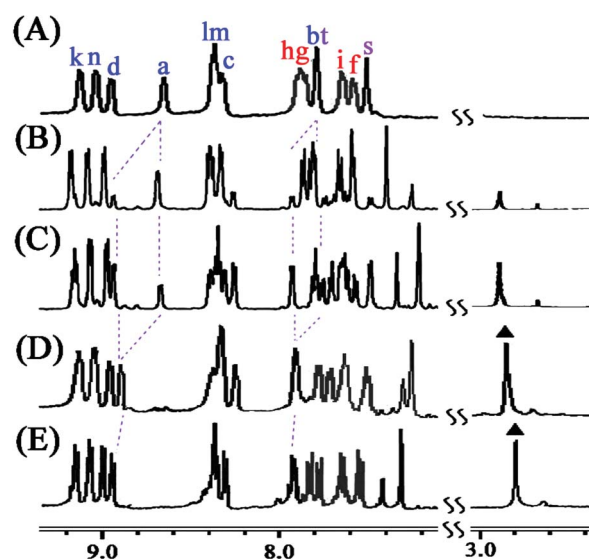


Fig. 1 Parts of the 1H NMR spectra (400 MHz in D_2O at 298 K) of A) $[L][NO_3]_3$, B) $[L][NO_3]_3$ + 0.1 eq. of $Pd(en)(NO_3)_2$, C) $[L][NO_3]_3$ + 0.3 eq. of $Pd(en)(NO_3)_2$, D) $[Pd-2L][NO_3]_8$ ($[L][NO_3]_3$ + 0.5 eq. of $Pd(en)(NO_3)_2$), E) $[Pt-2L][NO_3]_8$ ($[L][NO_3]_3$ + 0.5 eq. of $Pt(en)(NO_3)_2$). The black triangle marks the methylene protons of the coordinated ethylene diamine group.

efficiency *in situ*, as almost no peaks of $[L][NO_3]_3$ remained in the 1H NMR spectrum in Fig. 1D. H_a and H_b protons display great downfield shifts (from $\delta = 8.65$ to 8.89 for H_a , and from $\delta = 7.78$ to 7.89 for H_b), because of the coordination of the Pd(II) with two ligands *via* the pyridine nitrogen atoms. The shift of the methylene protons in ethylene diamine group to the value of 2.84 ppm appears to be gradual in Fig. 1. This would indicate slow Metal-Ligand exchange on the NMR timescale (Fig. 1A to 1D).

Keeping the mixture of $[L][NO_3]_3$ and $Pt(en)(NO_3)_2$ in a 2 : 1 ratio in D_2O at 333 K for 12 h resulted in the formation of $[Pt-2L][NO_3]_8$ (Scheme 1). The bis-coordinated Pt(II) complex revealed similar chemical shifts in 1H NMR spectrum in Fig. 1E as that of the Pd(II) complex in Fig. 1D, but H_a and H_b protons display greater downfield shifts to $\delta = 8.95$ and 7.93, respectively (Fig. 1E). The signals of the methylene protons also behave differently between the Pd(II) and Pt(II) systems where Metal-Ligand exchange rates would differ dramatically (see Fig. 1D and 1E). ESI mass spectrometry provides further evidence for the formation of this more stable bis-coordinated ensemble. In the mass spectrum of $[Pd-2L][NO_3]_8$, peak at $m/z = 1036.9$, corresponding to $[M-4NO_3]^{2+}$, is observed (Figure S1A, ESI †). Thus the reference compounds of the bis-branched molecular shuttles were obtained with high yield.

The hemi-rotaxane ligand $[L(\alpha-CD)][NO_3]_3$ was prepared from $[L][NO_3]_3$ by co-grind¹⁴ of the axle with 1 equiv. solid α -cyclodextrin for *ca.* 15 min. The uniformity of the well mixed sample can help enhance the inclusion rate of the host-guest structure in the aqueous solution. The NOEs pattern confirms that the α -CD ring dominantly stays at the azobenzene station in the initial state (see Fig. 4A).¹⁵ As cyclodextrin cavity has the primary and secondary site, some proton signals appearing in two different positions (*e.g.* two separate resonances for H_s , H_t in Fig. 2A) proves that two threading direction of α -CD are both involved in this supramolecular system. $[L(\alpha-CD)][NO_3]_3$ was

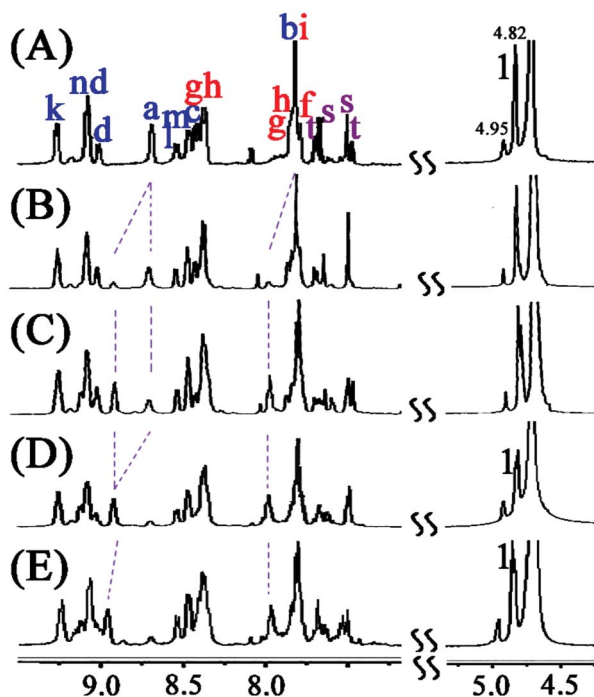


Fig. 2 Parts of the ^1H NMR spectra (400 MHz in D_2O at 298 K) of A) $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$, B) $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3 + 0.1$ eq. of $\text{Pd}(\text{en})(\text{NO}_3)_2$, C) $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3 + 0.3$ eq. of $\text{Pd}(\text{en})(\text{NO}_3)_2$, D) $[\text{Pd-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ ($[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3 + 0.5$ eq. of $\text{Pd}(\text{en})(\text{NO}_3)_2$), E) $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ ($[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3 + 0.5$ eq. of $\text{Pt}(\text{en})(\text{NO}_3)_2$). The denotation “1” stands for protons on the 1-position of $\alpha\text{-CD}$.

also reacted with a half equiv. of $\text{Pd}(\text{en})(\text{NO}_3)_2$ or $\text{Pt}(\text{en})(\text{NO}_3)_2$ to generate $[\text{M-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ ($\text{M} = \text{Pd}$ or Pt) *in situ* at the same condition as the formation of $[\text{M-2L}][\text{NO}_3]_8$ ($\text{M} = \text{Pd}$ or Pt) (Scheme 1). Still, NMR spectra for H_a and H_b protons reveal great downfield shifts (from $\delta = 8.70$ to 8.92 for H_a and from $\delta = 7.82$ to 7.97 for H_b) because of the $\text{Pd}(\text{II})$ coordination (see Fig. 2A and 2D). The $\text{Pt}(\text{II})$ coordination brought in a greater downfield shifts of H_a and H_b to $\delta = 8.98$ and 7.99 , respectively (Fig. 2E). Also, because the $\text{Pt}(\text{II})$ coordinated complex is more stable than the corresponding $\text{Pd}(\text{II})$ coordinated complex, the formation of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ can be well evidenced by ESI-MS shown in Figure S1B.† The peak at 1886.4 is assigned to $[\text{M-8NO}_3]^{2+}$. In this way, we have constructed a co-stopper with one metal center linked to two of the hemi-rotaxane ligands at a natural angle, thus leading to a new topology of closed multi-component molecular systems. The bis-branched complexes $[\text{M-2L}][\text{NO}_3]_8$ and $[\text{M-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ ($\text{M} = \text{Pd}$ or Pt) could be also prepared and isolated (see the details in Experimental Section). Once these samples are studied in solution, however, similar results are obtained to those studied *in situ* because of the slow exchange phenomena and the presence of minor equilibrium components.

Transformation of ring shuttling direction in bis-branched $\text{Pt}(\text{II})$ complex

Irradiation by 365 nm light caused the *trans*-to-*cis* photoisomerization of the azobenzene unit on the ligand $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ and the complex $[\text{M-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$, $\text{M} = \text{Pd}$ or Pt , which generates their corresponding photostationary states. The irradiation by

365 nm led to a cluster of new signals with the azobenzene group turning to *cis*-form, and the azobenzene protons are shifted dramatically towards upfield, for H_r to H_r' appearing at $\delta = 7.42 \sim 6.95$.¹⁶ Meanwhile, the $\alpha\text{-CD}$ ring displayed a shuttling motion along with the azobenzene's photoisomerization. However, it exhibits significant differences on the ring shuttling direction among the hemi-rotaxane ligand and the bis-branched complexes.

The proton H_1 of $\alpha\text{-cyclodextrin}$ will be shifted towards upfield to $\delta = 4.82$ when azobenzene moiety is located in the cavity, whereas the one of a small amount of free $\alpha\text{-cyclodextrin}$ appears at $\delta = 4.95$ in $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ (Fig. 2A). The peak at $\delta = 4.82$ dropped with the photoisomerization, but the one at $\delta = 4.95$ grew (see Fig. 3B). Comparing the proton signals in Fig. 3B with those in Fig. 3A, the cluster of new proton signals (H_e to H_r , and H_s , H_r') of $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ has appeared at the same positions as the corresponding protons of the photostationary state of $[\text{L}][\text{NO}_3]_3$. These results indicate that the $\alpha\text{-CD}$ host in $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ indeed took place a dethreading behavior with the photoisomerization, leaving a guest component with $\alpha\text{-CD}$ departed (Scheme 2). This phenomenon should be caused by the barrier effect of the electropositive viologen which blocks the ring shuttling inward. Similar to the case in $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$, the $\alpha\text{-CD}$ rings also reveal a dethreading behavior in bis-branched $\text{Pd}(\text{II})$

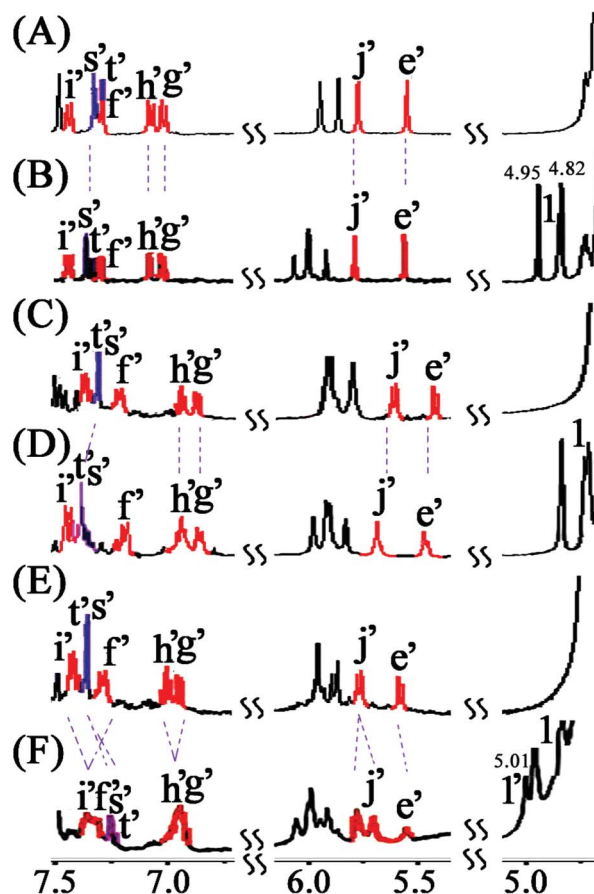
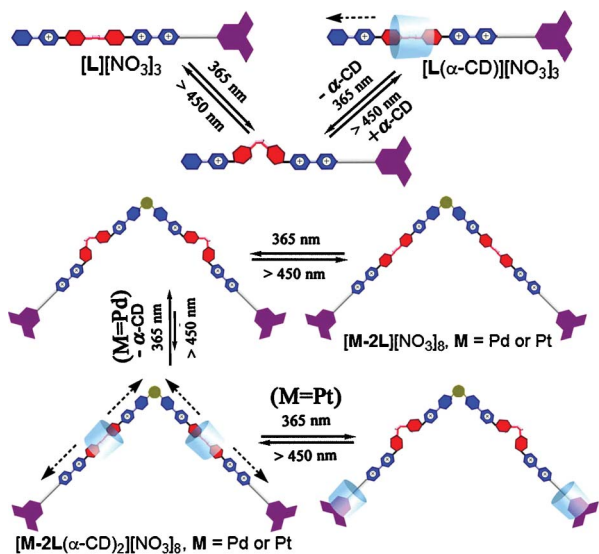


Fig. 3 Parts of the ^1H NMR spectra (400 MHz in D_2O at 298 K) of the photostationary states of A) $[\text{L}][\text{NO}_3]_3$; B) $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$; C) $[\text{Pd-2L}][\text{NO}_3]_8$; D) $[\text{Pd-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$; E) $[\text{Pt-2L}][\text{NO}_3]_8$ and F) $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$. The denotation “1” stands for protons on the 1-position of $\alpha\text{-CD}$.



Scheme 2 Interconversions of the bis-branched molecular shuttles with photoisomerization.¹⁵

complex (Scheme 2) because of the labile nature of the Pd(II)-Py bond even in room temperature.¹⁷ Such linkage is insufficient to help the ring overcome the barrier under the photoirradiation. This process is also confirmed by a similar comparison of the new emerged proton signals in Fig. 3D and 3C.

The case on the more stable bis-branched Pt(II) complex is totally different. Here we found that this co-stopper, formed by high-stable chelation of Pt(II) center, could originate a strong steric effect to transform the ring shuttling direction. The irradiation on $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ by 365 nm led to the emergence of a new peak at $\delta = 5.01$ shown in Fig. 3F, which should be assigned to the H_r of α -cyclodextrin encapsulating a deshielding moiety (the alkoxy isophthalate station) of the axle. In addition, the new proton signals (H_s to H_j , and H_s' , H_r') of the photostationary state of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ appeared at the different positions (Fig. 3F), while compared with the corresponding protons of the photostationary state of $[\text{Pt-2L}][\text{NO}_3]_8$ (Fig. 3E). $H_{g',h'}$ and $H_{r',r}$ are overlapped but H_r becomes split in Fig. 3F, showing another conformational structure is affecting the resonances of these protons while the α -CD ring has moved along the axle away from the azobenzene. Also, H_s and H_r in the photostationary state of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ are shifted towards upfield to $\delta = 7.26$ and 7.23, respectively, compared with those in the photostationary state of $[\text{Pt-2L}][\text{NO}_3]_8$. It is demonstrated that the ring should shuttle to the alkoxy isophthalate side with a major shielding effect on H_s and H_r .

A further investigation of the transformation of ring shuttling direction was carried out by 2D ^1H NOESY spectroscopy, which gave out precise information of the interconvert geometries in these α -CD based complexes. NOEs are observed from the azobenzene protons $H_{g,h}$, to the internal protons H_3 , H_5 of α -CD (Fig. 4A and 5A). These sets of NOEs show that the azobenzene stations are well encapsulated by α -CD in both of the initial states ($[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ and $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$). Irradiation by 365 nm on $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ caused the generation of its photostationary state. No NOE is found from the new emerged protons to the internal protons of α -CD (Fig. 4B), which can further

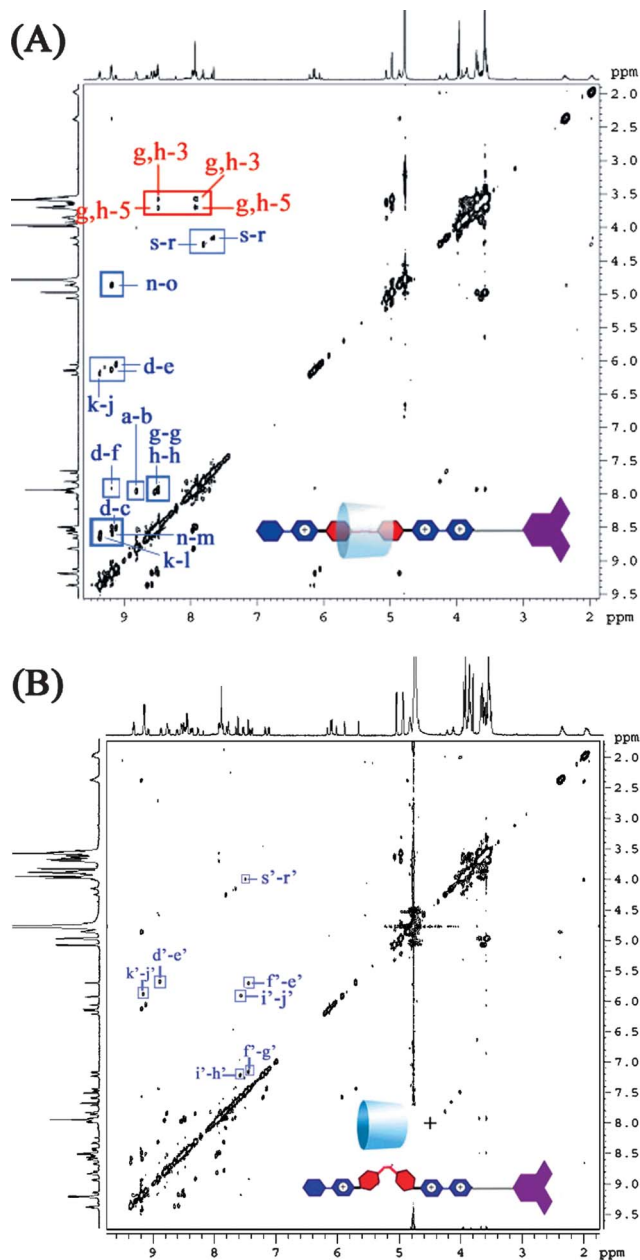


Fig. 4 The two-dimensional ^1H NOESY NMR spectra (500 MHz in D_2O at 298 K) of (A) $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$; B) irradiation on $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ by 365 nm for 2 h.

demonstrate that the structure is consistent with the geometry of the photostationary state of $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ shown in Scheme 2, where the α -CD ring is departed from the axle component. A completely different pattern of NOEs is observed in the bis-coordinated Pt(II) ensemble system. When $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ is photoisomerized to its photostationary state, new NOEs are found from the protons $H_{s',r'}$ to the internal protons H_5 of α -CD (Fig. 5B). The experimental results suggest that *cis*-formed azobenzene station has pushed the α -CD shuttling away, and the NOEs are consistent with the geometry of the photostationary state of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ shown in Scheme 2, where the α -CD ring stays at the alkoxy isophthalate unit (the second station) on the axle.¹⁸ The ring can be reset to encapsulate the azobenzene group

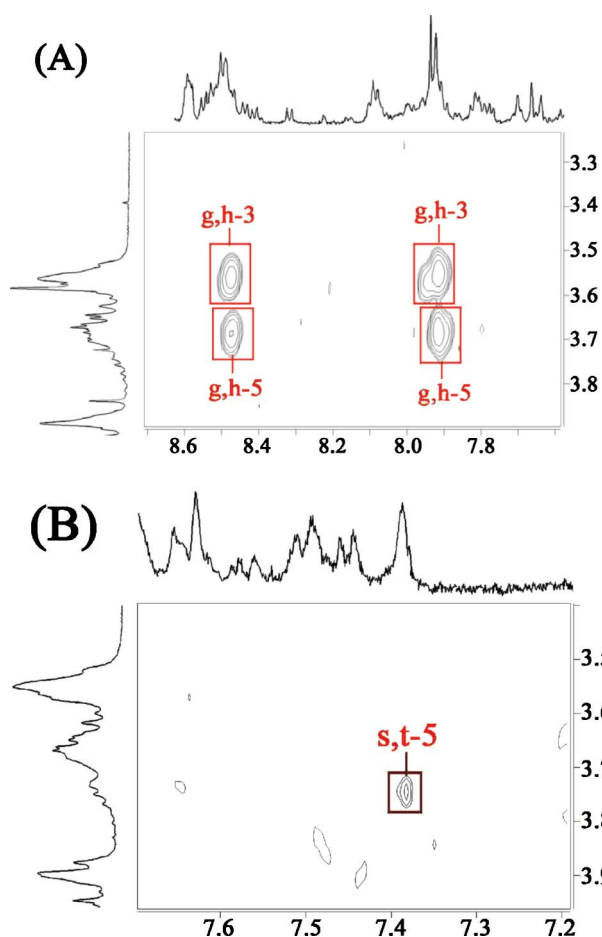


Fig. 5 The two-dimensional ^1H NOESY NMR spectra (500 MHz in D_2O at 298 K) of (A) $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$; B) irradiation on $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ by 365 nm for 2 h.

again for the full reversibility of the photochemical operations (Figure S3, ESI†).

Induced circular dichroism signal expression for the bis-branched molecular shuttle

Optical spectra could be channels of fast and convenient signal readout for this bis-branched molecular shuttle. Cyclodextrin-based host-guest structures are typical species which are sensitive to induced circular dichroism (ICD) signals.¹⁹ The encapsulation of $\alpha\text{-CD}$ to the azobenzene stations produces a positive cotton effect of ICD at about 330 nm, and a negative one at around 450 nm both in $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ and $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ (Fig. 6, curve a and c).²⁰ Both of the positive and the negative bands of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ have reached almost double altitude than those of $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ at the same concentration, because two of the hemi-rotaxane moieties are comprised in the bis-branched complex. This result shows an output signal amplification through the improvement of the chemical structure.²¹ As $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ is converted to its photostationary state, the intensity of the positive band at around 330 nm is drastically decreased from 9.6 to 4.5 mdeg, and the negative signal at around 450 nm is also weakened from -3.4 to -2.5 mdeg (Fig. 6, curve d). Such signal reduction is caused by the $\alpha\text{-CD}$ ring that has significantly shuttled far away from the azobenzene.²² The motion

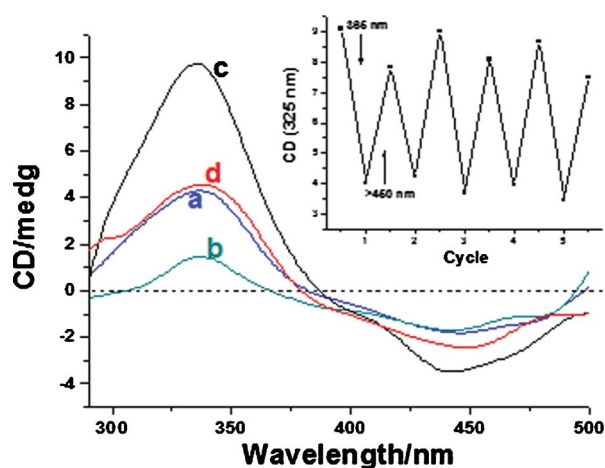


Fig. 6 ICD signals in water at 298 K of $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ a) in the initial state, b) after irradiation at 365 nm for 30 min and of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ c) in the initial state, d) after irradiation at 365 nm for 30 min. $[\text{L}(\alpha\text{-CD})][\text{NO}_3]_3$ and $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ were maintained at the same concentration of 1.25×10^{-4} M. Inset: changes in the ICD signal at 325 nm of $[\text{Pt-2L}(\alpha\text{-CD})_2][\text{NO}_3]_8$ for several cycles. In one cycle, 365-nm UV light and visible light irradiation was used to isomerize the azobenzene unit.

of the ring that shuttles back and forth between the two stations could be repeated for several cycles because of the reversibility of the photochemical operations (the inset of Fig. 6).

Conclusions

In summary, two novel bis-branched molecular shuttles have been prepared *via* quantitative coordination between one equiv. $\text{Pd}(\text{en})(\text{NO}_3)_2$ and $\text{Pt}(\text{en})(\text{NO}_3)_2$, respectively with two equiv. of hemi-rotaxane ligands. It is a highly efficient approach to prepare a coordinated host-guest architecture, which can be easily conducted *in situ*. In particular, transformation of ring shuttling direction was observed in the bis-branched $\text{Pt}(\text{II})$ complex. The $\alpha\text{-CD}$ ring in the hemi-rotaxane and in the bis-branched $\text{Pd}(\text{II})$ complex took place a dethreading behavior to depart from the axles, but the ring behaved an inward shuttling motion along the axles in the bis-branched $\text{Pt}(\text{II})$ ensemble. Therefore, it is a new approach for cooperatively modulating the components' relative motion by coordination-assembly. The bis-branched molecular shuttle can be repetitively operated. It provides a methodology for the design and construction of a new-type nano-machinery combination system, which may find application in fields of advanced molecular switches or digital information processings.²³

Experimental Section

Synthesis of compound A1: This compound was prepared as in our previous report.²⁴

Compound A2: Compound **A1** (4.2 g, 20 mmol) was added with magnetic stirring to a solution of 1, 4-dibromobutane (43.2 g, 0.2 mol) in acetone (*ca.* 150 mL). The mixture was then added upon K_2CO_3 (6.3 g, 45.6 mmol) and 18-Crown-6 (288 mg, 1.1 mmol). The solution was stirred refluxing for 14 h under Ar protection. The mixture was filtered. After the filtrate was concentrated in vacuo, the residue was applied to silica gel chromatography twice (petroleum ether as the eluent) to afford white compound **A2**

(5.66 g, 82.3%). M.p. 46 ~ 48 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 8.27 (s, 1H), 7.74 (s, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 3.93 (s, 6H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.09 (m, 2H), 1.99 (m, 2H). ¹³C NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 160.88, 153.68, 126.52, 117.76, 114.50, 62.23, 47.19, 28.03, 24.09, 22.46. HRMS (EI): *m/z*: 344.0259 (⁷⁹Br), 346.0239 (⁸¹Br).

Compound A3: A solution of **A2** (1.0 g, 2.9 mmol) and 4, 4'-bipyridine (3.2 g, 20.3 mmol) in acetonitrile (30 mL) was stirred for 2 days at 80 °C. The solvent was removed in vacuo, and the residue was dissolved in acetonitrile to applied to silica gel chromatography (dichloromethane:methanol = 50:3) to afford white compound **A3** (1.21 g, 83.4%). M.p. 203 ~ 204 °C. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 9.27 (d, *J* = 6.8 Hz, 2H), 8.88 (d, *J* = 6.0 Hz, 2H), 8.64 (d, *J* = 6.8 Hz, 2H), 8.07 (s, 1H), 8.03 (d, *J* = 6.4 Hz, 2H), 7.68 (s, 2H), 4.73 (t, *J* = 7.2 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 6H), 2.16 (m, 2H), 1.82 (m, 2H). ¹³C NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 165.15, 158.71, 152.23, 150.96, 145.36, 140.79, 131.46, 125.38, 121.87, 121.73, 119.24, 67.44, 59.94, 52.57, 27.48, 25.04. HRMS (ESI): *m/z*: 421.1755 [**A3** - Br]⁺.

Bis-(4-methyl-phenyl)-diazene (Compound B1): Cuprous chloride (30 g) was added slowly into anhydrous pyridine (200 mL), and the mixture was kept stirring at room temperature for 10 min. Then the solid was removed by filtration. p-toluidine (42.8 g, 0.44 mol) was added slowly into the above-mentioned filtrate, and the solution was kept stirring at room temperature for 12 h with air blowing. The pyridine solution was poured into 1300 mL water, and extracted with dichloromethane (180 mL ×3). The combined organic layer was washed with water (200 mL ×3), dried with anhydrous MgSO₄, and concentrated *in vacuo*. The residue was washed with 70 mL toluene to give out orange compound **B1** (14 g, 33.3%). M.p. 131 ~ 133 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 7.83 (d, *J* = 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.45 (s, 6H).

Bis-(4-bromomethyl-phenyl)-diazene (Compound B2): A mixture of **B1** (8.0 g, 38.04 mmol), NBS (16.3 g, 91.0 mmol), BPO (0.18 g, 0.74 mmol) and CCl₄ (360 mL) was refluxed for 20 h under an atmosphere of Ar gas. The resulting solution was filtered while it was hot. The filter cake was washed with water (350 mL), dried *in vacuo*, and then gave out orange compound **B2** (8.6 g, 61.4%). M.p. 178 ~ 180 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ = 7.90 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.0 Hz, 4H), 4.54 (s, 4H).

Compound A4: **B2** (4.0 g, 10.9 mmol) was dissolved in DMF (75 mL) at 90 °C. The solution was then added upon **A3** (0.78 g, 1.56 mmol) and stirred for 7 h at that temperature. It was filtered while it was hot. The filtrate was poured into toluene (300 mL) to precipitate some orange solid. The mixture was kept overnight and then filtered. The filter cake was washed with hot chloroform (30 mL), dried *in vacuo*, and then gave out pure orange compound **A4** (1.07 g, 78.7%). M.p. > 250 °C. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 9.59 (d, *J* = 6.8 Hz, 2H), 9.44 (d, *J* = 6.8 Hz, 2H), 8.83 (d, *J* = 6.8 Hz, 2H), 8.80 (d, *J* = 6.4 Hz, 2H), 8.07 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 6.10 (s, 2H), 4.82 (s, 2H), 4.80 (t, *J* = 7.6 Hz, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.89 (s, 6H), 2.19 (m, 2H), 1.83 (m, 2H). ¹³C NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 165.17, 158.74, 145.92, 145.81, 141.95, 137.20, 131.50, 130.52, 130.30, 130.24, 130.20, 127.15, 126.73, 123.22,

123.07, 123.00, 122.58, 121.75, 119.26, 67.46, 62.73, 60.46, 52.59, 33.50, 27.58, 25.06. HRMS (ESI): *m/z*: 708.1957 (⁷⁹Br), 710.1953 (⁸¹Br). [**A4**-2Br]⁺.

Target Ligand [L][NO₃]₃: 4, 4'-bipyridine (1.1 g, 6.9 mmol) was dissolved in DMF (85 mL) at 70 °C. **A4** (0.6 g, 0.69 mmol) was added into the solution and the mixture was stirred at 90 °C for 5 h. After cooling to room temperature, the mixture was filtered. And then the solid was washed with acetonitrile and gave an orange compound (**L**·3Br⁻) *ca.* 0.20 g. M.p. > 250 °C. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 9.59 (d, *J* = 6.4 Hz, 2H), 9.44 (d, *J* = 6.4 Hz, 2H), 9.41 (d, *J* = 6.8 Hz, 2H), 8.87 (d, *J* = 6.4 Hz, 2H), 8.83 (d, *J* = 6.8 Hz, 2H), 8.80 (d, *J* = 6.8 Hz, 2H), 8.69 (d, *J* = 6.8 Hz, 2H), 8.07 (s, 1H), 8.04 (d, *J* = 6.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 2H), 6.10 (s, 2H), 6.03 (s, 2H), 4.80 (t, *J* = 7.2 Hz, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.89 (s, 6H), 2.19 (m, 2H), 1.83 (m, 2H). AgNO₃ (89 mg, 0.52 mmol) was added to an aqueous solution (20 mL) containing [L][Br]₃ (180 mg, 0.17 mmol) and the mixture was stirred for 1 h at 65 °C in the dark. AgBr formed and was removed by filtration while it was hot. Evaporation of the filtrate and washing with a little water yielded **L** as an orange solid (125 mg, 74%). M.p. 161~162 °C. The chemical shift of its protons in ¹H NMR is almost the same as that of [L][Br]₃. ¹³C NMR (400 MHz, DMSO-*d*₆, 298 K, TMS): δ = 165.17, 158.74, 152.91, 152.14, 152.06, 151.00, 149.32, 148.61, 145.95, 145.82, 145.51, 140.83, 137.63, 137.37, 131.50, 130.21, 130.06, 127.14, 126.71, 125.92, 123.31, 122.00, 121.75, 119.26, 113.40, 67.45, 62.91, 62.40, 60.56, 52.58, 27.57, 25.07. MS (ESI): *m/z* = 423.1 [L-2NO₃⁻]²⁺. Elemental analysis calcd. for **L** (C₄₈H₄₅N₉O₁₄) (H₂O)₈: C 51.61, H 5.47, N 11.29; found: C 51.13, H 5.34, N 11.41.

Ethylene diamine palladium nitrate (Pd(en)(NO₃)₂): Ethylene diamine palladium chloride (73.6 mg, 0.31 mmol) was suspended in 20 mL water at room temperature. AgNO₃ (105.3 mg, 0.62 mmol) was added to the suspension and the mixture stirred for 0.5 h. A white solid of AgCl formed and was filtered off. The filtrate was evaporated *in vacuo* and the pale-yellow solid was directly used for the next step.

Ethylene diamine platinum nitrate (Pt(en)(NO₃)₂): Ethylene diamine platinum chloride (60 mg, 0.18 mmol) was suspended in 20 mL water at 50 °C. AgNO₃ (64 mg, 0.38 mmol) was added to the suspension and the mixture stirred for 2 h. A white solid of AgCl formed and was filtered off. The filtrate was evaporated *in vacuo* and the white solid was directly used for the next step.

[Pd-2L][NO₃]₈: An aqueous solution (10 mL) containing Pd(en)(NO₃)₂ (8.7 mg, 0.03 mmol) and [L][NO₃]₃ (60 mg, 0.0617 mmol) was stirred in the dark for 1 h at room temperature and a very small amount of precipitate was removed away by filtration. The filtrate was concentrated *in vacuo*. The residue was washed by deionized water (0.5 mL) and was dried to give the product (50.9 mg, 76%).

[Pt-2L][NO₃]₈: An aqueous solution (10 mL) containing Pt(en)(NO₃)₂ (11.4 mg, 0.03 mmol) and [L][NO₃]₃ (60 mg, 0.0617 mmol) was stirred in the dark for 18 h at 60 °C and a very small amount of precipitate was removed away by filtration. The filtrate was concentrated *in vacuo*. The residue was washed by deionized water (1 mL) and was dried to give the product (45.3 mg, 65%).

[Pd-2L(α-CD)₂][NO₃]₈: An aqueous solution (5 mL) containing Pd(en)(NO₃)₂ (8.7 mg, 0.03 mmol) and [L(α-CD)][NO₃]₃ (120 mg,

0.0617 mmol) was stirred in the dark for 1 h at room temperature. The solution was concentrated *in vacuo* and washed with a very small amount of deionized water to give the product (48.9 mg, 39%).

[Pt-2L(α -CD)₂][NO₃]₈: An aqueous solution (5 mL) containing Pt(en)(NO₃)₂ (11.4 mg, 0.03 mmol) and [L(α -CD)][NO₃]₃ (120 mg, 0.0617 mmol) was stirred in the dark for 18 h at 60 °C. The solution was concentrated *in vacuo* and washed with a very small amount of deionized water to give the product (32.0 mg, 25%).

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