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## Self-Assembly of Triangular and Hexagonal Molecular Necklaces

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## S Supporting Information

**ABSTRACT:** The formation of catenated systems can be simplified greatly if one or more rings are generated via self-assembly. Herein we exploit the orthogonality of coordination-driven self-assembly and crown-ether host–guest complexation to obtain a [4]molecular necklace and a [7]molecular necklace based on a well-developed recognition motif of 1,2-bis(pyridinium)ethane/dibenzo[24]crown-8. By adapting the bis(pyridinium) motif into the backbone of a donor building block, the resulting semirigid dipyrindyl species can serve both as a structural element in the formation of metallacycles and as a site for subsequent host–guest chemistry. The pseudo-linear nature of the donor precursor lends itself to the formation of triangular and hexagonal central metallacycles based on the complementary acceptor unit used. This exemplary system organizes up to 18 molecules from three unique species in solution to afford a single supramolecular ensemble.

Over the past two decades, a variety of supramolecular coordination complexes (SCCs) with well-defined shapes and sizes such as one-dimensional (1D) helices, two-dimensional (2D) polygons, and three-dimensional (3D) polyhedra have been prepared via the combinatorial utilization of carefully selected metal centers and organic ligands containing multiple binding sites.<sup>1</sup> The orthogonality<sup>2</sup> between coordination-driven self-assembly and other binding motifs developed by Lehn,<sup>3</sup> Sauvage,<sup>4</sup> Stoddart,<sup>5</sup> Sanders,<sup>6</sup> Beer,<sup>7</sup> Leigh,<sup>8</sup> Schmittel,<sup>9</sup> Nitschke,<sup>10</sup> Huang,<sup>11</sup> Stang,<sup>12</sup> and others<sup>13</sup> has been exploited in hierarchical schemes to construct complex supramolecular entities, such as metallacycles, metallacages, polypseudorotaxanes, rotaxanes, catenanes, knots, links, and supramolecular polymers. These systems are attractive in that they oftentimes possess facile syntheses that are reflective of the simple intermolecular interactions present, despite possessing degrees of structural complexity that would otherwise imply difficult routes of formation.

[*n*]Molecular necklaces ([*n*]MNs)<sup>14</sup> are a class of supramolecular constructs consisting of three or more subrings mechanically interlocked onto a central ring. [*n*]MNs are topological isomers of [*n*]catenanes and are uniquely defined

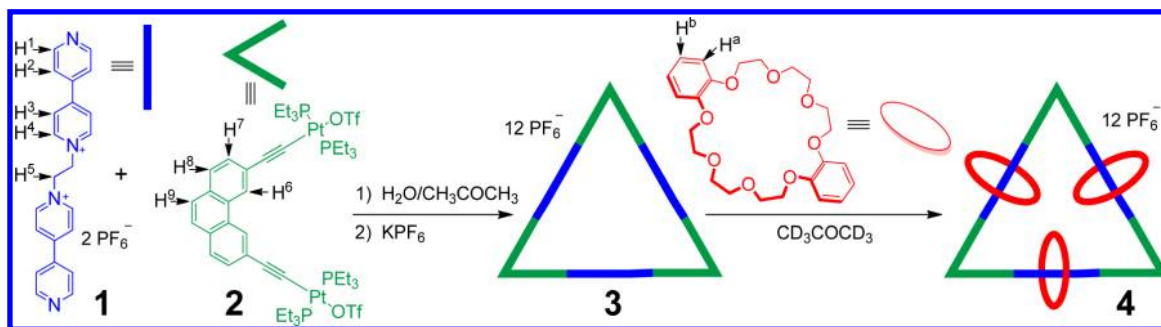
for a given value of *n*; the central ring is threaded by (*n* – 1) subrings. Sauvage et al. unexpectedly observed the existence of a mixture of [*n*]MN (*n* = 4–7) during the synthesis of a [3]catenane, as supported by electrospray ionization mass spectrometry (ESI-MS).<sup>14a</sup> Stoddart et al. obtained [4]MNs as byproducts during the synthesis of oligocatenanes<sup>14b</sup> and polyrotaxanes.<sup>14c</sup> Kim et al. have successfully constructed a [4]MN<sup>14d,f</sup> and a [5]MN<sup>14d,f</sup> using coordination-driven self-assembly along with cucurbit[6]uril-based host–guest chemistry. Later they reported the synthesis of a [6]MN<sup>14g</sup> utilizing selective host–guest complexation of cucurbit[8]uril with a guest molecule containing naphthalene and dipyrindylumethylene units. Recently, Wu et al. synthesized a kinetically stable [5]MN<sup>14h</sup> with dialkylammonium ions as recognition sites and DB24C8 as a macrocycle using olefin ring closing metathesis. A [7]MN homologue was unable to be formed using the same protocol. Herein, we present a highly efficient strategy to fabricate both a [4]MN and a [7]MN by utilizing the orthogonality of coordination-driven self-assembly and host–guest complexation based on a well-developed recognition motif of 1,2-bis(pyridinium)ethane/dibenzo[24]crown-8 (DB24C8).<sup>15</sup> To the best of our knowledge, [7]MNs are the highest order molecular necklaces prepared. Since the metal–ligand coordination and host–guest interactions do not disrupt one another, the entire synthesis can take place as a single self-assembly process, thus organizing up to 18 individual molecules from three unique species in solution to form a single product.

The hierarchical formation of the triangular [4]MN, **4**, was achieved via successive utilization of coordination-driven self-assembly and host–guest chemistry (Scheme 1). The unthreaded triangular metallacycle, **3**, was obtained by stirring 1,2-bis([4,4'-bipyridin]-1-ium)ethane (**1**) with an equimolar amount of a 60° Pt(II) acceptor (**2**) in water/acetone. The triflate counterions originating from the acceptor were exchanged such that the resulting cationic triangle was balanced exclusively by PF<sub>6</sub><sup>–</sup> anions. Multinuclear NMR (<sup>31</sup>P and <sup>1</sup>H) analysis of the reaction solution indicated the formation of a highly symmetric species. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** displayed a singlet at 12.75 ppm, flanked by <sup>195</sup>Pt satellites (Figure S1). The presence of isomer peaks in the <sup>1</sup>H NMR

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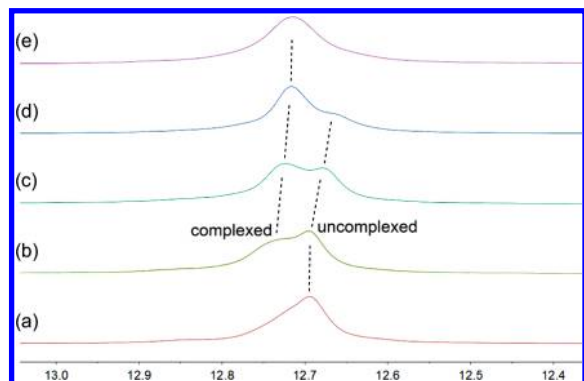
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Scheme 1. Self-Assembly of Supramolecular Triangle and [4]MN



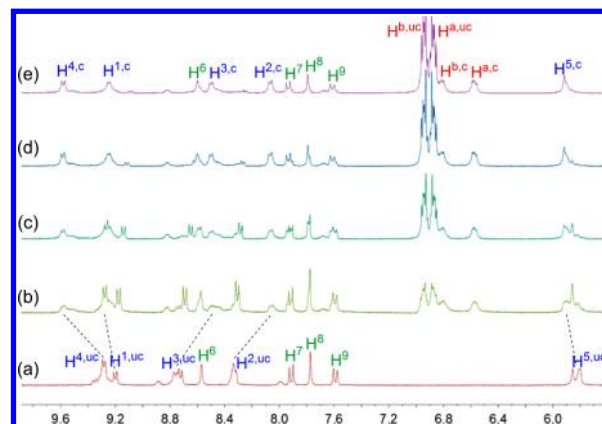
spectrum of **3** (Figure S2) was attributed to the conformational isomerism of ethylene group on **1** (Figure S10). The addition of DB24C8 to a solution of **3** resulted in the formation of [4]MN **4** after 3 days of stirring at room temperature. During the formation of **4**, a color change from pale to bright yellow was observed, suggestive of the presence of intermolecular charge-transfer transitions between the host and guest.

The threading process between triangle **3** and DB24C8 was characterized by  $^{31}\text{P}\{^1\text{H}\}$  (Figures 1 and S9) and  $^1\text{H}$  NMR



**Figure 1.** Partial  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetone- $d_6$ , 22 °C) spectra of (a) metallacycle **3** (1.0 mM), (b) **3** (1.0 mM) + DB24C8 (3.0 mM), (c) **3** (1.0 mM) + DB24C8 (6.0 mM), (d) **3** (1.0 mM) + DB24C8 (9.0 mM), and (e) **3** (1.0 mM) + DB24C8 (12.0 mM).

(Figure 2). When 1.0 equiv of DB24C8 per bis(pyridinium) ligand was added to a 1.0 mM solution of **3**, new sets of peaks appeared in both the  $^{31}\text{P}\{^1\text{H}\}$  NMR (Figure 1b) and the  $^1\text{H}$  NMR spectra (Figure 2b), corresponding to the generation of [4]MN **4**. The  $^1\text{H}$  NMR spectrum showed three sets of resonances corresponding to uncomplexed DB24C8, uncomplexed **3**, and **4**. The simultaneous observation of peaks associated with all three species is due to the slow rate of exchange of **4** on the  $^1\text{H}$  NMR time scale at room temperature. This slow exchange is consistent with complexation experiments between ligand **1** and DB24C8.<sup>15</sup> When additional DB24C8 was introduced, the peaks associated with threading intensified (Figures 1 and 2). After 4.0 equiv of DB24C8 per bis(pyridinium) ligand was added, almost all of the free metallacycle was threaded to form **4** (Figures 1e and 2e). The phenyl protons  $\text{H}^a$  and  $\text{H}^b$  of DB24C8 and pyridyl protons  $\text{H}^2$  and  $\text{H}^3$  of **1** move upfield upon the formation of **4**, while the pyridinium protons  $\text{H}^1$  and  $\text{H}^4$  and the ethylene protons  $\text{H}^5$  on **1** move downfield. Upon complete threading of **3**, the spectrum was clean and sharp (Figure 2e), indicative of the formation of a single, thermodynamically stable isomer. The conformational



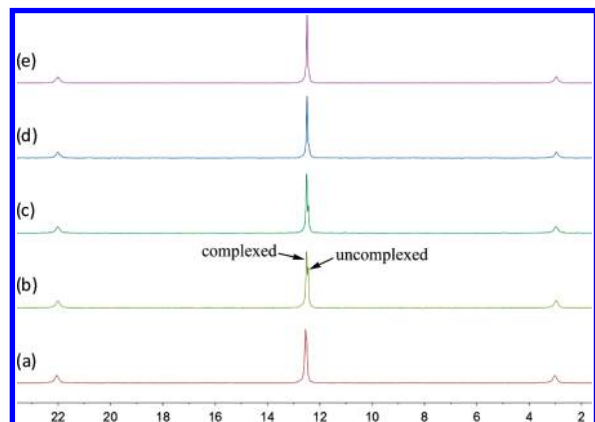
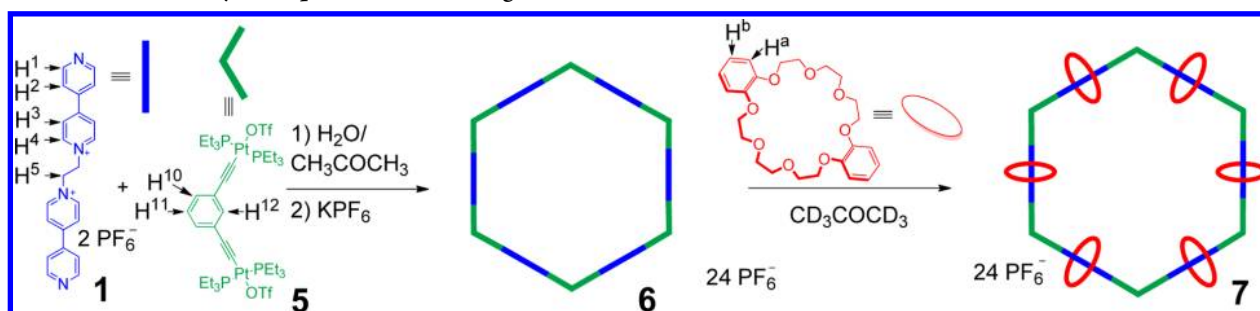
**Figure 2.** Partial  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 22 °C) spectra of (a) metallacycle **3** (1.0 mM), (b) **3** (1.0 mM) + DB24C8 (3.0 mM), (c) **3** (1.0 mM) + DB24C8 (6.0 mM), (d) **3** (1.0 mM) + DB24C8 (9.0 mM), and (e) **3** (1.0 mM) + DB24C8 (12.0 mM). Complexed and uncomplexed species are denoted by “c” and “uc”, respectively.

isomerization of the metallacycle core is therefore attenuated upon guest complexation.

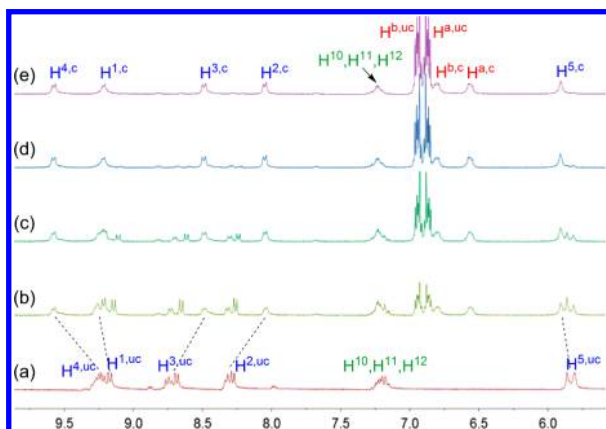
The hexagonal [7]MN, **7**, was synthesized using a similar strategy to that of **4** (Scheme 2). An initial self-assembly between **1** and a 120° Pt(II) acceptor (**5**) furnished a hexagonal core, **6**. Multinuclear NMR ( $^{31}\text{P}$  and  $^1\text{H}$ ) analysis of the reaction solution supported the formation of a discrete macrocyclic species. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** showed a singlet at 12.54 ppm, accompanied by  $^{195}\text{Pt}$  satellites (Figure S3). Topological isomers were also found in the  $^1\text{H}$  NMR spectrum of **6** as with **3** (Figure S4). Threading was similarly achieved by introducing DB24C8 to a solution of **6**, thus delivering [7]MN **7**. The threading processes between **6** and DB24C8 were characterized by  $^{31}\text{P}\{^1\text{H}\}$  (Figure 3) and  $^1\text{H}$  NMR (Figure 4) spectra. When DB24C8 was added into a solution of **6**, new sets of peaks appeared in both the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Figure 3b) and the  $^1\text{H}$  NMR spectrum (Figure 4b), indicative of the formation of **7**. After 4.0 equiv of DB24C8 per bis(pyridinium) ligand was added, almost all of the free metallacycle was threaded (Figures 3e and 4e). The changes in chemical shifts of protons on both the DB24C8 and **1** are similar to what was observed in the formation of [4]MN **4**. After hexagon **6** was thoroughly threaded, the  $^1\text{H}$  NMR spectrum also appeared sharper and clearer (Figure 4e), again indicating the presence of a single thermodynamically stable isomer.

The host–guest interactions in [4]MN **4** and [7]MN **7** were further confirmed by 2D NOESY NMR experiments. NOE was observed between the ether protons  $\text{H}^{\text{ether}}$  on DB24C8 and the

Scheme 2. Self-Assembly of Supramolecular Hexagon and [7]MN



**Figure 3.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.4 MHz, acetone- $d_6$ , 22 °C) spectra of (a) metallacycle **6** (0.5 mM), (b) **6** (0.5 mM) + DB24C8 (3.0 mM), (c) **6** (0.5 mM) + DB24C8 (6.0 mM), (d) **6** (0.5 mM) + DB24C8 (9.0 mM), and (e) **6** (0.5 mM) + DB24C8 (12.0 mM).

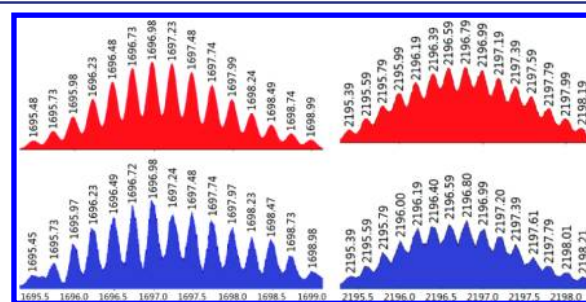


**Figure 4.** Partial  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , 22 °C) spectra of (a) metallacycle **6** (0.5 mM), (b) **6** (0.5 mM) + DB24C8 (3.0 mM), (c) **6** (0.5 mM) + DB24C8 (6.0 mM), (d) **6** (0.5 mM) + DB24C8 (9.0 mM), and (e) **6** (0.5 mM) + DB24C8 (12.0 mM). Complexed and uncomplexed species are denoted by “c” and “uc”, respectively.

pyridinium protons  $\text{H}^{4,c}$  on **3** in the NOESY NMR spectrum of a mixture of **3** and DB24C8 (Figure S11). NOEs were also found between the ether protons  $\text{H}^{\text{ether}}$  on DB24C8 and the pyridinium protons  $\text{H}^{3,c}$  and  $\text{H}^{4,c}$  on **6** in the NOESY NMR spectrum of a mixture of **6** and DB24C8 (Figure S12).

ESI-MS studies provided further evidence for the stoichiometry of formation of the assembled metallacycles and molecular necklaces. In the ESI mass spectrum for **4**, 10 related peaks (Figure S15) were observed that supported the [4]MN structural assignment, including a peak at  $m/z = 1696.98$ ,

attributed to  $[\mathbf{4} - 4\text{PF}_6]^{4+}$  (Figure S5). For **7**, four peaks (Figure S16) were found that supported the [7]MN structural



**Figure 5.** ESI-MS spectra of  $[\mathbf{4} - 4\text{PF}_6]^{4+}$  (left, bottom, blue) and  $[\mathbf{7} - 20\text{HPF}_6 + 1\text{K} + 1\text{Na} + 3\text{H}]^{5+}$  (right, bottom, blue), and their simulated spectra (top, red).

assignment, including a peak at  $m/z = 2196.59$ , attributed to  $[\mathbf{7} - 20\text{HPF}_6 + 1\text{K} + 1\text{Na} + 3\text{H}]^{5+}$  (Figure 5). Four related peaks were found for triangular metallacycle **3** (Figure S13), and two related peaks were found for hexagon **6** (Figure S14). All of these peaks were isotopically resolved and agreed very well with their calculated theoretical distributions.

In conclusion, we have described the highly efficient construction of two catenane systems, a [4]MN and a [7]MN. The facile syntheses of these structurally complex supramolecules are based on hierarchical assembly methods wherein coordination-driven self-assembly and the host–guest chemistry of DB24C8 and 1,2-bis([4,4′-bipyridin]-1-ium)-ethane are used in a complementary fashion. The dynamics of threading and structural studies on the resulting molecular necklaces were investigated using  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, 2D NOESY NMR, and ESI-MS. In the case of the [7]MN, 18 individual molecules from three unique species assemble quantitatively to deliver the final supramolecular ensemble. The highly efficient self-assembly of topologically complex supermolecules provides pathways to new nanoscopic designs with interesting structures and functions while avoiding the lengthy procedures associated with traditional synthetic routes.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Experimental procedures and characterization data for the metallacycles and molecular necklaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (c) Lee, S. J.; Hupp, J. T. *Coord. Chem. Rev.* **2006**, *250*, 1710. (d) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618. (e) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418. (f) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 1650. (g) Northrop, B. H.; Zheng, Y.-R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554. (h) Jin, P.; Dalgarno, S. J.; Atwood, J. L. *Coord. Chem. Rev.* **2010**, *254*, 1760. (i) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (j) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734. (k) Cook, T. R.; Vajpayee, V.; Lee, M. H.; Stang, P. J.; Chi, K.-W. *Acc. Chem. Res.* **2013**, *46*, 2464. (l) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728. (m) Ward, M. D.; Raithby, P. R. *Chem. Soc. Rev.* **2013**, *42*, 1619. (n) Pollock, J. B.; Schneider, G. L.; Cook, T. R.; Davies, A. S.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 13676. (o) Harris, K.; Sun, Q.-F.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2013**, *135*, 12497. (p) Zhao, C.; Sun, Q.-F.; Hart-Cooper, W. M.; DiPasquale, A. G.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2013**, *135*, 18802. (q) Samanta, S. K.; Schmittel, M. J. *Am. Chem. Soc.* **2013**, *135*, 18794. (r) Mahata, K.; Frischmann, P. D.; Würthner, F. J. *Am. Chem. Soc.* **2013**, *135*, 15656.
- (2) (a) Huck, W. T. S.; Hulst, R.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006. (b) Lehn, J.-M. *Chem. Soc. Rev.* **2007**, *36*, 151. (c) Wong, C.-H.; Zimmerman, S. C. *Chem. Commun.* **2013**, *49*, 1679. (d) Saha, M. L.; De, S.; Pramanik, S.; Schmittel, M. *Chem. Soc. Rev.* **2013**, *42*, 6860.
- (3) (a) Nitschke, J. R.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 11970. (b) Lehn, J.-M. *Angew. Chem., Int. Ed.* **2013**, *52*, 2836.
- (4) (a) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Top. Curr. Chem.* **2005**, *262*, 29–62. (b) Durot, S.; Reviriego, F.; Sauvage, J.-P. *Dalton Trans.* **2010**, *39*, 10557. (c) Joosten, A.; Trolez, Y.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2012**, *134*, 1802.
- (5) (a) Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S.-H.; Cave, G. W. V.; Atwood, J. L.; Stoddart, J. F. *Science* **2004**, *304*, 1308. (b) Pentecost, C. D.; Peters, A. J.; Chichak, K. S.; Cave, G. W. V.; Cantrill, S. J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 4099. (c) Pentecost, C. D.; Chichak, K. S.; Peters, A. J.; Cave, G. W. V.; Cantrill, S. J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 218. (d) Meyer, C. D.; Joiner, C. S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 1705. (e) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434.
- (6) (a) Try, A. C.; Harding, M. M.; Hamilton, D. G.; Sanders, J. K. M. *Chem. Commun.* **1998**, 723. (b) Gunter, M. J.; Bampos, N.; Johnstone, K. D.; Sanders, J. K. M. *New J. Chem.* **2001**, *25*, 166.
- (7) (a) Beer, P. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1678. (b) Hancock, L. M.; Beer, P. D. *Chem. Commun.* **2011**, *47*, 6012. (c) Hancock, L. M.; Marchi, E.; Ceroni, P.; Beer, P. D. *Chem.—Eur. J.* **2012**, *18*, 11277.
- (8) (a) Ayme, J.-F.; Beves, J. E.; Leigh, D. A.; McBurney, R. T.; Rissanen, K.; Schultz, D. *Nat. Chem.* **2012**, *4*, 15. (b) Ayme, J.-F.; Beves, J. E.; Leigh, D. A.; McBurney, R. T.; Rissanen, K.; Schultz, D. *J. Am. Chem. Soc.* **2012**, *134*, 9488. (c) Ayme, J.-F.; Beves, J. E.; Campbell, C. J.; Leigh, D. A. *Chem. Soc. Rev.* **2013**, *42*, 1700.
- (9) (a) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555. (b) Saha, M. L.; Schmittel, M. *J. Am. Chem. Soc.* **2013**, *135*, 17743.
- (10) (a) Nitschke, J. R. *Acc. Chem. Res.* **2007**, *40*, 103. (b) Black, S. P.; Stefankiewicz, A. R.; Smulders, M. M. J.; Sattler, D.; Schalley, C. A.; Nitschke, J. R.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5749.
- (11) (a) Zhu, K.; He, J.; Li, S.; Liu, M.; Wang, F.; Zhang, M.; Abliz, Z.; Yang, H.-B.; Li, N.; Huang, F. *J. Org. Chem.* **2009**, *74*, 3905. (b) Wang, F.; Zhang, J.; Ding, X.; Dong, S.; Liu, M.; Zheng, B.; Li, S.; Wu, L.; Yu, Y.; Gibson, H. W.; Huang, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1090. (c) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042.
- (12) (a) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Zheng, Y.-R.; Lyndon, M. M.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 14187. (b) Ghosh, K.; Yang, H.-B.; Northrop, B. H.; Lyndon, M. M.; Zheng, Y.-R.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 5320. (c) Li, S.; Huang, J.; Cook, T. R.; Pollock, J. B.; Kim, H.; Chi, K.-W.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 2084. (d) Yan, X.; Li, S.; Pollock, J. B.; Cook, T. R.; Chen, J.; Zhang, Y.; Ji, X.; Yu, Y.; Huang, F.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15585. (e) Yan, X.; Jiang, B.; Cook, T. R.; Zhang, Y.; Li, J.; Yu, Y.; Huang, F.; Yang, H.-B.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 16813.
- (13) (a) Thordarson, P.; Coumans, R. G. E.; Elemans, J. A. A. W.; Thomassen, P. J.; Visser, J.; Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4755. (b) Yoon, I.; Narita, M.; Shimizu, T.; Asakawa, M. *J. Am. Chem. Soc.* **2004**, *126*, 16740. (c) Blanco, V.; Chas, M.; Abella, D.; Peinador, C.; Quintela, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 13978. (d) Liu, Y.; Bruneau, A.; He, J.; Abliz, Z. *Org. Lett.* **2008**, *10*, 765. (e) Peinador, C.; Blanco, V.; Quintela, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 920. (f) Blanco, V.; García, M. D.; Peinador, C.; Quintela, J. M. *Chem. Sci.* **2011**, *2*, 2407.
- (14) (a) Bitsch, F.; Dietrichbuecker, C. O.; Khemiss, A. K.; Sauvage, J. P.; Vandorsselaer, A. *J. Am. Chem. Soc.* **1991**, *113*, 4023. (b) Amabilino, D. B.; Ashton, P. R.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1998**, *4*, 460. (c) Whang, D. M.; Park, K. M.; Heo, J.; Ashton, P.; Kim, K. *J. Am. Chem. Soc.* **1998**, *120*, 4899. (d) Roh, S. G.; Park, K. M.; Park, G. J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 638. (e) Chiu, S. H.; Rowan, S. J.; Cantrill, S. J.; Ridvan, L.; Ashton, P. R.; Garrell, R. L.; Stoddart, J. F. *Tetrahedron* **2002**, *58*, 807. (f) Park, K. M.; Kim, S. Y.; Heo, J.; Whang, D.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2002**, *124*, 2140. (g) Ko, Y. H.; Kim, K.; Kang, J. K.; Chun, H.; Lee, J. W.; Sakamoto, S.; Yamaguchi, K.; Fetting, J. C.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 1932. (h) Dasgupta, S.; Wu, J. *Org. Biomol. Chem.* **2011**, *9*, 3504.
- (15) (a) Loeb, S. J.; Wisner, J. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2838. (b) Loeb, S. J.; Tiburcio, J.; Vella, S. J.; Wisner, J. A. *Org. Biomol. Chem.* **2006**, *4*, 667. (c) Loeb, S. J. *Chem. Soc. Rev.* **2007**, *36*, 226. (d) Li, S.; Zheng, B.; Chen, J.; Dong, S.; Ma, Z.; Huang, F.; Gibson, H. W. *J. Polym. Sci.: Polym. Chem.* **2010**, *48*, 4067. (e) Suhan, N. D.; Allen, L.; Gharib, M. T.; Viljoen, E.; Vella, S. J.; Loeb, S. J. *Chem. Commun.* **2011**, *47*, 5991.