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A Bis(*m*-phenylene)-32-crown-10/Paraquat [2]Rotaxane

Shijun Li,[a] Kelong Zhu,[a] Bo Zheng,[a] Xianhong Wen,[b] Ning Li,[a] and Feihe Huang*[a]

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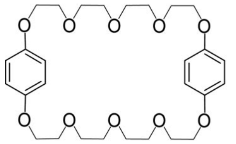
The successful preparation of the first bis(*m*-phenylene)-32-crown-10/paraquat [2]rotaxane showed unambiguously that psuedorotaxane-type complexation, rather than the taco-complex-type complexation previously observed in the solid state and in solution, exists – in solution – for complexation between bis(*m*-phenylene)-32-crown-10 derivatives and paraquat derivatives.

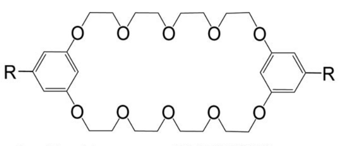
Introduction

Mechanically interlocked threaded structures, such as rotaxanes and catenanes, have attracted much attention not only because of their topological importance but also as a result of their application in the preparation of artificial molecular machines.[1] Paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) have been widely used as guests in the preparation of these mechanically interlocked structures, not only because they are easy to prepare and have interesting oxidation/reduction properties, but also because they can form pseudorotaxane-type complexes in solution with bis(*p*-phenylene) and bis(*o*-phenylene) crown ethers such as bis(*p*-phenylene)-34-crown-10 (BPP34C10) and dibenzo-24-crown-8 (DB24C8).[2–4] For the construction of more complicated mechanically interlocked threaded structures based on paraquat derivatives, it becomes worthwhile to functionalize bis(*p*-phenylene) and bis(*o*-phenylene) crown ethers. However, the use of mono- and difunctionalized bis(*p*-phenylene) and bis(*o*-phenylene) crown ether hosts leads inevitably to complications as a result of the formation of stereoisomeric complexes when two or more hosts participate.[5] One strategy by which to solve this symmetry-based problem would be the introduction of bis(*m*-phenylene) crown ethers, such as bis(*m*-phenylene)-32-crown-10 (BMP32C10, **1a**).[5c,6–8] Because of their symmetric natures, (5-)-mono- and (5,5′-)-difunctional derivatives of bis(*m*-phenylene) crown ethers can be easily prepared as pure compounds without tedious isomer separation and have simpler NMR spectra than their substituted bis(*o*-phenylene) analogues.[5c,6–8]

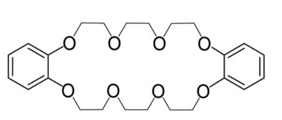
Therefore, this symmetry-based problem can be solved if we use (5-)-mono- and (5,5′-)-difunctional BMP32C10 derivatives instead of functionalized BPP34C10 and DB24C8 derivatives to prepare mechanically interlocked structures with paraquat derivatives. Before we can do this, we have to show that pseudorotaxane-type complexation (Figure 1a) exists in solution between BMP32C10 and paraquat derivatives. However, it had previously been observed that BMP32C10 derivatives such as **1a** and **1b** formed taco complexes with paraquat derivatives such as **2** and **3** in the solid state (Figure 2).[8a,8c,8e,8f] Taco-complex-type complexation (Figure 1b) should also exist between BMP32C10 deriva-



BPP34C10

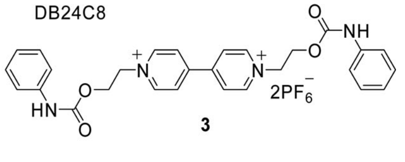


1a: R = H BMP32C10
1b: R = CH$_2$OH BMP32C10 diol



DB24C8

2



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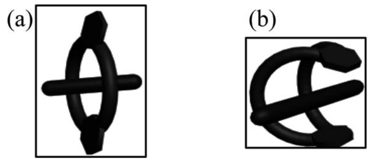

Figure 1. (a) Psuedorotaxane-type complexation and (b) taco-complex-type complexation between BMP32C10 and paraquat derivatives.

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[a] Department of Chemistry, Zhejiang University,
Hangzhou 310027, P. R. China
Fax: +86-571-8795-3189
E-mail: fhuang@zju.edu.cn
[b] Department of Chemistry, Zhejiang Forest University,
Hangzhou 311300, P. R. China

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tives and paraquat derivatives in solution because BMP32C10-based supramolecular cryptand structures can form in solution.[8b,8d]

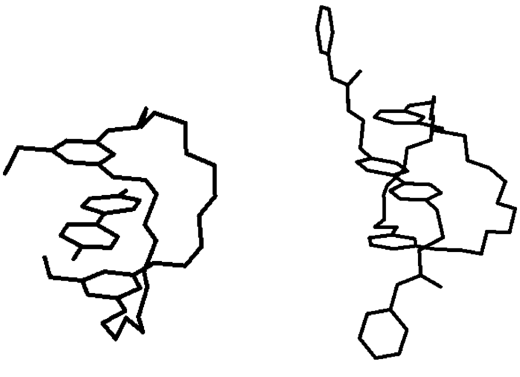


Figure 2. X-ray taco complex structures of **1b·2**[8a] and **1a·3**.[8c]

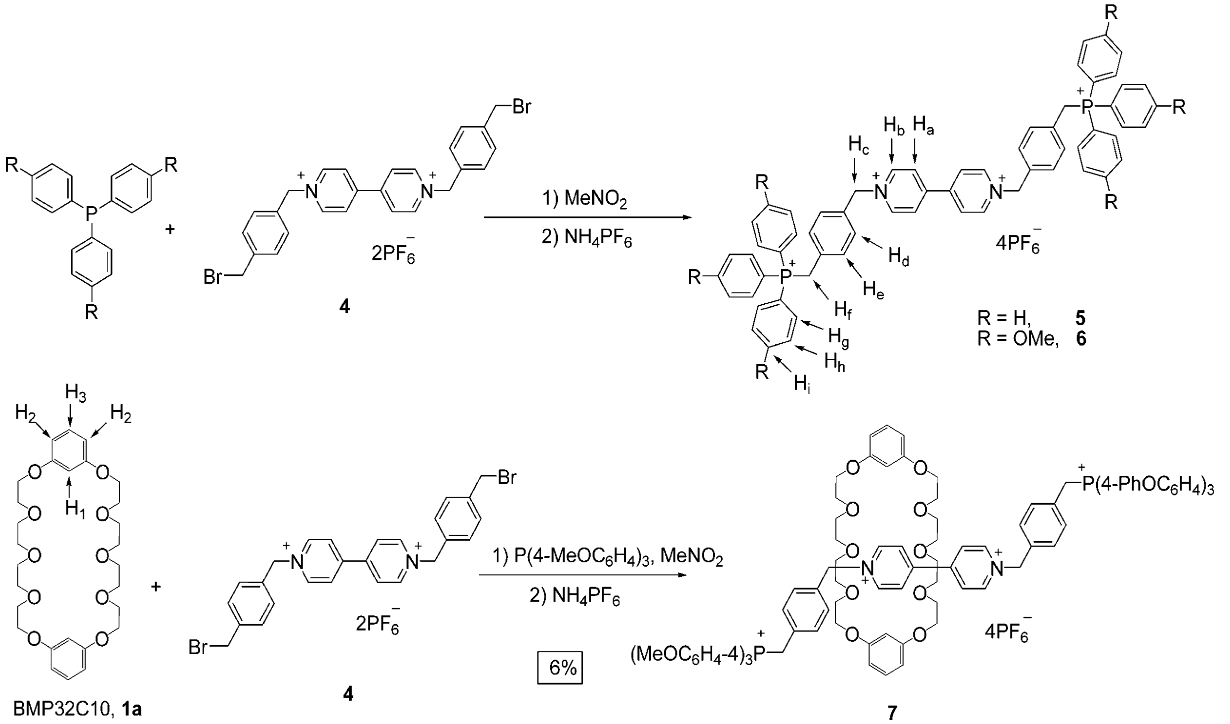
To establish whether we might be able to use paraquat derivatives to prepare mechanically interlocked threaded structures with BMP32C10 derivatives, and because the manner in which a guest is incorporated into a host (or how a host is threaded onto a guest) is very important in supramolecular chemistry,[9] we wanted to study whether pseudorotaxane-type complexation between BMP32C10 and paraquat derivatives exists in solution.

One direct method by which to establish whether pseudorotaxane-type complexation between BMP32C10 and paraquat derivatives exists in solution would be to confirm whether a rotaxane can be synthesized from a paraquat derivative with BMP32C10 as the macrocycle. Here we report the successful preparation of the first rotaxane based on the BMP32C10/paraquat recognition motif, which unambiguously demonstrates that pseudorotaxane-type complexation, rather than the previously reported taco-complex-type complexation, also exists in solution between BMP32C10 derivatives and paraquat derivatives.

Results and Discussion

The synthesis of the BMP32C10-based rotaxane by the threading-followed-by-stoppering strategy[4,5b,10,12] was attempted. After equimolar quantities of BMP32C10 and paraquat dibromide derivative **4**[4,11] had been mixed in $MeNO_2$, tris(4-methoxyphenyl)phosphane was added (Scheme 1). After counterion exchange, the [2]rotaxane **7** with tris(4-methoxyphenyl)phosphane stoppers was isolated in 6% yield, which unambiguously showed that pseudorotaxane-type complexation between BMP32C10 and paraquat derivatives does exist in solution. The low yield was due to only a small proportion of the BMP32C10 and **4** molecules forming pseudorotaxanes in solution.

When triphenylphosphane was used instead of tris(4-methoxyphenyl)phosphane, no rotaxane was obtained. This demonstrated that the tris(4-methoxyphenyl)phosphane groups are large enough to act as stoppers to form rotaxanes from BMP32C10 whereas the triphenylphosphane groups are not large enough, which could be further confirmed by comparing the cavity size of BMP32C10 with the diameters of triphenylphosphane and tris(4-methoxyphenyl)phosphane salts. X-ray analysis by Stoddart and co-workers showed BMP32C10 to have a 7.8×4.9 Å^2 cavity in the solid state.[5a] In solution, the BMP32C10 cavity may



Scheme 1. Syntheses of BMP32C10/paraquat [2]rotaxane **7** and dumbbell-shaped compounds **5**[12] and **6**.[12]

expand to larger sizes. The previously reported X-ray structure showed that the triphenylphosphane group has a diameter of only about 7.8 Å, equal to the size of the macrocyclic ring of BMP32C10.[4] The triphenylphosphane groups are therefore obviously not large enough to act as stoppers to form rotaxanes from BMP32C10. The X-ray structures of similar tris(4-methoxyphenyl)phosphane salts, however, showed them to have diameters of about 10.5 Å,[13] larger than the size of BMP32C10, so tris(4-methoxyphenyl)phosphane groups are large enough to act as stoppers for the formation of rotaxanes from BMP32C10.

Partial proton NMR spectra of BMP32C10 **1a**, rotaxane **7** and dumbbell-shaped component **6**[12] in CD_3SOCD_3 are shown in Figure 3. After the formation of rotaxane **7**, the signals of the aromatic protons of BMP32C10 (H_1, H_2 and H_3) were dramatically shifted upfield. Significant upfield shifts were also observed for the signals of pyridinium protons H_a and H_b on **6**, whereas the phenyl protons H_d and H_e were shifted slightly downfield.

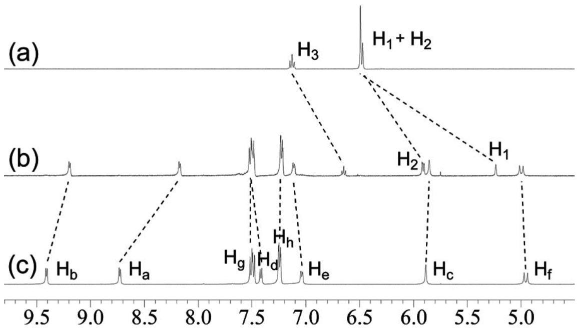


Figure 3. Partial proton NMR spectra (400 MHz, CD_3SOCD_3, 22 °C) of (a) BMP32C10, (b) rotaxane **7**, and (c) dumbbell-shaped compound **6**.

The formation of the mechanically interlocked [2]rotaxane **7** was further confirmed by its low- and high-resolution ESIMS. Three relevant peaks were observed in its low-resolution ESIMS: the peak at *m*/*z* (%) = 2037.0 (15) corresponds to $[\mathbf{7} - HPF_6 - H]^+$, the peak at *m*/*z* (%) = 1908.3 (18) corresponds to $[\mathbf{7} - 2\ HPF_6 - H + H_2O]^+$, and the peak at *m*/*z* (%) = 1657.6 (100) corresponds to $[\mathbf{7} - 3\ HPF_6 - PhOCH_3 + H_2O]^+$. One relevant peak was found in its high-resolution ESIMS: calcd. for $C_{96}H_{106}F_6N_2O_{16}P_3$ $[\mathbf{7} - 3\ PF_6]^{3+}$ 583.2220; found 583.2191 (error –5.0 ppm).

The existence of psuedorotaxane-type complexation between BMP32C10 derivatives and paraquat derivatives in solution was also confirmed by the difference in the association constants (K_a) of BMP32C10·**5** and BMP32C10·**6**. The stoichiometries of the complexation between BMP32C10 and the two paraquat derivatives **5**[12] and **6** were both determined to be 1:1 in acetone by Job plots[14] (Figure 4) based on UV/Vis absorption spectroscopy data at 403 nm. Initial UV/Vis absorption studies were carried out with solutions with constant concentrations of **5** or **6** (0.136 mM) and varying concentrations of BMP32C10 (up to 38.0 mM). From these absorption data (Figure 5), the association constants (K_a) of BMP32C10·**5** and BMP32C10·**6** in acetone were then calculated by use of a modified Benesi–Hildebrand equation[15] to be 313 (±7) M^{-1} and 220 (±10) M^{-1}, respectively. Because the structures of compounds **5** and **6** are very similar, their complexation abilities with BMP32C10 should be almost the same. The decrease in the association constants on going from $K_{a,BMP32C10\cdot\mathbf{5}}$ to $K_{a,BMP32C10\cdot\mathbf{6}}$ should be due to the fact that BMP32C10 and **5** molecules can form taco complexes and pseudorotaxanes at the same time in solution, whereas BMP32C10 and **6** molecules can form only taco complexes in solution, because the tris(4-methoxyphenyl)phosphane groups at the two ends of paraquat derivative **6** cannot be threaded over by BMP32C10, whereas the triphenylphosphane groups at the two ends of paraquat derivative **5** can.

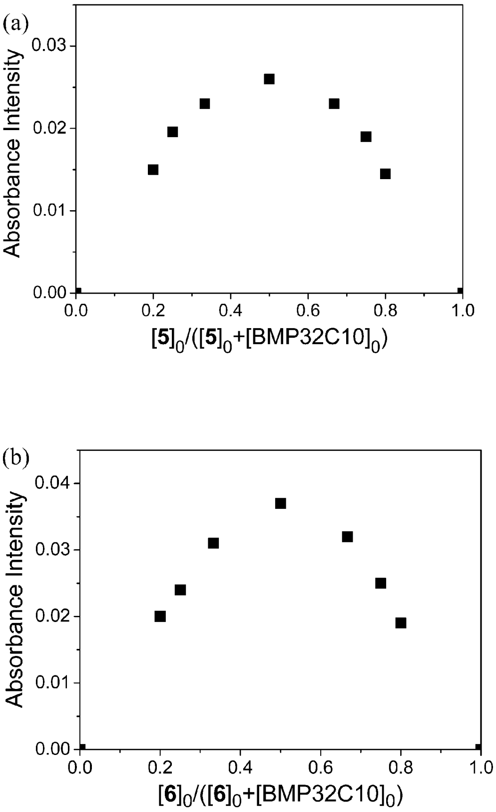


Figure 4. Job plots showing the 1:1 stoichiometries of the complexation between BMP32C10 and paraquat derivative guest **5** (a) and between BMP32C10 and paraquat derivative guest **6** (b) in acetone by plotting of the absorbance intensity at λ = 403 nm (the host–guest charge-transfer band) against the mol fraction of **5** or **6**. $[BMP32C10]_0$, $[\mathbf{5}]_0$ and $[\mathbf{6}]_0$ are initial concentrations of BMP32C10, **5** and **6**, respectively. $[BMP32C10]_0 + [\mathbf{5}]_0 = [BMP32C10]_0 + [\mathbf{6}]_0 = 5.0 \times 10^{-4}$ M.

Further confirmation of the existence of psuedorotaxane-type complexation in solution was provided by proton NMR characterization. The chemical shifts of the signals of the pyridinium protons H_a and H_b are almost the same for the two paraquat derivatives **5** and **6** (Figure 6a and d) before their complexation with BMP32C10. However, the

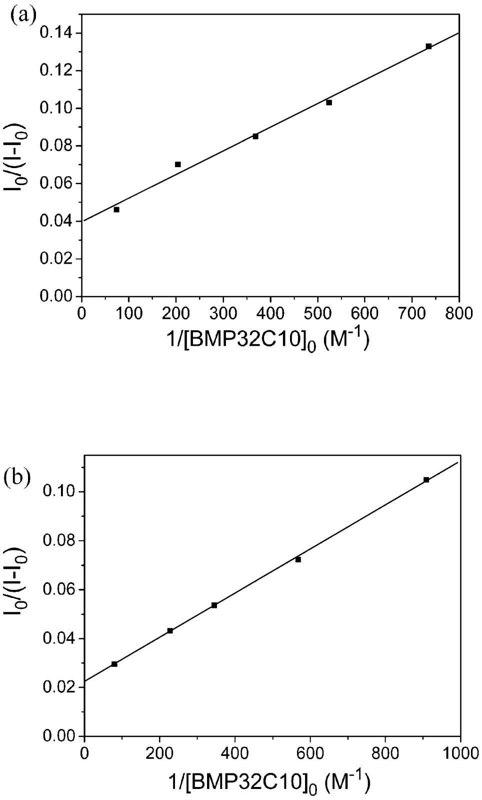


Figure 5. Plots of the modified Benesi–Hildebrand equation $I_0/(I - I_0) = \{a/(b - a)\}\{(1/K_a)[\text{BMP32C10}]_0^{-1} + 1\}$ for the complexation between BMP32C10 and the two paraquat derivative guests **5** (a) and **6** (b) in acetone, based on the UV/Vis absorption titration data at λ = 403 nm. Here *a* and *b* are constants whereas *I* and I_0 are the UV/Vis absorbance intensities at λ = 403 nm with concentrations of $[\text{BMP32C10}]_0$ and 0, respectively.

signals corresponding to H_a and H_b moved upfield more when **5** was mixed with BMP32C10 than when **6** was mixed with BMP32C10. This should also be due to the BMP32C10 and **5** molecules being able to form taco complexes and pseudorotaxanes at the same time in solution, whereas BMP32C10 and **6** can form only taco complexes in solution. The ^{1}H NMR spectrum of a mixture of dumbbell-shaped compound **6** and [2]rotaxane **7** (Figure 6e) shows two sets of signals from each species because each component cannot exchange, which gives further strong evidence for the formation of the [2]rotaxane structure.

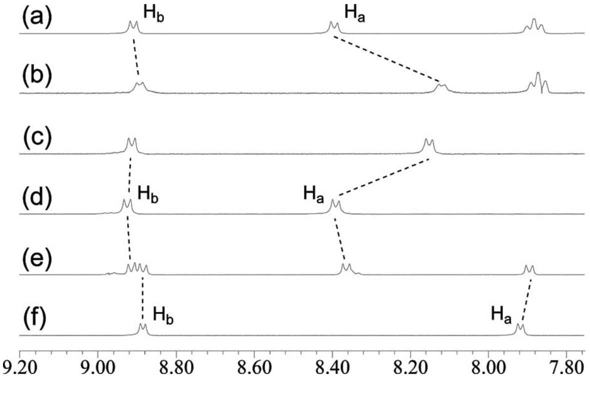


Figure 6. Partial proton NMR spectra (400 MHz, CD_3CN, 22 °C) of (a) **5**, (b) a mixture of BMP32C10 (2.00 mm) and **5** (2.00 mm), (c) a mixture of BMP32C10 (2.00 mm) and **6** (2.00 mm), (d) **6**, (e) a mixture of **6** (2.00 mm) and rotaxane **7** (2.00 mm), and (f) rotaxane **7**.

Conclusions

We have synthesized the first rotaxane based on the BMP32C10/paraquat recognition motif and have demonstrated that pseudorotaxane-type complexation also exists in solution between BMP32C10 derivatives and paraquat derivatives, in addition to the previously reported taco-complex-type complexation. Further intended work will include the application of paraquat derivatives in the preparation of more complicated mechanically interlocked threaded structures with symmetric (5-)-mono- and (5,5′-)-difunctional BMP32C10 derivatives.

Experimental Section

General: All reagents were purchased from commercial suppliers and were used as received. Paraquat derivative dibromide **4**,[11] BMP32C10 (**1a**)[7] and dumbbell-shaped component **6**[12] were prepared according to published literature procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer.

Synthesis of [2]Rotaxane 7: Tris(4-methoxyphenyl)phosphane (52.8 mg, 0.150 mmol) was added to a solution of BMP32C10 (26.8 mg, 0.0500 mmol) and paraquat derivative **4** (40.7 mg, 0.0500 mmol) in $MeNO_2$ (5 mL). The reaction mixture was stirred at room temperature overnight. Et_2O was then added, and the resulting precipitate was filtered and washed with Et_2O. The air-dried precipitate was dissolved in H_2O, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The resulting solid was filtered, washed with H_2O and dried. The crude compound was purified by preparative thin layer chromatography [SiO_2, MeOH/NH_4Cl (2 M)/$MeNO_2$, 17:2:1] to give [2]rotaxane **7** (6.0 mg, 6.0%) as a yellow solid. M.p. 220–222 °C (dec.). ^{1}H NMR (500 MHz, CD_3CN, 22 °C): δ = 8.88 (d, J = 6.5 Hz, 4 H), 7.92 (d, J = 6.5 Hz, 4 H), 7.45–7.39 (m, 16 H), 7.14–7.08 (m, 16 H), 6.72 (t, J = 8.0 Hz, 2 H), 5.90 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 4 H), 5.76 (s, 4 H), 5.19 (s, 2 H), 4.50 (d, J = 14.5 Hz, 4 H), 3.86 (s, 18 H), 3.65–3.60 (m, 16 H), and 3.54–3.47 (m, 16 H) ppm. Low-resolution ESIMS: *m/z* (%) = 2037.0 (15) $[\mathbf{7} - HPF_6 - H]^+$, 1908.3 (18) $[\mathbf{7} - 3\ HPF_6 - PhOCH_3 + H_2O]^+$, 1657.6 (100) $[\mathbf{7} - 2\ HPF_6 - H + H_2O]^+$. High-resolution ESIMS: calcd. for $C_{96}H_{106}F_6N_2O_{16}P_3$ $[\mathbf{7} - 3PF_6]^{3+}$ 583.2220; found 583.2191 (error –5.0 ppm).

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectrum and low-resolution electrospray ionization mass spectrum of rotaxane **7**, and determination of association constants of BMP32C10·**5** and BMP32C10·**6**.

Acknowledgments

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[1] J.-P. Sauvage, J.-M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, New York, **1995**; J.-P. Sauvage, C. O. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, Germany, **1999**; V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952; M. Andersson, M. Linke, J.-C. Chambron, J. Davidsson, V. Heitz, L. Hammarstrom, J.-P. Sauvage, *J. Am. Chem. Soc.* **2002**, *124*, 4347–4362; F. Huang, H. W. Gibson, *Prog. Polym. Sci.* **2005**, *30*, 982–1018; G. Wenz, B.-H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782–817; E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; S. J. Loeb, *Chem. Soc. Rev.* **2007**, *36*, 226–235; H. Tian, Q.-C. Wang, *Chem. Soc. Rev.* **2007**, *36*, 361–374; C. D. Meyer, C. S. Joiner, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 1705–1723; S.-Y. Hsueh, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu, *Angew. Chem. Int. Ed.* **2007**, *46*, 2013–2017; S. Nygaard, S. W. Hansen, J. C. Huffman, F. Jensen, A. H. Flood, J. O. Jeppesen, *J. Am. Chem. Soc.* **2007**, *129*, 7354–7363; C. Yang, Y. H. Ko, N. Selvapalam, Y. Origane, T. Mori, T. Wada, K. Kim, Y. Inoue, *Org. Lett.* **2007**, *9*, 4789–4792; Y. Liu, A. Bruneau, J. He, Z. Abliz, *Org. Lett.* **2008**, *10*, 765–768; J. Berná, S. M. Goldup, A.-L. Lee, D. A. Leigh, M. D. Symes, G. Teobaldi, F. Zerbetto, *Angew. Chem. Int. Ed.* **2008**, *47*, 4392–4396; D. Nishimura, T. Oshikiri, Y. Takashima, A. Hashidzume, H. Yamaguchi, A. Harada, *J. Org. Chem.* **2008**, *73*, 2496–2502; W. Deng, H. Yamaguchi, Y. Takashima, A. Harada, *Chem. Asian J.* **2008**, *3*, 687–695; G. Fioravanti, N. Haraszkiewicz, E. R. Kay, S. M. Mendoza, C. Bruno, M. Marcaccio, P. G. Wiering, F. Paolucci, P. Rudolf, A. M. Brouwer, D. A. Leigh, *J. Am. Chem. Soc.* **2008**, *130*, 2593–2601.

[2] a) T. Han, C.-F. Chen, *Org. Lett.* **2007**, *9*, 4207–4210; b) Y. Liu, A. H. Flood, P. A. Bonvallet, S. A. Vignon, B. H. Northrop, H.-R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C.-M. Ho, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759.

[3] a) B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart, D. J. Williams, *J. Chem. Soc., Chem. Commun.* **1987**, 1064–1066; b) F. M. Raymo, K. N. Houk, J. F. Stoddart, *J. Am. Chem. Soc.* **1998**, *120*, 9318–9322; c) K. Patel, O. Š. Miljanić, J. F. Stoddart, *Chem. Commun.* **2008**, 1853–1855; d) Y. Liu, A. Bruneau, J. He, Z. Abliz, *Org. Lett.* **2008**, *10*, 765–768.

[4] A. B. Braunschweig, C. M. Ronconi, J.-Y. Han, F. Arico, S. J. Cantrill, J. F. Stoddart, S. I. Khan, A. J. P. White, D. J. Williams, *Eur. J. Org. Chem.* **2006**, *8*, 1857–1866.

[5] a) B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart, D. J. Williams, *J. Chem. Soc., Chem. Commun.* **1987**, 1058–1061; b) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297; c) T. Chang, A. M. Heiss, S. J. Cantrill, M. C. T. Fyfe, A. R. Pease, S. J. Rowan, J. F. Stoddart, A. J. P. White, D. J. Williams, *Org. Lett.* **2000**, *2*, 2947–2950; d) H. W. Gibson, H. Wang, K. Bonrad, J. W. Jones, C. Slebodnick, L. N. Zackharov, A. L. Rheingold, B. Habenicht, P. Lobue, A. E. Ratliff, *Org. Biomol. Chem.* **2005**, *3*, 2114–2121; e) H. W. Gibson, H. Wang, C. Slebodnick, J. Merola, W. S. Kassel, A. L. Rheingold, *J. Org. Chem.* **2007**, *72*, 3381–3393.

[6] a) P. R. Ashton, R. A. Bartsch, S. J. Cantrill, R. E. Hanes Jr, S. K. Hickingbottom, J. N. Lowe, J. A. Preece, J. F. Stoddart, V. S. Talanov, Z.-H. Wang, *Tetrahedron Lett.* **1999**, *40*, 3661–3664; b) S. J. Cantrill, D. A. Fulton, A. M. Heiss, A. R. Pease, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2000**, *6*, 2274–2287; c) S.-H. Chiu, S. J. Rowan, S. J. Cantrill, P. T. Glink, R. L. Garrell, J. F. Stoddart, *Org. Lett.* **2000**, *2*, 3631–3634.

[7] a) D. S. Nagvekar, N. Yamaguchi, F. Wang, W. S. Bryant, H. W. Gibson, *J. Org. Chem.* **1997**, *62*, 4798–4803; b) W. S. Bryant, I. A. Guzei, A. L. Rheingold, J. S. Merola, H. W. Gibson, *J. Org. Chem.* **1998**, *63*, 7634–7639.

[8] a) W. S. Bryant, J. W. Jones, P. E. Mason, I. A. Guzei, A. L. Rheingold, D. S. Nagvekar, H. W. Gibson, *Org. Lett.* **1999**, *1*, 1001–1004; b) J. W. Jones, L. N. Zakharov, A. L. Rheingold, H. W. Gibson, *J. Am. Chem. Soc.* **2002**, *124*, 13378–13379; c) F. Huang, F. R. Fronczek, H. W. Gibson, *Chem. Commun.* **2003**, 1480–1481; d) F. Huang, I. A. Guzei, J. W. Jones, H. W. Gibson, *Chem. Commun.* **2005**, 1693–1695; e) F. Huang, P. Gantzel, D. S. Nagvekar, A. L. Rheingold, H. W. Gibson, *Tetrahedron Lett.* **2006**, *47*, 7841–7844; f) Y. Yang, H.-Y. Hu, C.-F. Chen, *Tetrahedron Lett.* **2007**, *48*, 3505–3509.

[9] a) W. H. Chen, M. Fukudome, D. Q. Yuan, T. Fujioka, K. Mihashi, K. Fujita, *Chem. Commun.* **2000**, 541–542; b) A. Harada, *Acc. Chem. Res.* **2001**, *34*, 456–464; c) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2003**, *42*, 1491–1495; d) T. Felder, C. A. Schalley, *Angew. Chem. Int. Ed.* **2003**, *42*, 2258–2260; e) H. Onagi, C. J. Blake, C. J. Easton, S. F. Lincoln, *Chem. Eur. J.* **2003**, *9*, 5978–5988; f) J. D. Badjic, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845–1849; g) J. V. Hernandez, E. R. Kay, D. A. Leigh, *Science* **2004**, *306*, 1532–1537; h) A. Scarso, H. Onagi, J. Rebek Jr, *J. Am. Chem. Soc.* **2004**, *126*, 12728–12729; i) A. Scarso, L. Trembleau, J. Rebek Jr, *J. Am. Chem. Soc.* **2004**, *126*, 13512–13518; j) T. Oshikiri, Y. Takashima, H. Yamaguchi, A. Harada, *Chem. Eur. J.* **2007**, *13*, 7091–7098; k) J. Zhang, F. Huang, N. Li, H. Wang, H. W. Gibson, P. Gantzel, A. L. Rheingold, *J. Org. Chem.* **2007**, *72*, 8935–8938.

[10] a) S. J. Rowan, S. J. Cantrill, J. F. Stoddart, *Org. Lett.* **1999**, *1*, 129–132; b) S. H. Chiu, J. F. Stoddart, *J. Am. Chem. Soc.* **2002**, *124*, 4174–4175.

[11] D. B. Amabilino, P. R. Ashton, L. Perez-Garcia, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2378–2380.

[12] S. Li, M. Liu, J. Zhang, B. Zheng, C. Zhang, X. Wen, N. Li, F. Huang, *Org. Biomol. Chem.* **2008**, *6*, 2103–2107.

[13] J. K. Bera, S. S. Lau, P. E. Fanwick, R. A. Walton, *J. Chem. Soc., Dalton Trans.* **2000**, 4277–4284; X. Fang, B. L. Scott, K. D. John, G. J. Kubas, J. G. Watkin, *New J. Chem.* **2000**, *24*, 831–833.

[14] P. Job, *Ann. Chim.* **1928**, *9*, 113–203.

[15] a) N. J. Rose, R. S. Drago, *J. Am. Chem. Soc.* **1959**, *81*, 6138–6141; b) X. Zhang, H. Xu, Z. Dong, Y. Wang, J. Liu, J. Shen, *J. Am. Chem. Soc.* **2004**, *126*, 10556–10557; c) S. Zhang, A. Palkar, A. Fragoso, P. Prados de Mendoza, L. Echegoyen, *Chem. Mater.* **2005**, *17*, 2063–2068; d) X. Zhang, C. Zhai, N. Li, M. Liu, S. Li, K. Zhu, J. Zhang, F. Huang, H. W. Gibson, *Tetrahedron Lett.* **2007**, *48*, 7537–7541.

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