Phosphine oxide functional group based three-station molecular shuttle

ARTICLE *in* CHEMICAL SCIENCE · MARCH 2013

Impact Factor: 9.21 · DOI: 10.1039/C3SC22048F

11 AUTHORS, INCLUDING:

Li Liu
University of Tennessee
508 PUBLICATIONS **6,359** CITATIONS
SEE PROFILE

Xiao-Yu Hu
Nanjing University
35 PUBLICATIONS **862** CITATIONS
SEE PROFILE

Yang Yang
Changzhou University
85 PUBLICATIONS **682** CITATIONS
SEE PROFILE

Jing Ma
Nanjing University
194 PUBLICATIONS **3,760** CITATIONS
SEE PROFILE

Chemical Science

RSC Publishing

EDGE ARTICLE

View Article Online
View Journal | View Issue

Phosphine oxide functional group based three-station molecular shuttle†

Cite this: *Chem. Sci.*, 2013, **4**, 1701

Li Liu,[a] Yuanyuan Liu,[a] Pingying Liu,[a] Jie Wu,[a] Yangfan Guan,[a] Xiaoyu Hu,[a] Chen Lin,[a] Yang Yang,[b] Xiaoqiang Sun,[b] Jing Ma[a] and Leyong Wang*[a]

Received 22nd November 2012
Accepted 30th January 2013

DOI: 10.1039/c3sc22048f

www.rsc.org/chemicalscience

A switchable three-station rotaxane based molecular shuttle with phosphine oxide, dibenzylammonium, and urea functional groups has been developed, where the macrocycle can be easily switched between three different binding sites along the rotaxane thread by addition of acid/base or anions resulting in three stable states. Phosphine oxide is shown to be a potential recognition unit for rotaxane based molecular shuttles and plays an important role as one of three "stations", allowing the design of a new class of molecular shuttles.

Introduction

Mechanically interlocked molecules (MIMs), in particular rotaxanes and catenanes, have attracted much attention not only for their nontrivial topological structures[1] but also for their potential applications in molecular machines.[2] Among these artificial molecular systems, rotaxane based molecular shuttles that can be switched by external stimuli represent the archetype of molecular machines.

Most reported molecular shuttles have focused on dual station [2]rotaxanes.[3–7] Various stimuli have been employed to drive the shuttling motion of the macrocycle along the rotaxane thread, such as acid/base,[3] ion binding,[4] configurational changes,[5] photochemical,[6] electrochemical[7] stimuli and so on. To the best of our knowledge, only a few examples of molecular shuttles with three different stations have been described so far.[8] The first tristable molecular shuttle, which could be controlled by photochemical and temperature stimuli, was elaborately designed by Leigh and Zerbetto *et al.*[8a] Later, Coutrot and co-workers reported a glycorotaxane molecular shuttle with three different stations,[8d] and a three-station [2]rotaxane with multilevel fluorescence responses was prepared by Li and coworkers.[8e] More recently, Chiu *et al.* have constructed a three-station [2]-rotaxane in which the motion of the macrocycle can be switched by oppositely charged ions.[8f] Although some progress has been made in the development of rotaxane based three-station molecular shuttles, it is still a challenge to construct a system where a macrocycle can be easily and reversibly switched between three different binding sites by external stimuli-control.

Various hydrogen bonding acceptors, such as amide,[9] ester,[3i,10] squaraines,[11] urea,[4b,9c,12] pyridone,[13] azodicarboxamide,[14] and sulfoxide[15] have been applied to construct benzylic amide macrocycle based rotaxanes and catenanes. However, the related phosphorus-containing analogues have seldom been reported as functional moieties for rotaxanes.[16] Phosphine oxide, which played a great role in the development of coordination chemistry and organometallic catalysis,[17] is an attractive moiety for inclusion in interlocked structures due to its good hydrogen bonding acceptor properties. Recently, Leigh *et al.* reported a series of [2]rotaxanes based on hydrogen bonding between benzylic amide macrocycles and phosphorus-based functional groups where the macrocycle might be used to hinder or expose the binding sites for metal-based catalysts.[16d] However, to the best of our knowledge, no molecular shuttle featuring a phosphine oxide functional moiety has been reported. Therefore, the introduction of phosphine oxide as a potential recognition binding unit for rotaxane-based molecular shuttles would provide a novel class of molecular shuttles.

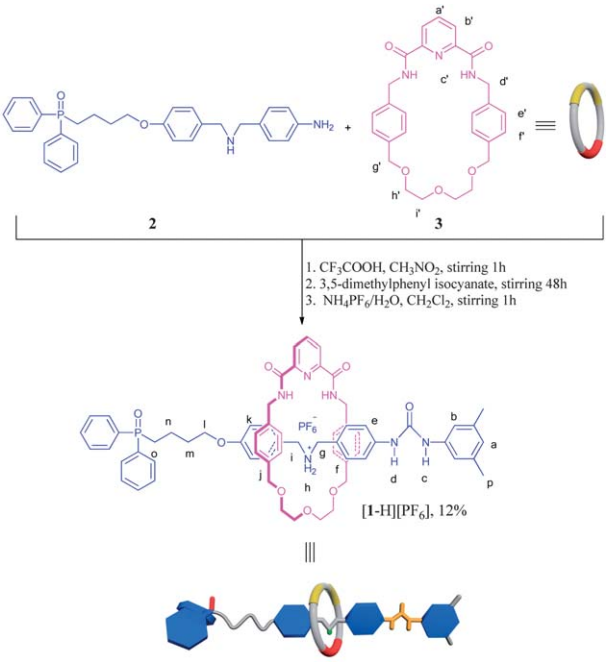
Results and discussion

The switchable three-station molecular shuttle [**1**-H][PF_6] was designed (Scheme 1), which incorporates dibenzylammonium (DBA^+), urea, and phosphine oxide stations in the thread and a 2,6-pyridinediamide and polyether chain in the macrocycle **3**.[9c,13] In this designed molecular shuttle (Scheme 2), the DBA^+ group (station **A**), which is a good recognition site for the macrocycle containing a polyether chain, is selectively protonated (DBA, station **A′**) to form the strongest hydrogen-bond donor for the

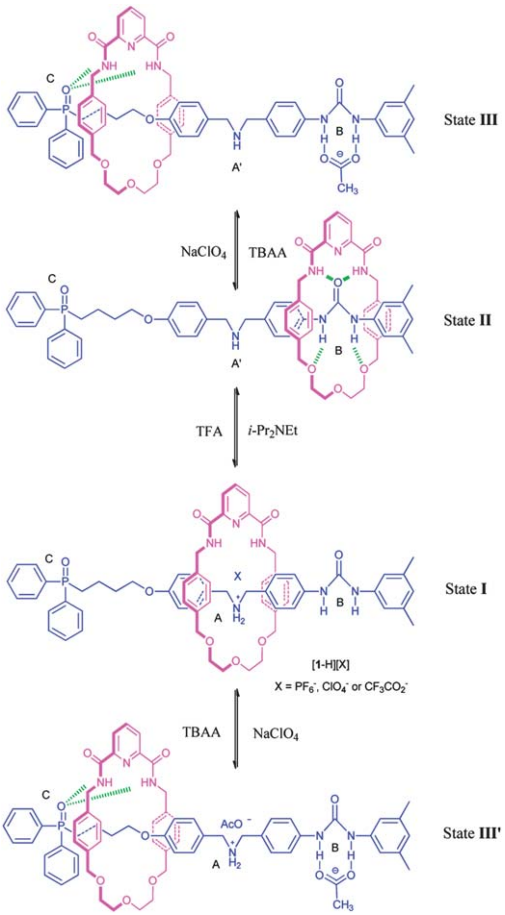
[a]*Key Laboratory of Mesoscopic Chemistry of MOE, Center for Multimolecular Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: lywang@nju.edu.cn; Fax: +86 25-83597090*

[b]*School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China*

† Electronic supplementary information (ESI) available: Experimental details, ^{1}H NMR, COSY and ROESY spectra of individual compounds, details of the X-ray analyses including CIF file and theoretical calculations. CCDC 900778. For ESI and crystallographic data see DOI: 10.1039/c3sc22048f



Scheme 1 Synthesis of phosphine oxide based [2]rotaxane [**1**-H][PF_6].



Scheme 2 The shuttling process of the macrocycle **3** along the rotaxane thread.

macrocycle **3**, and is also able to strongly bind acetate ions.[4b] The urea group (station **B**), which has been widely studied in receptors for anion recognition, such as for carboxylate anions,[18] can not only act as a good hydrogen bond donor, but also effectively bind acetate ions, which block its binding ability to the macrocycle **3**.[4b,9c] The third binding site, a phosphine oxide group (station **C**), is both difficult to protonate and unable to effectively bind acetate ions, but can act as a hydrogen bond acceptor.[19] Consequently, using two stimuli (acid/base and acetate addition) the molecular shuttle could exist in three possible states. In State **I**, the DBA^+ group would bind the macrocycle **3** most strongly. In State **II**, the system is neutral and the urea group could have a higher affinity for the macrocycle **3** over the neutral amine and phosphine oxide group. The addition of acetate anions to the neutral system could generate State **III** where the urea group could selectively and strongly bind the acetate anion and drive the displacement of the macrocycle **3** to preferentially bind the phosphine oxide over the neutral DBA group due to the better hydrogen bond acceptor properties of phosphine oxide group. The addition of acetate anions to the acidic system in State **I** could generate a very similar state to State **III**, State **III′** where the DBA^+ and the urea units could bind acetate anions strongly,[4b,6d] and the macrocycle **3** could be bound to the phosphine oxide station. Therefore, herein we report a switchable molecular shuttle with three different stations for the macrocycle **3** (phosphine oxide, urea and DBA^+ functional moieties) which can be operated by exploiting the relative pK_a values and acetate-binding affinities of the three binding sites, allowing the binding of the macrocycle **3** to be reversibly manipulated by addition of acid/base or by addition/removal of acetate anions (Scheme 2).

Molecular shuttle [**1**-H][PF_6] was prepared from compound **2**, macrocycle **3** and 3,5-dimethylphenyl isocyanate using a threading-followed-by-stoppering route as shown in Scheme 1 in 12% yield (see Section S2 for details, ESI†). The ^{1}H NMR spectra of [2]rotaxane [**1**-H][PF_6], the dumbbell-shaped thread and the free macrocycle **3** in $CDCl_3$–CD_3CN (1 : 1, v/v) (Fig. S18†) indicate that the interlocked structure formed with the macrocycle **3** preferentially encircles station **A** of the thread under acidic conditions. The signals for the protons adjacent to DBA^+ (H_i, H_g, H_f and H_j) exhibited upfield shifts compared with those of the free thread without the macrocycle **3**, which was attributed to the aromatic shielding effect of the macrocycle **3** on station **A**. Moreover, the 2D ROESY spectrum of [2]rotaxane further confirmed this assignment (Fig. S25 and S26†).

Single crystals of [**1**-H][PF_6] (see Section S8, ESI†) suitable for X-ray crystallography were obtained by slow evaporation of its $CHCl_3$–CH_3CN (1 : 1, v/v) solution.‡ The solid-state structure unambiguously confirmed the macrocycle **3** was located at the DBA^+ recognition site, as found in solution *via* the 2D ROESY NMR spectrum. The DBA^+ functional group of the thread forms hydrogen bonds with the diethylene glycol units of the macrocycle **3** (Fig. 1a, N^+–H···O, 2.945–3.105 Å). Two water molecules act as a "water bridge" between the carbonyl groups of the urea unit of the thread and the carbonyl groups of the macrocycle **3** belonging to an adjacent [2]rotaxane (Fig. 1b). Intermolecular hydrogen bonds between phosphine oxide and urea protons of

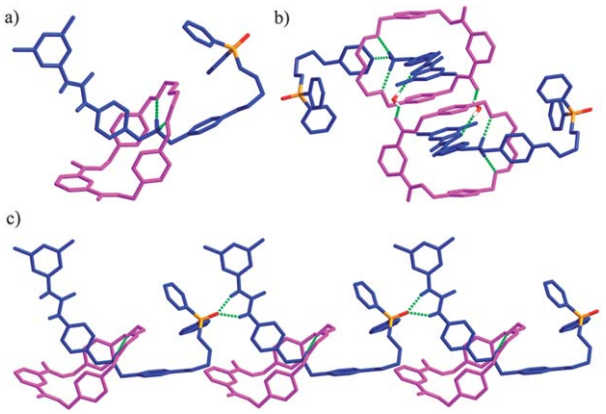


Fig. 1 X-Ray crystal structure of the [2]rotaxane [**1**-H][PF_6]. (a) The intramolecular H-bonds in [2]rotaxane [**1**-H][PF_6], (b) the linkage of two rotaxane molecules through water bridges in [**1**-H][PF_6], (c) the packing structure of [**1**-H][PF_6] along the *c* axis *via* N–H···O bonds. For clarity, the macrocycles are shown in pink and the threads in blue; phosphine atoms are depicted in yellow, only the oxygen atoms involved in hydrogen bonding are shown in red and all PF_6 counterions have been omitted. Intra- and intermolecular hydrogen bonds are in green.

a neighboring molecule were also observed (Fig. 1c, P═O···HN, 2.798 Å and 2.914 Å, respectively).

Initially, in order to investigate the difference of the binding abilities among the urea, DBA^+, and phosphine oxide moieties to the macrocycle **3**, a model compound, phosphine oxide derivative **10**, was synthesized (see Section S2, ESI†), and then its binding ability with macrocycle **3** was measured by ^{1}H NMR titration experiments in $CDCl_3$.[20] The obtained association constant (K_a) between model compound **10** and macrocycle **3** is $14.2 \pm 1.5\ M^{-1}$, which is lower than those of the urea and DBA^+ moieties with macrocycle **3** respectively, as expected.[4b,9c,16f] Sequentially, the shuttling properties of [**1**-H][PF_6] between three stations were investigated by ^{1}H NMR and 2D ROESY. Upon addition of 1.5 equiv. of *i*-Pr_2NEt to neutralize the DBA^+ group of [**1**-H][PF_6], the ^{1}H NMR spectra (Fig. 2b and c) showed significant downfield shifts of the methylene protons of the DBA group (H_i and H_g), indicating the disappearance of the aromatic shielding effect of the macrocycle **3** and the leaving of the macrocycle **3** from station **A**. The formerly broad signals of the urea protons of the thread were shifted upfield and the amide protons signals of the macrocycle **3** ($\Delta\delta H_{c'} = 0.16$ ppm) were shifted downfield, suggesting the formation of hydrogen bonds between the urea group and macrocycle **3** (Fig. 2b). Supporting this assignment, the aromatic protons adjacent to the urea group of the thread ($\Delta\delta H_e = -0.32$ ppm and $H_b = -0.39$ ppm) were significantly shifted upfield due to the aromatic shielding effect of the macrocycle **3** on station **B**. A 2D ROESY NMR spectrum revealed cross peaks between the ethylene glycol protons ($H_{h'}$ and $H_{i'}$) of the macrocycle **3** and the urea group (H_c and H_d), providing further confirmation of the movement of the macrocycle **3** from station **A** to station **B** (Fig. S28†). The addition of trifluoroacetic acid (TFA) to a solution of the shuttle in State **II** gave a similar spectrum to that of the original [**1**-H][PF_6] with minor differences for the signals of the DBA^+ group, indicating that the macrocycle **3** was switched back to station **A** (Fig. S19†). These results demonstrated that [**1**-H][PF_6] acts as an acid/base-controllable molecular shuttle.

The anion controllable shuttling of the molecular shuttle in State **II** was also investigated. Tetrabutylammonium acetate (TBAA, 2.0 equiv.) was added to a $CDCl_3$–CD_3CN (1 : 1, v/v) solution of the shuttle in State **II** (*i.e.* State **I** with the addition of 1.5 equiv. of *i*-Pr_2NEt), and the ^{1}H NMR spectrum was recorded (Fig. 2a). Significant downfield shifts of the signals of the aromatic protons ($\Delta\delta H_e = 0.14$ ppm and $H_b = 0.13$ ppm) adjacent to the urea group were observed due to the disappearance of the aromatic shielding effect of the macrocycle **3**, suggesting the urea binding site was blocked by an acetate anion to displace the macrocycle **3**. Similarly, signals of the alkyl chain, especially the methylene group ($\Delta\delta H_l = -0.15$ ppm) adjacent to the phenol of the thread, also showed upfield shifts after the addition of TBAA due to the aromatic shielding effect of the macrocycle **3** on station **C**, indicating it had moved to the phosphine oxide recognition site of the thread. A downfield chemical shift of $H_{c'}$ ($\Delta\delta H_{c'} = 0.16$ ppm) of the macrocycle **3** was observed which was attributed to the formation of new hydrogen bonds between the phosphine oxide unit of the thread and NH groups of the macrocycle **3**, and there was slight change in the chemical shift of the methylene protons of the DBA group of the thread. All the above results confirmed that the macrocycle **3** moved over station **A′**, to form a stable interaction at station **C**, showing that the addition of TBAA successfully drove the molecular shuttle from State **II** to State **III** as expected. To switch the molecular shuttle from State **III** back to State **II**, 3.0 equiv. of $NaClO_4$ was added to remove the acetate by precipitation as NaOAc and eliminate the binding interaction between acetate anion and the urea group. The resulting ^{1}H NMR spectrum (Fig. S20†) was similar to that of the molecular shuttle in State **II**, in agreement with the shuttling of the macrocycle **3** from the phosphine oxide site to the urea binding site. Consequently, we have realized the switchable property between State **II** and State **III**.

The addition of 3.0 equiv. of TBAA to a $CDCl_3$–CD_3CN (1 : 1, v/v) solution of shuttle in State **I**, resulted in significant changes in the ^{1}H NMR spectrum (Fig. 2d) to give a spectrum similar to that of the shuttle in State **III** (Fig. 2a), indicating the macrocycle **3** switched from station **A** to station **C** due to the strong binding interaction between acetate anions and both the DBA^+ and urea groups, resulting in State **III′** (Scheme 2). The addition of $NaClO_4$ removed the acetate and efficiently translocated the macrocycle **3** back to the DBA^+ site (Fig. S21†), demonstrating the reversible movement of the macrocycle **3** between the DBA^+ and phosphine oxide sites.

Theoretical calculations based on hybrid DFT with the 6-31G** basis set were carried out on models of the macrocycle **3** located at three different stations; and all computations were performed with the Gaussian 09 software.[21] The calculated NMR chemical shifts of the hydrogen atoms based on four optimized structures which were consistent with experimental data are shown in Fig. S32.† The optimized structure of State **I** was consistent with the crystal structure (Fig. S33†) and the other geometry optimization structures gave a visual indication of States **II**, **III**, and **III′** (Fig. 3).

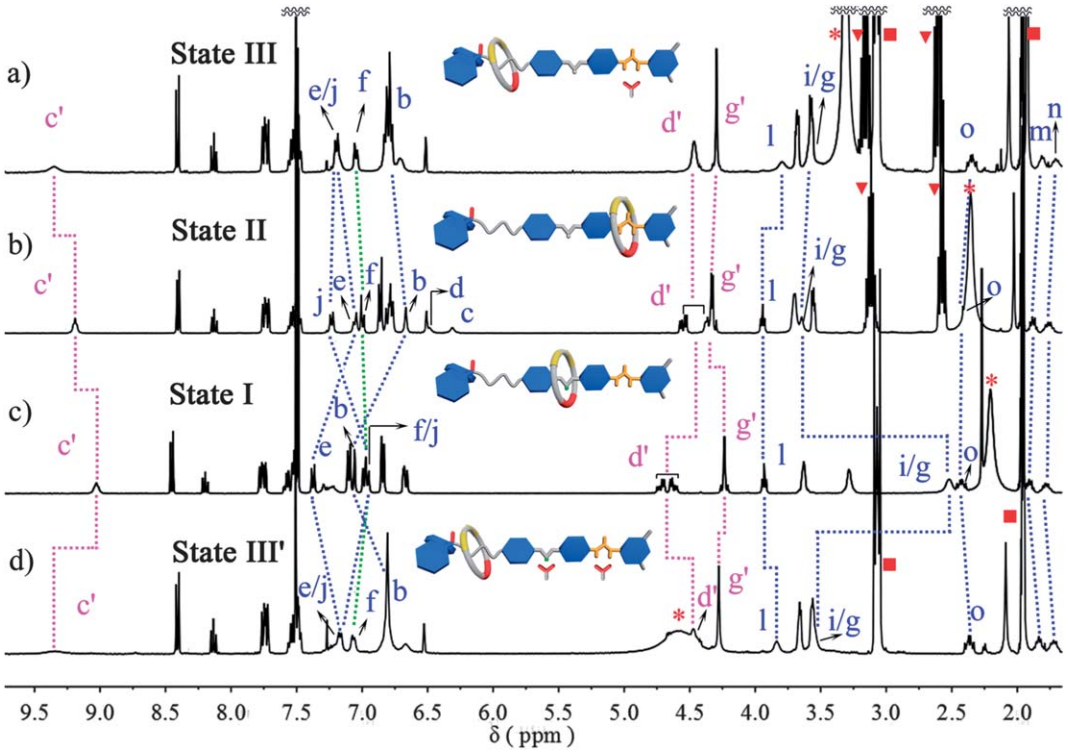


Fig. 2 Shuttling of [**1**-H][PF_6] driven by base and acetate addition. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$–CD_3CN = 1 : 1, 298 K) of (a) the mixture obtained after adding *i*-Pr_2NEt (1.5 equiv.) and TBAA (2.0 equiv.) to [**1**-H][PF_6] (5.0 mM), (b) the mixture obtained after adding *i*-Pr_2NEt (1.5 equiv.) to [**1**-H][PF_6] (5.0 mM), (c) molecular shuttle [**1**-H][PF_6] (5.0 mM), and (d) the mixture obtained after adding TBAA (3.0 equiv.) to [**1**-H][PF_6] (5.0 mM) (the peaks marked with * are ascribed to H_2O from the solvent, the peaks marked with ▼ are ascribed to *i*-Pr_2NEt and the peaks marked with ■ are ascribed to TBAA).

Conclusions

We have developed a switchable three-station molecular shuttle with phosphine oxide, DBA^+, and urea recognition sites where the macrocycle can be selectively and readily shuttled between these three different binding stations by addition of acid/base or by addition/removal of acetate anions. The macrocycle in State **I** is preferentially bound at the DBA^+ site, which can be shifted to the urea site by base addition (change from State **I** to State **II**), a process fully reversible upon acid/base addition. The position of the macrocycle in State **II** could also be reversibly switched between the urea site and the phosphine oxide site by addition/removal of acetate anions, a process which occurs with and without the presence of acetate anions (States **III** and **II**, respectively). The addition and removal of acetate anions in State **I** could also realize the reversible switch between States **I** and **III**′. Phosphine oxide based molecular shuttle, [**1**-H][PF_6], represents a type of molecular shuttle with excellent switchable and reversible properties, which will have a bright future in the development of switchable ligands and supramolecular catalysts.[22]

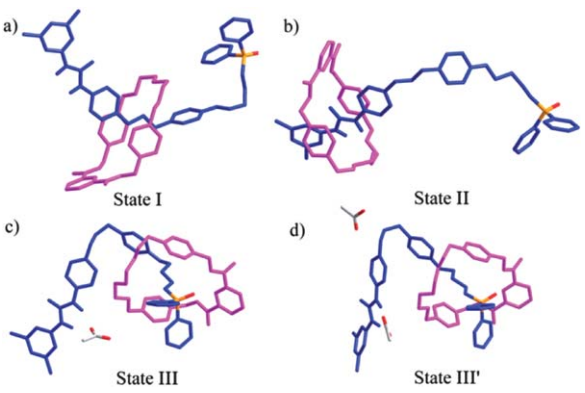


Fig. 3 The geometry optimized structures of the molecular shuttle obtained *via* theoretical calculations in (a) State **I**, (b) State **II**, (c) State **III**, and (d) State **III**′.

Acknowledgements

We gratefully thank the National Basic Research Program of China (2011CB808600, 2013CB922101) and the National Natural Science Foundation of China (no. 20932004, 21072093, 91227106) for financial support. We thank Prof. Dunru Zhu (Nanjing University of Technology) for the collection of X-ray data, and Dr Jon Beves (Nanjing University) for fruitful discussions.

Notes and references

‡ Crystal data for [**1**-H][PF_6]: $C_{66}H_{72}F_6N_6O_8P_2\cdot(H_2O)_2$, M_r = 1289.27, triclinic, space group $P\bar{1}$, a = 14.9639(11), b = 16.2074(10), c = 16.6904(12) Å, V = 16.6904(12) Å^3, ρ_{calcd} = 1.244 g cm^{-3}, μ (MoKa) = 0.40 mm^{-1}, T = 291(2) K,

colorless block; 26.00 independent measured reflections, F^2 refinement, $R_1 = 0.0577$, w$R_2 = 0.1132$.

1 (*a*) D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725–2828; (*b*) J.-P. Sauvage and C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots: A Journey Through the World of Molecular Topology*, Wiley-VCH, Weinheim, Germany, 2007; (*c*) X. Ma and H. Tian, *Chem. Soc. Rev.*, 2010, **39**, 70–80.

2 (*a*) J.-P. Sauvage, *Molecular Machines and Motors*, Springer, Berlin, Heidelberg, Germany, 2001; (*b*) V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines: A Journey into the Nano World*, Wiley-VCH, Weinheim, Germany, 2003; (*c*) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, Germany, 2001; (*d*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348–3391; (*e*) E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191.

3 For examples of acid/base molecular shuttles, see: (*a*) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gomez-Lopez, M. V. Martinez-Diaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1998, **120**, 11932–11942; (*b*) J. D. Badjic, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845–1849; (*c*) D. A. Leigh and A. R. Thomson, *Org. Lett.*, 2006, **8**, 5377–5379; (*d*) S. J. Vella, J. Tiburcio and S. J. Loeb, *Chem. Commun.*, 2007, 4752–4754; (*e*) F. Coutrot and E. Busseron, *Chem.–Eur. J.*, 2009, **15**, 5186–5190; (*f*) Q. Jiang, H.-Y. Zhang, M. Han, Z.-J. Ding and Y. Liu, *Org. Lett.*, 2010, **12**, 1728–1731; (*g*) Y. Jiang, J.-B. Guo and C.-F. Chen, *Org. Lett.*, 2010, **12**, 4248–4251; (*h*) H. Zheng, W. Zhou, J. Lv, X. Yin, Y. Li, H. Liu and Y. Li, *Chem.–Eur. J.*, 2009, **15**, 13253–13262; (*i*) S. Suzuki, K. Nakazono and T. Takata, *Org. Lett.*, 2010, **12**, 712–715; (*j*) Y. Tokunaga, M. Kawabata and N. Matsubara, *Org. Biomol. Chem.*, 2011, **9**, 4948–4953; (*k*) Q. Gan, Y. Ferrand, C. Bao, B. Kauffmann, A. Grélard, H. Jiang and I. Huc, *Science*, 2011, **331**, 1172–1175.

4 For examples of molecular shuttles driven by ion binding, see: (*a*) C.-F. Lin, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Chem.–Eur. J.*, 2007, **13**, 4350–4355; (*b*) S.-Y. Hsueh, C.-T. Kuo, T.-W. Lu, C.-C. Lai, Y.-H. Liu, H.-F. Hsu, S.-M. Peng, C.-h. Chen and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2010, **49**, 9170–9173; (*c*) B. Champin, P. Mobian and J.-P. Sauvage, *Chem. Soc. Rev.*, 2007, **36**, 358–366; (*d*) C. M. Keaveney and D. A. Leigh, *Angew. Chem., Int. Ed.*, 2004, **43**, 1222–1224; (*e*) G. T. Spence, M. B. Pitak and P. D. Beer, *Chem.–Eur. J.*, 2012, **18**, 7100–7108; (*f*) K. Zhu, V. N. Vukotic and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2012, **51**, 2168–2172.

5 For examples of shuttles driven by configuration changes, see: (*a*) Q. C. Wang, D. H. Qu, J. Ren, K. C. Chen and H. Tian, *Angew. Chem., Int. Ed.*, 2004, **43**, 2661–2665; (*b*) C. A. Stanier, S. J. Alderman, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2002, **41**, 1769–1772; (*c*) A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2003, **42**, 2296–2300.

6 For examples of shuttles controlled by light, see: (*a*) K. Hirose, Y. Shiba, K. Ishibashi, Y. Doi and Y. Tobe, *Chem.–Eur. J.*, 2008, **14**, 3427–3433; (*b*) S. Saha and J. F. Stoddart, *Chem. Soc. Rev.*, 2007, **36**, 77–92; (*c*) H. Zhang, X. X. Kou, Q. Zhang, D. H. Qu and H. Tian, *Org. Biomol. Chem.*, 2011, **9**, 4051–4056; (*d*) H. Zhang, J. Hu and D.-H. Qu, *Org. Lett.*, 2012, **14**, 2334–2337.

7 For examples of shuttles controlled by redox properties, see: (*a*) R. A. Bissell, E. Cordova, A. E. Kaifer and J. F. Stoddart, *Nature*, 1994, **369**, 133–137; (*b*) A. Altieri, F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin and J. K. Y. Wong, *J. Am. Chem. Soc.*, 2003, **125**, 8644–8654; (*c*) W.-Q. Deng, A. H. Flood, J. F. Stoddart and W. A. Goddard, *J. Am. Chem. Soc.*, 2005, **127**, 15994–15995; (*d*) G. Fioravanti, N. Haraszkiewicz, E. R. Kay, S. M. Mendoza, C. Bruno, M. Marcaccio, P. G. Wiering, F. Paolucci, P. Rudolf, A. M. Brouwer and D. A. Leigh, *J. Am. Chem. Soc.*, 2008, **130**, 2593–2601; (*e*) J. F. Stoddart, S. K. Dey, A. Coskun, A. C. Fahrenbach, G. Barin, A. N. Basuray, A. Trabolsi and Y. Y. Botros, *Chem. Sci.*, 2011, **2**, 1046–1053; (*f*) A. Joosten, Y. Trolez, J.-P. Collin, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2012, **134**, 1802–1809.

8 For examples of three-station shuttles, see: (*a*) G. Bottari, F. Dehez, D. A. Leigh, P. J. Nash, E. M. Perez, J. K. Y. Wong and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2003, **42**, 5886–5889; (*b*) ([2]- and [3]catenanes) D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174–179; (*c*) J.-P. Collin, F. Durola, J. Lux and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2009, **48**, 8532–8535; (*d*) E. Busseron, C. Romuald and F. Coutrot, *Chem.–Eur.J.*, 2010, **16**, 10062–10073; (*e*) Y. Zhao, Y. Li, S.-W. Lai, J. Yang, C. Liu, H. Liu, C.-M. Che and Y. Li, *Org. Biomol. Chem.*, 2011, **9**, 7500–7503; (*f*) Y.-C. You, M.-C. Tzeng, C.-C. Lai and S.-H. Chiu, *Org. Lett.*, 2012, **14**, 1046–1049.

9 (*a*) J. Berna, G. Bottari, D. A. Leigh and E. M. Perez, *Pure Appl. Chem.*, 2007, **79**, 39–54; (*b*) C. A. Schalley, W. Reckien, S. Peyerimhoff, B. Baytekin and F. Vögtle, *Chem.–Eur. J.*, 2004, **10**, 4777–4789; (*c*) Y.-L. Huang, W.-C. Hung, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 6629–6633.

10 (*a*) F. G. Gatti, D. A. Leigh, S. A. Nepogodiev, A. M. Z. Slawin, S. J. Teat and J. K. Y. Wong, *J. Am. Chem. Soc.*, 2001, **123**, 5983–5989; (*b*) X. Fradera, M. Márquez, B. D. Smith, M. Orozco and F. J. Luque, *J. Org. Chem.*, 2003, **68**, 4663–4673.

11 J. J. Gassensmith, S. Matthys, J.-J. Lee, A. Wojcik, P. V. Kamat and B. D. Smith, *Chem.–Eur. J.*, 2010, **16**, 2916–2921.

12 S. J. Cantrill, D. A. Fulton, M. C. T. Fyfe, J. F. Stoddart, A. J. P. White and D. J. Williams, *Tetrahedron Lett.*, 1999, **40**, 3669–3672.

13 D. Philp and A. Vidonne, *Tetrahedron*, 2008, **64**, 8464–8475.

14 J. Berna, M. Alajarin and R. A. Orenes, *J. Am. Chem. Soc.*, 2010, **132**, 10741–10747.

15 A. Altieri, V. Aucagne, R. Carrillo, G. J. Clarkson, D. M. D'Souza, J. A. Dunnett, D. A. Leigh and K. M. Mullen, *Chem. Sci.*, 2011, **2**, 1922–1928.

16 For examples of phosphorus-containing rotaxanes, see (*a*) S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White and D. J. Williams, *Org. Lett.*, 2000, **2**, 759–762; (*b*) A. Theil, C. Mauve, M. T. Adeline, A. Marinetti and J. P. Sauvage, *Angew. Chem., Int. Ed.*, 2006, **45**, 2104–2107; (*c*) S. Li, M. Liu, J. Zhang, B. Zheng, X. Wen, N. Li and F. Huang, *Eur. J. Org. Chem.*, 2008, 6128–6133; (*d*) R. Ahmed, A. Altieri, D. M. D'Souza, D. A. Leigh, K. M. Mullen, M. Papmeyer, A. M. Z. Slawin, J. K. Y. Wong and J. D. Woollins, *J. Am. Chem. Soc.*, 2011, **133**, 12304–12310; (*e*) T. Oku, Y. Furusho and T. Takata, *Org. Lett.*, 2003, **5**, 4923–4925; (*f*) W. C. Hung, L. Y. Wang, C. C. Lai, Y. H. Liu, S. M. Peng and S. H. Chiu, *Tetrahedron Lett.*, 2009, **50**, 267–270.

17 (*a*) J. R. Dilworth and N. Wheatley, *Coord. Chem. Rev.*, 2000, **199**, 89–158; (*b*) N. V. Dubrovina and A. Börner, *Angew. Chem., Int. Ed.*, 2004, **43**, 5883–5886; (*c*) V. V. Grushin, *Chem. Rev.*, 2004, **104**, 1629–1662; (*d*) T. M. Shaikh, C.-M. Weng and F.-E. Hong, *Coord. Chem. Rev.*, 2012, **256**, 771–803.

18 (*a*) P. A. Gale, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker Inc., New York, USA, 1st edn, 2004, pp. 31–41; (*b*) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094–3117; (*c*) J. L. Sessler, P. A. Gale and W.-S. Cho, *Anion Receptor Chemistry*, Royal Society Chemistry, Cambridge, UK, 2006; (*d*) V. Amendola, L. Fabbrizzi and L. Mosca, *Chem. Soc. Rev.*, 2010, **39**, 3889–3915.

19 C. A. Hunter, *Angew. Chem., Int. Ed.*, 2004, **43**, 5310–5324.

20 K. A. Connors, *Binding Constants*, Wiley, New York, 1987.

21 All calculations were performed using the Gaussian 09 program suite. M. J. Frisch, *et al*. *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford, CT, 2010. See the ESI† for details.

22 (*a*) F. Würthner and J. Rebek, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 446–448; (*b*) H. J. Yoon, J. Kuwabara, J.-H. Kim and C. A. Mirkin, *Science*, 2010, **330**, 66–69; (*c*) J. Wang and B. L. Feringa, *Science*, 2011, **331**, 1429–1432; (*d*) U. Lüning, *Angew. Chem., Int. Ed.*, 2012, **51**, 8163–8165; (*e*) V. Blanco, A. Carlone, K. D. Hänni, D. A. Leigh and B. Lewandowski, *Angew. Chem., Int. Ed.*, 2012, **51**, 5166–5169; (*f*) M. Schmittel, S. De and S. Pramanik, *Angew. Chem., Int. Ed.*, 2012, **51**, 3832–3836; (*g*) D. Wilson and N. R. Branda, *Angew. Chem., Int. Ed.*, 2012, **51**, 5431–5434; (*h*) S. Mortezaei, N. R. Catarineu and J. W. Canary, *J. Am. Chem. Soc.*, 2012, **134**, 8054–8057; (*i*) B. M. Neilson and C. W. Bielawski, *J. Am. Chem. Soc.*, 2012, **134**, 12693–12699.

