Molecular Devices

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Fine-Tuning Conformational Motion of a Self-Assembled Metal–Organic Macrocycle by Multiple C–H···Anion Hydrogen Bonds**

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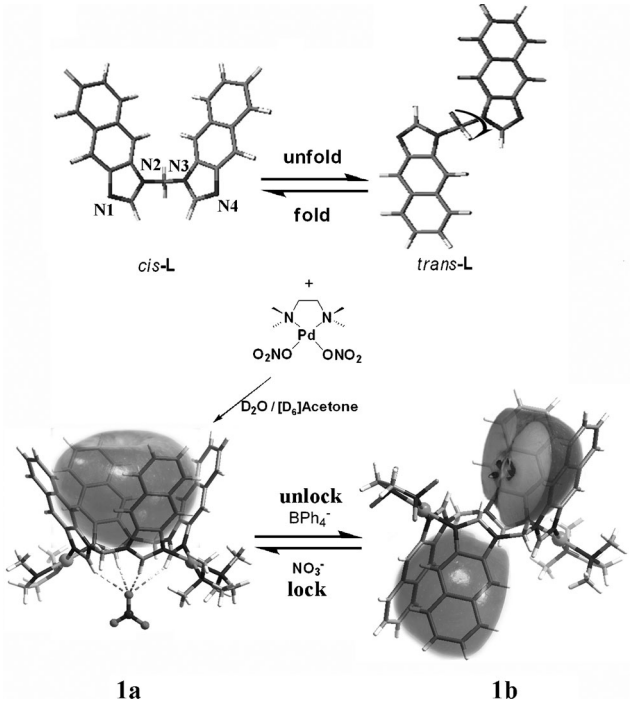
Biological molecular motor proteins that exist ubiquitously in nature have inspired the design of supramolecular systems of controllable motions,[1,2] for example, rotation,[3] shuttling,[4] and folding.[5] Based on these motions, artificial molecular devices and machines have been intensively developed, which are controlled with external stimuli, such as metal-cation coordination,[6] chemical reaction,[7] redox processes,[8] and light sensitivity.[9] Recently, artificial molecular devices driven by anions in organic host systems have received increasing interest because the anion species play important roles both in environmental and biological processes.[10,11] In contrast, metal–organic self-assembled systems employed to construct anion controlled molecular devices have rarely been reported to date.[12] Herein, we present a novel anion-switchable self-assembled metal–organic macrocyclic system, the conformation of which can be directly controlled by C–H···anion hydrogen bonding (Scheme 1). Furthermore, the conformations and the transformation process of two relatively stable states have been observed both in solution by NOESY and ESI-MS and in the solid state by X-ray crystallographic analysis.

The metal–organic macrocycle was synthesized from the reaction of a palladium(II) nitrate prescursor with di(1H-naphtho[2,3-d]imidazol-1-yl)methane (**L**), which contains two naphthoimidazole units linked with a methylene bridge and exists as two stable conformations (*cis* and *trans*; Scheme 1). Treating **L** with one equivalent of [(tmen)Pd(NO_3)$_2$] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in H_2O/acetone (1:1 v/v) at 60 °C for 2 h, the complex **1a**·4NO_3^- ([$\mathbf{M_2L_2}$]·4NO_3^-, where **M** = {(tmen)Pd^{II}}) with a fixed bowl-shaped conformation was formed in quantitative yield. Subsequent addition of an excess of sodium tetraphenylborate to the solution of **1a**·4NO_3^- in H_2O/acetonitrile (1:1 v/v) afforded complex **1b**·4BPh_4^- with a freed partial-chair conformation. Similarly, **1b**·4 PF_6^- was obtained by stirring the complex of nitrate in aqueous ammonium hexafluorophosphate.



Scheme 1. Self-assembly of complex **1a**, and the conformational motion between **1a** and **1b** (free anions and solvent molecules were omitted for clarity).

In the ^{1}H NMR spectrum of **1a**·4NO_3^- in D_2O/[D_6]acetone (1:1 v/v), the signals of the methylene bridge protons of **L** ($\delta = 7.19$, 6.92 ppm) split into a pair of doublets (Supporting Information, Figure S2). The diastereotopic environment of the methylene bridges protons cannot be averaged, which suggests a highly symmetric structure. Furthermore, the four methyl groups on the tmen units also split into two groups of singlets, and three pairs of peaks with chemical shift values between $\delta = 7.30$ and 9.35 ppm can be assigned to the aromatic protons on the naphthanoimidazolium moieties. The results imply that the complex **1a**·4NO_3^- keeps a fixed cone conformation in solution at room temperature.

The ESI-MS measurements of **1a**·4NO_3^- confirmed the existence of the cationic macrocycle **1** in methanol solution. Three intense peaks were observed at $m/z = 285$, 401, and 632 corresponding to the cations $[\mathbf{1a}]^{4+}$, $[\mathbf{1a}\cdot NO_3^-]^{3+}$, and $[\mathbf{1a}\cdot 2NO_3^-]^{2+}$, respectively (Supporting Information, Figure S28). This is in accordance with the results from a solution study and X-ray crystallography study shown below.

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The crystallographic data from a single crystal (Figure 1) revealed the formation of a bowl-shaped structure made up of two ligands connected with two half-protected Pd^{II} atoms. The dimensions of the molecular bowl are as follows: 6.49 Å and

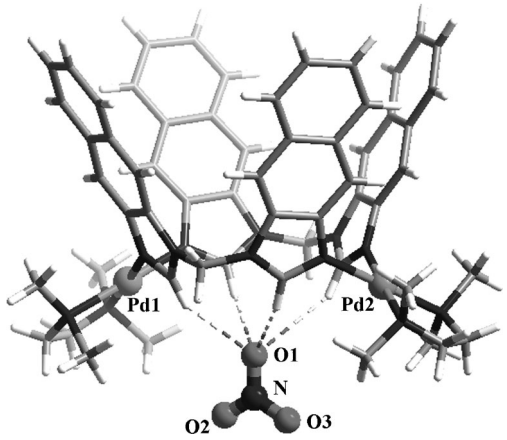

Figure 1. Crystal structure of **1a**·4 NO_3^- (free solvent molecules and nonbonding anions were omitted for clarity).

7.41 Å for the upper-rim lengths (that is, the distances between the centers of the upper rings of **L**); 2.38 Å and 2.87 Å for the lower-rim lengths between the protons of naphthanoimidazolium units, and 7.8 Å in depth. Also of note is that there is a nitrate anion bound to the bottom of the bowl by quadruple hydrogen bonds between the oxygen atom of the nitrate and the C2 hydrogen atoms of the naphthanoimidazolium moieties of **1a**·4 NO_3^-. The distances are 2.62 Å and 2.67 Å, and the angles of C–H···O are 147 and 151°, respectively. This indicates that the nitrate anion locks the four naphthanoimidazolium moieties toward one direction when this bowl-shaped structure is formed. Although it is very common that imidazolium interacts with anions, this phenomenon was not found in the case of homo-metallocalix[3]-naphthanoimidazoliums with rigid cone conformation in our previously studies,[13] or any other metal–imidazolium complexes, because of the electron-withdrawing ability of the metal cations and the environment in aqueous media. It indicates that the imidazolium protons in the metal–organic macrocycles (**1a**, **1b**, **2a**) still retain the ability to bind some anions even in the presence of Pd^{II} or Pt^{II}.

The complex **1b** with a partial chair conformation was obtained by adding of eight equivalents of sodium tetraphenylborate to the solution of **1a** in H_2O/MeCN (1:1 v/v) with nitrate anions, which gave rise to a total precipitation of a neat partial chair complex. The ^{1}H NMR spectrum of this complex is shown in the Supporting Information, Figure S3. A series of signals were observed that are totally different to **1a**·4 NO_3^- with a bowl-shaped structure. The pair of doublets for the methylene bridge between naphthanoimidazolium moieties was replaced by only one peak. This observation means that the driving force of NO_3^- to keep this macrocycle in a cone conformation has been destroyed by utilizing the solubility difference between the nitrate and tetraphenylborate. After numerous attempts to obtain a pure partial chair solution, we established that this process should be performed only in the presence of acetonitrile owing to its weak hydrogen bonding interaction, which is shown by the X-ray structure (see below).

The ^{1}H NMR spectrum of complex **1b**·4 BPh_4^- showed that by changing the anions to tetraphenylborate, a relatively stable partial chair conformer can be produced at room temperature (Supporting Information, Figure S3). The most characteristic peak was the signal of protons at the imidazolium rings, which remarkably shifted upfield to $\delta = 8.1$ ppm compared to that of $\delta = 9.4$ ppm in molecular bowl **1a**. This considerable upfield shift suggests that the aromatic planes linked by palladium form a half-closed cavity and causes an obvious shielding effect. In the spectrum, it showed only one signal for the protons of the methylene bridges, indicating that the naphthanoimidazolium moieties quickly fold around the methylene bridges on the ^{1}H NMR timescale. Additional evidence of the partial chair conformation is provided by 2D ^{1}H–^{1}H NOESY NMR spectroscopy (Supporting Information, Figure S7). The NOE correlations ((H_a, H_j) and (H_d, H_k) between the methyl protons of tmen units and adjacent protons confirm that the conformation is a partial chair. The ESI-MS spectrum of an acetonitrile solution of **1b**·4 BPh_4^- showed an intense signal at m/z 2101 corresponding to the cation [**1b**·3 BPh_4^-]$^+$, which is consistent with the results of the ^{1}H NMR and NOESY spectrum.

Now that it has been established that complexes **1a** and **1b** can be distinguished by large conformational differences only because they have different anions, the details of transformation between the two conformers were then studied. The investigation of anion-switching conformation transformation was performed by a ^{1}H NMR titration experiment. Upon addition of the nitrate to the solution of the partial chair conformer **1b**·4 BPh_4^-, dramatic changes occurred as shown in the ^{1}H NMR spectrum (Figure 2). A new series of peaks is different for every proton from those of the partial chair. The change between the two conformers (bowl-shaped conformer represented by a′–i′, partial chair conformer represented by a–i) could be observed directly on the NMR timescale because the conformation transformation equilibrium is slow. The signal for the protons on the imidazolium ring shifts downfield ($\delta = 9.65$ ppm), demonstrating that the nitrate anion is associated with the binding sites on the imidazolium rings. The more obvious feature is that part of the signal for the singlet corresponding to the methylene bridges split into two pairs of doublets. This result showed that the nitrate anion serves as a driving force to switch the partial chair conformation into the fixed bowl-shaped conformation. After addition of excessive nitrate, the peaks ascribed to the partial chair disappeared, indicating that the partial chair conformer gradually turned into the bowl conformer on the ^{1}H NMR timescale (yield 92%). The binding constant K_a of 5800 L mol^{-1} is calculated according to Stoddart;[14] the free-energy change $\Delta G = -21.5$ kcal mol^{-1} is obtained at 298 K (Supporting Information, Table S1). Furthermore, we have performed titration experiments with other anions, such as HSO_4^-, $H_2PO_4^-$, $CF_3SO_3^-$, ClO_4^-, PF_6^-, and carboxylates, with **1b**·4 BPh_4^-. The K_a and ΔG values are listed in the Supporting Information. The results revealed that

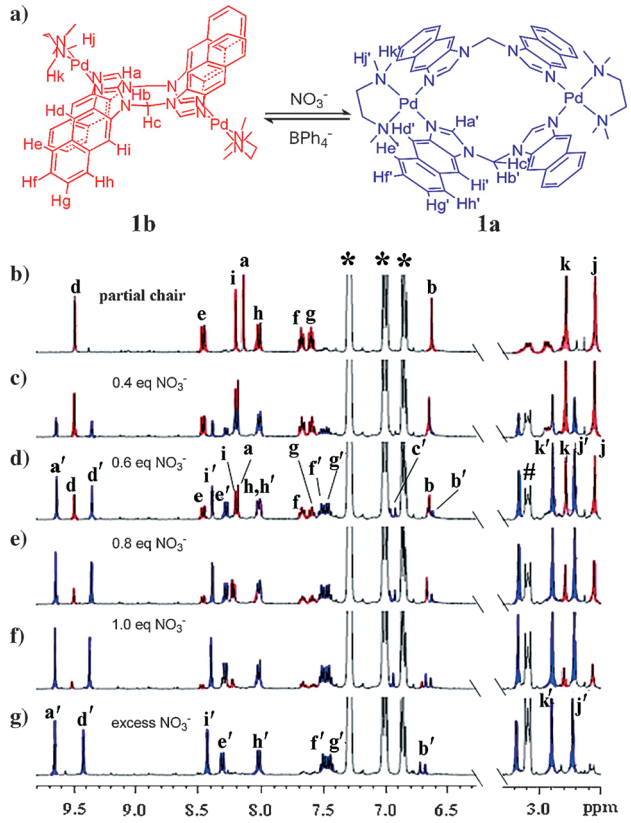

Figure 2. a) The conformation transformation between partial-chair and bowl-shaped structure; and ^{1}H NMR spectra (in [D_3]acetonitrile at 298 K) of b) complex **1b**·4 BPh_4^-; after adding c) 0.4 equiv; d) 0.6 equiv; e) 0.8 equiv; f) 1 equiv; g) excess (based on **1b**·4 BPh_4^-) of [*n*Bu_4N]NO_3. (Bowl-shaped conformer represented by a′–i′; partial chair conformer represented by a–i; * signals from BPh_4^-; # signals from *t*Bu_4N^+).

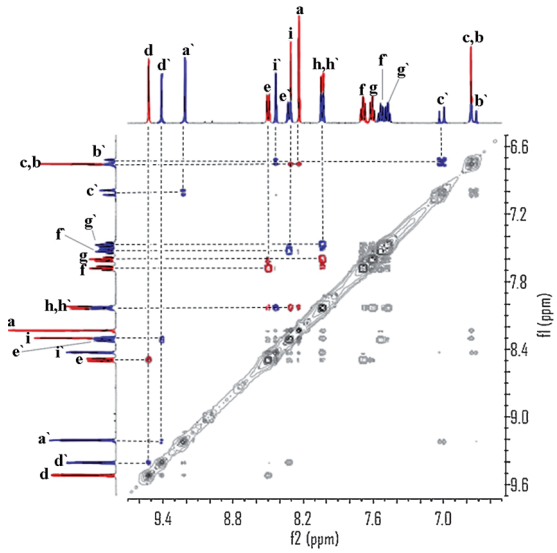

Figure 3. Partial NOESY spectra of complex **1b**·4 PF_6^- in [D_3]acetonitrile solution at 298 K.

the anions of NO_3^-, HSO_4^-, $H_2PO_4^-$, and carboxylic acid could switch the partial chair conformer of **1b** into the bowl-shaped conformer almost completely, while the $CF_3SO_3^-$ and ClO_4^- anions could change the conformation partially even after adding a more than 50-fold excess of anions to the solution used for NMR spectroscopy studies, and there was no change at all when adding PF_6^- anion.

We also examined the halide anions. Unfortunately, the hydrogen-bonding interactions between naphthanoimidazolium moieties and the halides were so strong that the coordination bonds of Pd–N were destroyed (Supporting Information, Figure S16). Therefore, integrating the degree of conformation conversion and the chemical shift, it is found that the intensity of anion binding to the complex **1b** is in the order $NO_3^- > HSO_4^- \approx$ terephthalate $> H_2PO_4^- > CF_3SO_3^- \approx ClO_4^- > PF_6^-$.

To study the details of the intermediate in the conformation transformation, we adopted a novel method. The ^{1}H NMR spectra displayed such a dramatic phenomenon that there were two sets of high-resolution signals observed in CD_3CN solution at room temperature. In this solution, a bowl-shaped conformer was accompanied by a partial chair conformer in a 1:2 molar ratio. The NOESY spectrum (Figure 3) of this mixture illustrated couplings that were consistent with the presence of two conformers in solution: the proton of single peak at $\delta = 6.76$ ppm (H_c and H_b were in the same environment) had a strong contact with H_a in imidazolium ring and H_i nearby, indicating that it belonged to partial chair conformer clearly. Meanwhile, the protons c′ (toward the bottom of the bowl) and b′ (toward the upper rim of the bowl) of CH_2 bridges between the naphthanoimidazolium moieties belonging to bowl-shaped conformer split into two groups of doublets ($\delta = 6.76$, 7.05 ppm) have contact with H_i' and H_a', separately. In the upfield of the spectrum (Supporting Information, Figure S8), the methyl groups on tmen units were all split into two groups, because one group of them was on the shielding effect from the aromatic cavity, and the other was on deshielding effect, and had strong contact with the hydrogen atoms on the naphthanoimidazolium rings. These results could be considered as the intermediate state and have further shown that an equilibrium exists between the two stable conformers during the process of conformation conversion in the solution at room temperature.

Although the analogue of the partial chair with hexafluorophosphate anions has a 1:3 molar ratio in acetonitrile solution, the single crystal suitable for X-ray analysis was grown by evaporating the solution of complex **1b**·4 PF_6^- slowly in a pure form. It showed a partial chair conformation, which was consistent with the ^{1}H NMR spectrum of **1b**·4 BPh_4^- (Figure 4). In this structure, both ligands **L** adopt a *trans* conformation, and every two naphthanoimidazolium moieties with a Pd^{II} linkage were oriented toward one direction. The separation between two palladium atoms was a little longer than in the cone conformer. Remarkably, two acetonitrile molecules were located along the central axis of the partial chair, the nitrogen atoms of which were bound at the protons on imidazolium rings through double hydrogen bonding interactions. The associated C···N and H···N distances are 3.20 and 2.49 Å, respectively; the corresponding angle of C–H···N is 132.8°. Moreover, the methyl part of the actonitrile was stabilized by the adjacent two aromatic planes

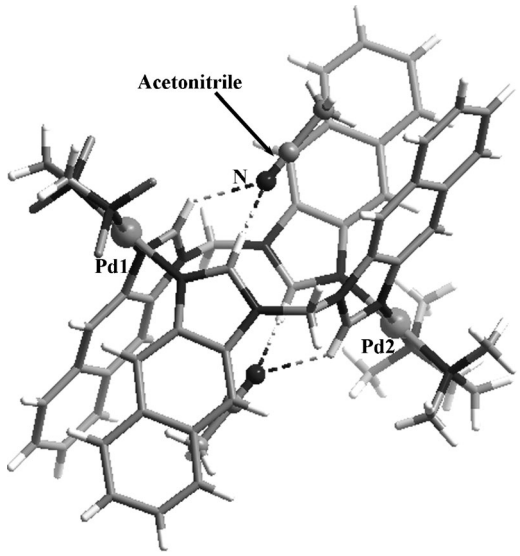

Figure 4. Crystal structure of $\mathbf{1b}\cdot 4\,PF_6^-$ (free solvent molecules and nonbonding anions were omitted for clarity).

by a C–H···π interaction. The crystal structure provided further evidence to the conformation of $\mathbf{1b}\cdot 4\,BPh_4^-$ in the ^{1}H NMR spectroscopy solution.

According the resulting properties of the palladium(II)-based macrocycles (**1a**, **1b**), we designed and synthesized an anion receptor of **2a** as the platinum analogue of **1a** by the same procedure, which has been confirmed by ^{1}H NMR spectroscopy (Supporting Information, Figure S6), ESI-MS (Supporting Information, Figure S23), and single-crystal X-ray analysis (Figure 5). The complex $\mathbf{2a}\cdot 4\,PF_6^-$ retained a fixed bowl-shaped conformation both in solution and solid state that is the same as $\mathbf{1a}\cdot 4\,NO_3^-$, but without conformation changing because of the inertness of the Pt–N bond.[6d] The interactions between $\mathbf{2a}\cdot 4\,PF_6^-$ and a variety of anions were studied by ^{1}H NMR titration experiments in [D$_6$]DMSO and CD_3CN solution. Even in highly competitive solvents and under the tiny influence of the weak hydrogen-bonding interaction between the cation and hexafluorophosphate anion, the metallomacrocyclic receptor showed a strong hydrogen-bonding interaction with these anions, and the complex preserved a bowl-shaped structure on addition of halogen anions, which was totally different from the complex $\mathbf{1b}\cdot 4\,BPh_4^-$ owing to the inert Pt–N bonds. The titration experiments support the formation of a 1:1 receptor/anion-binding model, and the association constants were obtained by fitting the respective titration data to a 1:1 host–guest binding model (Table 1).[15] Addition of $H_2PO_4^-$ to $\mathbf{2a}\cdot 4\,PF_6^-$ induced the largest downfield shift ($\Delta\delta = 1.32$ ppm) in [D$_6$]DMSO, with $K_a = 7.65\times10^5\ L\,mol^{-1}$.

Table 1: Binding constants K_a [$L\,mol^{-1}$] at 298 K between molecular bowl $\mathbf{2a}\cdot 4\,PF_6^-$ and anionic guests in [D$_6$]DMSO or CD_3CN.

Anions[a]	Binding constants[b]	
	K_a ([D$_6$]DMSO)	K_a (CD_3CN)
$H_2PO_4^-$	7.65×10^5	4.73×10^4
Cl^-	6.54×10^4	8.38×10^3
Br^-	6.97×10^4	1.17×10^4
I^-	3.43×10^3	3.49×10^4
F^-	1.43×10^4	3.43×10^3
NO_3^-	2.57×10^4	4.00×10^3

[a] The counterion is $[n\mathrm{Bu_4N}]^+$. [b] Binding constants were calculated by winEQNMR2 program; estimated errors are within ±10%.[15]

In summary, we have demonstrated that flexible ligand **L** with a methylene bridge can be employed to coordinate with dynamic palladium(II) complex to develop a form of metal–organic macrocycle that is capable of performing well-defined movement switched by different anions through C–H···anion hydrogen-bonding interactions. Regarding the effect of anions, the conformation of the macrocycle can be changed from fixed bowl-shaped to a relatively stable partial chair shape, and then return to the bowl shape to complete a cycle. Moreover, we also synthesized a potential receptor capable of selectively binding anions in competitive solution. Further investigation into the host–guest function of these motional metal–organic macrocycles is in progress.

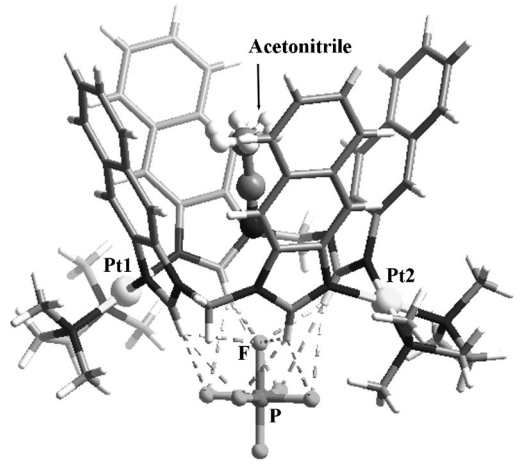

Figure 5. Crystal structure of $\mathbf{2a}\cdot 4\,PF_6^-$ (free solvent molecules and nonbonding anions were omitted for clarity).

Experimental Section

Full experimental details are presented in the Supporting Information. CCDC 780677 ($\mathbf{1a}\cdot 4\,NO_3^-$), CCDC 780678 ($\mathbf{1b}\cdot 4\,PF_6^-$), and CCDC 823548 ($\mathbf{2a}\cdot 4\,PF_6^-$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal data for $\mathbf{1a}\cdot 4\,NO_3^-$: $C_{58}H_{64}N_{12}O_{12}Pd_2$, $M_r = 1334.04$, yellow prism, $0.30\times0.24\times0.22\ mm^3$, trigonal, space group $R\bar{3}m$, $a = 39.7698(17)$ Å, $b = 39.7698(17)$ Å, $c = 25.444(2)$ Å, $V = 34851(4)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.298\ g\,cm^{-3}$, $F_{000} = 14046$, MoK_α radiation, $\lambda = 0.71073$ Å, $T = 291(2)$ K, $2\theta_{max} = 52°$, 64908 reflections collected, 7986 unique ($R_{int} = 0.0633$). Final GooF = 1.044, $R_1 = 0.0458$, $wR_2 = 0.1093$, R indices based on 5775 unique reflections with $I > 2\sigma(I)$, $\mu = 0.0483\ mm^{-1}$.

Crystal data for $\mathbf{1b}\cdot 4\,PF_6^-$: $C_{66}H_{84}F_{24}N_{16}O_4P_4Pd_2$, $M_r = 1958.17$, yellow prism, $0.28\times0.24\times0.22\ mm^3$, monoclinic, space group $C2/m$, $a = 17.723(3)$ Å, $b = 18.217(3)$ Å, $c = 15.004(2)$ Å, $\beta = 117.392(2)°$, $V = 4301.1(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.512\ g\,cm^{-3}$, $F_{000} = 1984$, MoK_α

radiation, $\lambda = 0.71073$ Å, $T = 291(2)$ K, $2\theta_{max} = 52°$, 12295 reflections collected, 4374 unique ($R_{int} = 0.0620$). Final GooF = 1.032, $R_1 = 0.0508$, $wR_2 = 0.1137$, R indices based on 3518 unique reflections with $I > 2\sigma(I)$, $\mu = 0.0630$ mm^{-1}.

Crystal data for **2a**·4 PF_6^-: $C_{66}H_{80}F_{24}N_{16}O_4P_4Pt_2$, $M_r = 2099.52$, yellow prism, $0.28 \times 0.22 \times 0.20$ mm^3, monoclinic, space group $P2_1/m$, $a = 13.5874(8)$ Å, $b = 21.8048(12)$ Å, $c = 15.4898(9)$ Å, $\beta = 110.5750(10)°$, $V = 4296.4(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.623$ g cm^{-3}, $F_{000} = 2072$, Mo K_α radiation, $\lambda = 0.71073$ Å, $T = 291(2)$ K, $2\theta_{max} = 52°$, 26869 reflections collected, 6645 unique ($R_{int} = 0.0597$). Final GooF = 1.060, $R_1 = 0.0459$, $wR_2 = 0.1066$, R indices based on 3518 unique reflections with $I > 2\sigma(I)$, $\mu = 0.0498$ mm^{-1}.

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[1] a) J.-P. Sauvage, C. D. Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, **1999**; b) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; c) *Molecular Motors* (Ed.: M. Schliwa), Wiley-VCH, Weinheim, **2002**; d) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, **2004**; e) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines, 2nd ed.*, Wiley-VCH, Weinheim, **2008**.

[2] For reviews on molecular machines and devices, see: a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725 – 2828; b) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53 – 61; c) V. W.-W. Yam, K. K.-W. Lo, *Chem. Soc. Rev.* **1999**, *28*, 323 – 334; d) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484 – 3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348 – 3391; e) Special issue on molecular machines, *Acc. Chem. Res.* **2001**, *34*, 410 – 522; f) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281 – 1376; g) K. Kinbara, T. Aida, *Chem. Rev.* **2005**, *105*, 1377 – 1400; h) W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* **2006**, *1*, 25 – 35; i) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77 – 92; j) B. Champin, P. Mobian, J.-P. Sauvage, *Chem. Soc. Rev.* **2007**, *36*, 358 – 366; k) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2006**, *119*, 72 – 196; *Angew. Chem. Int. Ed.* **2006**, *46*, 72 – 191; l) J. W. Canary, S. Mortezaei, J. Liang, *Coord. Chem. Rev.* **2010**, *254*, 2249 – 2266; m) M. von Delius, D. A. Leigh, *Chem. Soc. Rev.* **2011**, *40*, 3656 – 3676.

[3] For molecular rotation, see: a) T. Shima, F. Hampel, J. A. Gladysz, *Angew. Chem.* **2004**, *116*, 5653 – 5656; *Angew. Chem. Int. Ed.* **2004**, *43*, 5537 – 5540; b) M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, *Science* **2004**, *303*, 1849 – 1851; c) M. M. Pollard, M. Lubomska, P. Rudolf, B. L. Feringa, *Angew. Chem.* **2007**, *119*, 1300 – 1302; *Angew. Chem. Int. Ed.* **2007**, *46*, 1278 – 1280.

[4] For molecular shuttling, see: a) P. L. Anelli, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1991**, *113*, 5131 – 5133; b) R. A. Bissell, E. Cordova, A. E. Kaifer, J. F. Stoddart, *Nature* **1994**, *369*, 133 – 137; c) D. J. Cárdenas, A. Livoreil, J.-P. Sauvage, *J. Am. Chem. Soc.* **1996**, *118*, 11980 – 11981.

[5] For molecular folding, see: Q. Gan, Y. Ferrand, C. Bao, B. Kauffmann, A. Grélard, H. Jiang, I. Huc, *Science* **2011**, *331*, 1172 – 1175.

[6] For cation-induced molecular motion, see: a) W.-W. Yam, C.-K. Li, C.-L. Chan, *Angew. Chem.* **1998**, *110*, 3041 – 3044; *Angew. Chem. Int. Ed.* **1998**, *37*, 2857 – 2859; b) V. W.-W. Yam, X.-X. Lu, C.-C. Ko, *Angew. Chem.* **2003**, *115*, 3507 – 3510; *Angew. Chem. Int. Ed.* **2003**, *42*, 3385 – 3388; c) A. Petitjean, N. Kyritsakas, J.-M. Lehn, *Chem. Eur. J.* **2005**, *11*, 6818 – 6828; d) K. Yamashita, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2007**, *129*, 1850 – 1851; e) F. Durola, J. Rebek, Jr., *Angew. Chem.* **2010**, *122*, 3257 – 3259; *Angew. Chem. Int. Ed.* **2010**, *49*, 3189 – 3191; f) A.-M. Stadler, J. R. Rez, J.-M. Lehn, *Chem. Eur. J.* **2010**, *16*, 5369 – 5378; g) G. J. E. Davidson, S. Sharma, S. J. Loeb, *Angew. Chem.* **2010**, *122*, 5058 – 5062; *Angew. Chem. Int. Ed.* **2010**, *49*, 4938 – 4942.

[7] For chemically induced molecular motion, see: a) D. Zehm, W. Fudickar, T. Linker, *Angew. Chem.* **2007**, *119*, 7833 – 7836; *Angew. Chem. Int. Ed.* **2007**, *46*, 7689 – 7692; b) M. von Delius, E. M. Geertsema, D. A. Leigh, D.-T. D. Tang, *J. Am. Chem. Soc.* **2010**, *132*, 16134 – 16145.

[8] For redox-induced molecular motion, see: a) J. M. Spruell, W. F. Paxton, J.-C. Olsen, D. Benítez, E. Tkatchouk, C. L. Stern, A. Trabolsi, D. C. Friedman, W. A. Goddard, J. F. Stoddart, *J. Am. Chem. Soc.* **2009**, *131*, 11571 – 11580; b) K. Parimal, E. H. Witlicki, A. H. Flood, *Angew. Chem.* **2010**, *122*, 4732 – 4736; *Angew. Chem. Int. Ed.* **2010**, *49*, 4628 – 4632.

[9] For light-driven molecular motion, see: a) T. Muraoka, K. Kinbara, Y. Kobayashi, T. Aida, *J. Am. Chem. Soc.* **2003**, *125*, 5612 – 5613; b) M. J. Barrell, A. G. Campaña, M. Delius, E. M. Geertsema, D. A. Leigh, *Angew. Chem.* **2011**, *123*, 299 – 304; *Angew. Chem. Int. Ed.* **2011**, *50*, 285 – 290; c) L. Fang, C. Wang, A. C. Fahrenbach, A. Trabolsi, Y. Y. Botros, J. F. Stoddart, *Angew. Chem.* **2011**, *123*, 1845 – 1849; *Angew. Chem. Int. Ed.* **2011**, *50*, 1805 – 1809.

[10] a) J. L. Sessler, P. A. Gale, W.-S. Cho, *Anion Receptor Chemistry*, RSC, London, **2006**; b) M. D. Lankshear, P. D. Beer, *Acc. Chem. Res.* **2007**, *40*, 657 – 668; c) K. M. Mullen, P. D. Beer, *Chem. Soc. Rev.* **2009**, *38*, 1701 – 1713; d) P. A. Gale, *Chem. Soc. Rev.* **2010**, *39*, 3746 – 3771; e) T. B. Gasa, C. Valente, J. F. Stoddart, *Chem. Soc. Rev.* **2011**, *40*, 57 – 78.

[11] a) L. O. Abouderbala, W. J. Belcher, M. G. Boutelle, P. J. Cragg, J. W. Steed, D. R. Turner, K. J. Wallace, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5001 – 5006; b) C. M. Keaveney, D. A. Leigh, *Angew. Chem.* **2004**, *116*, 1242 – 1244; *Angew. Chem. Int. Ed.* **2004**, *43*, 1222 – 1224; c) B. W. Laursen, S. Nygaard, J. O. Jeppesen, J. F. Stoddart, *Org. Lett.* **2004**, *6*, 4167 – 4170; d) K. A. Nielsen, W.-S. Cho, J. O. Jeppesen, V. M. Lynch, J. Becher, J. L. Sessler, *J. Am. Chem. Soc.* **2004**, *126*, 16296 – 16297; e) P. D. Beer, M. R. Sambrook, D. Curiel, *Chem. Commun.* **2006**, 2105 – 2117; f) Y.-L. Huang, W.-C. Hung, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, *Angew. Chem.* **2007**, *119*, 6749 – 6753; *Angew. Chem. Int. Ed.* **2007**, *46*, 6629 – 6633; g) T.-C. Lin, C.-C. Lai, S.-H. Chiu, *Org. Lett.* **2009**, *11*, 613 – 616; h) H.-Y. Gong, B. M. Rambo, E. Karnas, V. M. Lynch, J. L. Sessler, *Nat. Chem.* **2010**, *2*, 406 – 409; i) Y. Hua, A. H. Flood, *J. Am. Chem. Soc.* **2010**, *132*, 12838 – 12840; j) I. M. Jones, A. D. Hamilton, *Angew. Chem.* **2011**, *123*, 4693 – 4696; *Angew. Chem. Int. Ed.* **2011**, *50*, 4597 – 4600.

[12] a) K.-H. Kim, R. Ju, H.-J. Kim, M.-J. Jun, K. M. Kim, *Bull. Korean Chem. Soc.* **2011**, *32*, 3497 – 3500.

[13] a) S.-Y. Yu, H. Huang, H.-B. Liu, Z.-N. Chen, R. Zhang, M. Fujita, *Angew. Chem.* **2003**, *115*, 710 – 714; *Angew. Chem. Int. Ed.* **2003**, *42*, 686 – 690; b) S.-H. Li, H.-P. Huang, S.-Y. Yu, Y.-Z. Li, H. Huang, Y. Sei, K. Yamaguchi, *Dalton Trans.* **2005**, 2346 – 2348; c) L.-X. Liu, H.-P. Huang, X. Li, Q.-F. Sun, C.-R. Sun, Y.-Z. Li, S.-Y. Yu, *Dalton Trans.* **2008**, 1544 – 1546; d) G.-H. Ning, T.-Z. Xie, Y.-J. Pan, Y.-Z. Li, S.-Y. Yu, *Dalton Trans.* **2010**, *39*, 3203 – 3211.

[14] M. B. Nielsen, J. O. Jeppesen, J. Lau, C. Lomholt, D. Damgaard, J. P. Jacobsen, J. Becher, J. F. Stoddart, *J. Org. Chem.* **2001**, *66*, 3559 – 3563.

[15] M. J. Hynes, *J. Chem. Soc. Dalton Trans.* **1993**, 311.

