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Formation of [3]Catenanes from 10 Precursors via Multicomponent Coordination-Driven Self-Assembly of Metallarectangles

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Ⓢ *Supporting Information*

ABSTRACT: We describe the formation of a suite of [3]catenanes via multicomponent coordination-driven self-assembly and host−guest complexation of a rectangular scaffold comprising a 90° Pt-based acceptor building block with a pseudorotaxane bis(pyridinium)ethane/dibenzo-24-crown-8 linear dipyridyl ligand and three dicarboxylate donors. The doubly threaded [3]catenanes are formed from a total of 10 molecular components from four unique species. Furthermore, the dynamic catenation process is reversible and can be switched off and on in a controllable manner by successive addition of KPF_6 and 18-crown-6, as monitored by ^1H and ^{31}P NMR spectroscopy.

[*n*]Catenanes are a class of supramolecular constructs consisting of *n* interlocked macrocycles, ranging from simple double rings ($n = 2$) to infinite chains. These fascinating molecules have attracted attention not only because of their topological importance but also as a result of their interesting physical properties and potential applications in molecular machines, supramolecular polymers, nanomaterials, and biomaterials.[1] The formation of catenanes oftentimes exploits molecular recognition and/or host−guest chemistry based on non-covalent interactions, thereby facilitating the preorganization of molecular components to provide a notable improvement in synthetic efficiency. A variety of promising template-directed methods, including metal/organic ligand coordination,[2] intermolecular hydrogen bonding,[3] anion templation,[4] donor/acceptor interaction,[5] hydrophilic/hydrophobic interaction,[6] and radical−radical interaction templating strategies,[7] have been developed to provide convenient routes for obtaining catenanes.

Coordination-driven self-assembly is a well-established methodology for the synthesis of discrete supramolecular coordination complexes (SCCs). Over the past three decades, many two-dimensional (2D) and three-dimensional (3D) finite SCCs with various predetermined shapes and sizes have been prepared via the combinatorial coordination of transition-metal-based acceptor fragments and nitrogen/carboxylate donor precursors.[8] While the use of directional bonding, wherein building blocks with specific angularities are employed to give single, thermodynamic products, typically produces regular polygons, polyhedra, and prismatic cages, the modularity and versatility of this design strategy has lent itself to the construction of mechanically interlocked molecules.[6a,9] Recent examples of catenane formation by Quintela and co-workers[10] and Stoddart and co-workers[11] have used pyridine-based ligands with Pd^{II}(en) or Pt^{II}(en) corners (en = ethylenediamine) to make a series of electron-deficient molecular squares. When self-assembled under thermodynamic control in the presence of electron-rich aromatic crown ethers, these squares can form catenanes,[10a−c,e,11] a Solomon link,[10d] and a ring-in-ring complex.[11] These simple mono- and dinuclear examples consist of three to six building blocks in total because of the use of traditional two-component assembly. Here we describe a method for utilizing multi-component coordination-driven self-assembly (i.e., the use of three or more unique building blocks) to expand the structural complexity of [*n*]catenanes. These exemplary systems organize 10 molecules in solution to afford a single reaction product.

Our recently demonstrated strategy for the selective self-assembly of multicomponent 2D and 3D metallosupramolecules is based on heteroligated Pt centers.[12] With suitable stoichiometries and directionalities of 90° Pt(II) acceptors with pyridyl and carboxylate ligands, three-component 2D rectangles and 3D prisms were obtained from multicomponent mixtures as a result of the energetic preference for Pt−N,O coordination. On the basis of these results, we envisioned that multicomponent rectangular SCCs formed partly from ligands with electron-deficient pyridinium cores might be particularly effective scaffolds from which mechanically interlocked structures can be generated. The work described herein focused on the preparation, characterization, and reversible threading/dethreading studies of [3]catenanes based on coordination-driven self-assembly and the well-developed 1,2-bis(pyridinium)ethane/dibenzo-24-crown-8 (DB24C8) recognition motif, the latter of which has been widely used in the synthesis of interlocked molecules, metal−organic rotaxane frameworks, and supramolecular polymers.[13] These [3]catenanes were formed with up to 10 components, including 1,2-bis(4,4′-bipyridin-1-ium)ethane (**1**), *cis*-$Pt(PEt_3)_2(OTf)_2$ (**2**), ditopic carboxylate ligands (**3a−c**), and DB24C8 in a 2:4:2:2 ratio.

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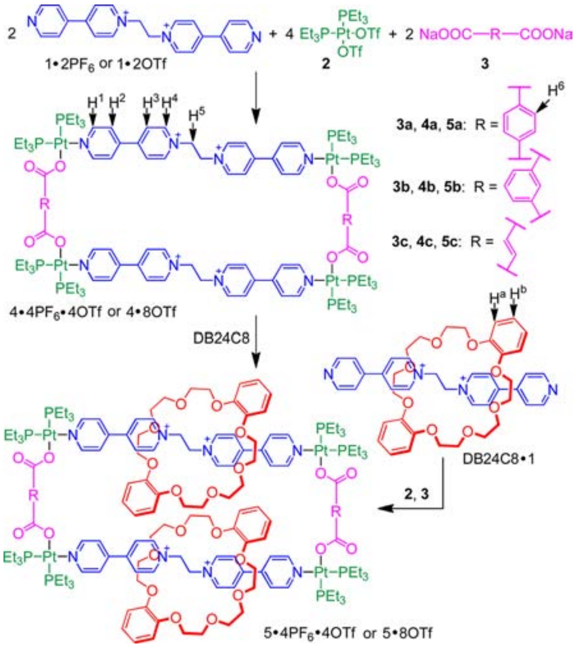
Scheme 1. Synthesis of Metallacycles and [3]Catenanes



As shown in Scheme 1, the guest-containing metallacycles $4\cdot4PF_6\cdot4OTf$ and $4\cdot8OTf$ were synthesized in one pot by stirring a salt of **1** ($1\cdot2PF_6$ or $1\cdot2OTf$, respectively), **2**, and a dicarboxylate ligand (**3a**, **3b**, or **3c**) in a 1:2:1 ratio in D_2O/acetone-d_6 and then acetone-d_6. Multinuclear NMR (^{31}P and ^{1}H) spectroscopy of the reaction solution indicated the formation of single, discrete assemblies. The $^{31}P\{^{1}H\}$ NMR spectra of **4** displayed two coupled doublets of approximately equal intensity with concomitant ^{195}Pt satellites, indicating that the Pt(II) centers of **4** bear a heteroligated N,O coordination motif with one pyridyl and one carboxylate moiety per metal center (Figures S1−S12 in the Supporting Information). Following the formation of the assembled rectangles **4a**−**c**, DB24C8 was added to the solutions in situ, and the mixtures were shaken for several minutes at room temperature to allow the generation of [3]catenanes **5a**−**c**. After DB24C8 was added, the color of the solutions changed from colorless to bright yellow, consistent with absorptions due to intermolecular charge-transfer transitions between the host and guest. The [3]catenanes **5** could also be obtained by initial formation of [2]pseudorotaxane DB24C8·**1** and subsequent assembly with **2** and **3** (Figures S23 and S24), suggesting that the system is under thermodynamic control with the catenane as the energetically preferred product.

The threading processes of rectangles **4a**−**c** and DB24C8 were characterized by $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy. When 0.5 equiv of DB24C8 was added into a 5 mM solution of **4a**, almost no change was observed in the $^{31}P\{^{1}H\}$ NMR spectrum (Figure 1b), while the addition of 1.0 equiv or more of DB24C8 led to the appearance of a new set of peaks corresponding to the [3]catenane **5a** (Figure 1c,d). After 4.0 equiv of DB24C8 was added, almost all of the free metallacycle was threaded to form **5a** (Figure 1e). This trend was also observed in an ^{1}H NMR titration experiment (Figure 2). After 1.0 and 2.0 equiv of DB24C8 were added, the ^{1}H NMR spectra showed three sets of resonances for uncomplexed DB24C8, uncomplexed **4a**, and [3]catenane **5a**. The simultaneous observation of peaks associated with all three species was possible because of the slow exchange of the [3]catenane on the ^{1}H NMR time scale at room temperature. This slow exchange is consistent with complexation experiments between ligand **1** and DB24C8.[13a,b] The signals of the aromatic protons H^a and H^b of DB24C8 and the ethylene protons H^5 and pyridinium protons H^1, H^2, and H^3 of **1** move upfield upon the formation of [3]catenane **5a**, while those of H^6 on the carboxylate ligand and the pyridyl protons H^4 on **1** move downfield. The threading processes forming [3]catenanes **5b** and **5c**, which differ by the carboxylate ligand used, showed similar $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra ($5b\cdot4PF_6\cdot4OTf$, Figures S13 and S14; $5c\cdot4PF_6\cdot4OTf$, Figures S15 and S16; **5a**-**5c**·8OTf, Figures S17−S22).

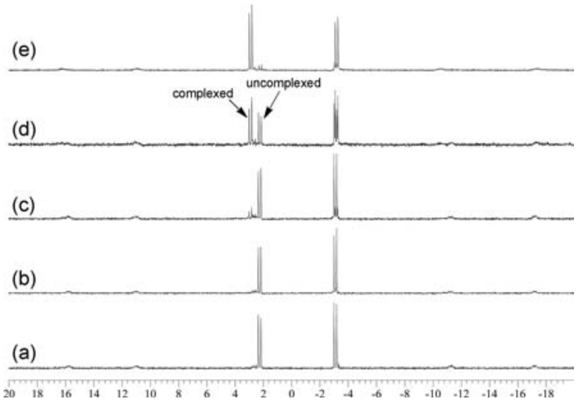


Figure 1. $^{31}P\{^{1}H\}$ NMR spectra (121.4 MHz, acetone-d_6, 22 °C) of (a) metallacycle $4a\cdot4PF_6\cdot4OTf$ (5 mM), (b) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (2.5 mM), (c) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (5 mM), (d) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (10 mM), and (e) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (20 mM).

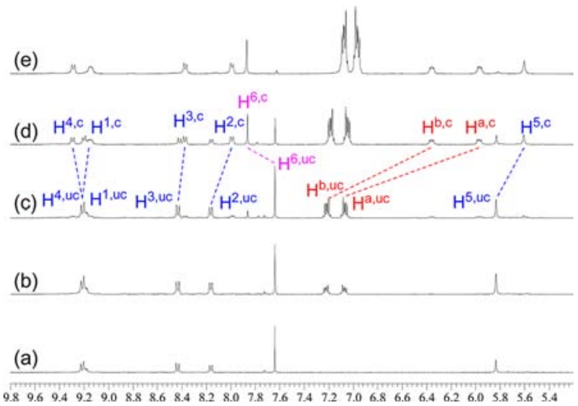


Figure 2. Partial ^{1}H NMR spectra (300 MHz, acetone-d_6, 22 °C) of (a) metallacycle $4a\cdot4PF_6\cdot4OTf$ (5 mM), (b) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (2.5 mM), (c) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (5 mM), (d) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (10 mM), and (e) $4a\cdot4PF_6\cdot4OTf$ (5 mM) + DB24C8 (20 mM). Complexed and uncomplexed species are denoted by "c" and "uc", respectively.

Electrospray ionization mass spectrometry (ESI-MS) studies further supported the formation of the assembled metallacycles and [3]catenanes. The ESI mass spectrum for [3]catenane $5a\cdot8OTf$ (Figure 3) showed peaks at m/z 1458.7 and 1608.4, corresponding to $[M - 3OTf]^{3+}$ and $[M + 3H]^{3+}$, respectively. For [3]catenane $5b\cdot8OTf$, two related peaks were similarly found at m/z 1458.6 and 1608.4, attributed to $[M - 3OTf]^{3+}$ and $[M + 3H]^{3+}$, respectively (Figure S28). For [3]catenane $5c\cdot8OTf$, one related peak was found at m/z 1425.4, corresponding to $[M - 3OTf]^{3+}$ (Figure S29). The ESI mass spectra for the isomers $4a\cdot8OTf$ and $4b\cdot8OTf$ showed peaks at m/z 1962.2 and 1835.3,

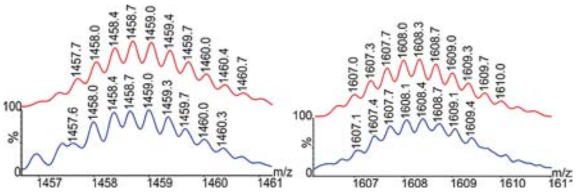


Figure 3. Experimental (blue) and simulated (red) ESI-MS spectra of (left) [**5a**·8OTf − 3OTf]$^{3+}$ and (right) [**5a**·8OTf + 3H]$^{3+}$.

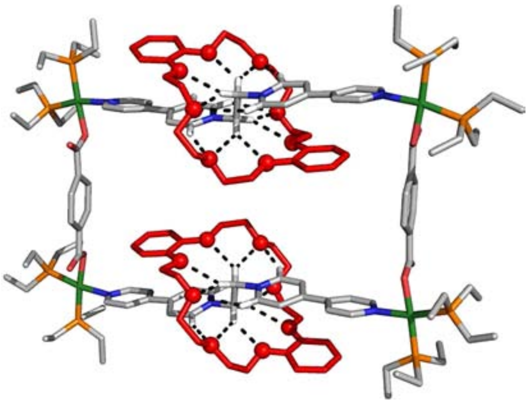


Figure 4. Crystal structure of the [3]catenane **5a**·4PF$_6$·4OTf. Solvent molecules, counterions, and H atoms except for the ones involved in hydrogen bonding have been omitted for clarity. Color code: green = Pt; orange = P; gray = C; red = O; blue = N; the two crown ethers are also shown in red.

corresponding to [M + 2H]$^{2+}$ and [M − 2HOTf + 2Na]$^{2+}$, respectively (Figures S25 and S26). For metallacycle **4c**·8OTf, one peak was found at m/z 1324.5, attributed to [M − 7HOTf − OTf + Na]$^{2+}$ (Figure S27). All of these peaks were isotopically resolved and agreed very well with their calculated theoretical distributions.

The formation of the 10-component [3]catenanes was further confirmed by single-crystal X-ray analysis (Figure 4). X-ray-quality red single crystals of [3]catenane **5a**·4PF$_6$·4OTf were grown by vapor diffusion of ethyl acetate into an acetone solution of **4a**·4PF$_6$·4OTf (5 mM) with excess DB24C8 (20 mM). The solid-state structure of **5a**·4PF$_6$·4OTf revealed that the two units of **1** are threaded through two DB24C8 molecules and stabilized by hydrogen bonding and face-to-face π-stacking interactions. The configuration of DB24C8 and **1** is similar to the previously reported solid-state structure of the [2]pseudorotaxane DB24C8·**1**:[13b] the pyridinium rings of the SCC ligands are held roughly parallel to the phenyl rings of DB24C8.

Furthermore, the reversibility of catenane formation was investigated using **5a**·8OTf as a platform. DB24C8 forms a stronger complex with potassium ions than with ligand **1**,[13b,14] and this fact was utilized herein to promote controllable threading/dethreading processes. The processes were monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy (Figures 5 and 6). When a slight excess of KPF$_6$ was added to a yellow solution of **5a**, the color vanished as the catenane dissociated to furnish metallacycle **4a** and the K$^+$/DB24C8 complex. The ^{31}P{^{1}H} NMR and ^{1}H NMR spectra clearly show the disappearance of the catenane resonances and the appearance of peaks associated with metallacycle **4a** (Figures 5c and 6c). This process could be reversed by titration with 18-crown-6 (18C6), which forms a stronger complex with K$^+$ than DB24C8.[15] After excess 18C6 was added, DB24C8 released its K$^+$ ions and rethreaded into metallacycle **4a** to reform the [3]catenane (Figures 5d and 6d).

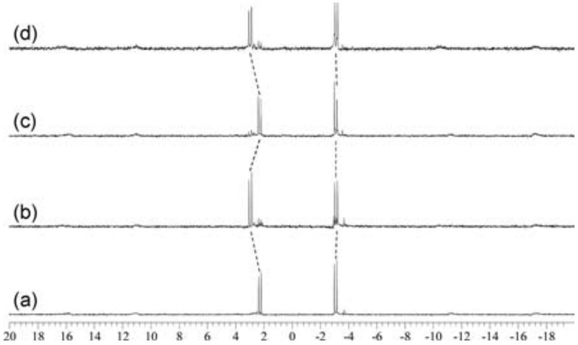


Figure 5. ^{31}P{^{1}H} NMR spectra (121.4 MHz, acetone-d_6, 22 °C) of (a) **4a**·8OTf (5 mM), (b) **4a**·8OTf (5 mM) + DB24C8 (20 mM), (c) **4a**·8OTf (5 mM) + DB24C8 (20 mM) + KPF$_6$ (22 mM), and (d) **4a**·8OTf (5 mM) + DB24C8 (20 mM) + KPF$_6$ (22 mM) + 18C6 (24 mM).

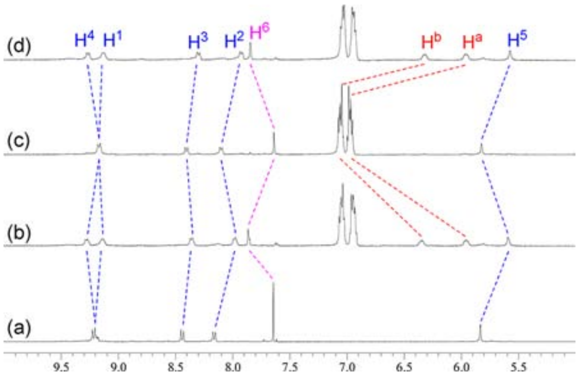


Figure 6. ^{1}H NMR spectra (300 MHz, acetone-d_6, 22 °C) of (a) **4a**·8OTf (5 mM), (b) **4a**·8OTf (5 mM) + DB24C8 (20 mM), (c) **4a**·8OTf (5 mM) + DB24C8 (20 mM) + KPF$_6$ (22 mM), and (d) **4a**·8OTf (5 mM) + DB24C8 (20 mM) + KPF$_6$ (22 mM) + 18C6 (24 mM).

In conclusion, we have described the highly efficient multicomponent coordination-driven self-assembly of [3]-catenanes comprising 10 total building blocks based on the recognition motif between DB24C8 and 1,2-bis(4,4′-bipyridin-1-ium)ethane. The formation of these dynamic [3]catenanes and the resultant structures were characterized via multinuclear NMR spectroscopy, ESI-MS, and X-ray crystallography. Furthermore, the catenation process could be switched off and on in a controllable manner by successive addition of KPF$_6$ and 18C6. These studies reveal the power of parallel non-covalent interactions, wherein metal coordination, hydrogen bonding, π-stacking, and charge transfer can all be exploited in a single system to furnish a unique, thermodynamically favored supramolecular ensemble. The cooperative self-assembly resulting from these multivalent interactions demonstrated here provides a foundation for the preparation of complicated molecular devices and materials under relatively simple synthetic conditions.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental procedures and characterization data for all metallacycles and catenanes. 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) *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C., Eds.; Wiley-VCH: Weinheim, Germany, 1999. (b) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (c) Stoddart, J. F. *Chem. Soc. Rev.* **2009**, *38*, 1802. (d) Niu, Z.; Gibson, H. W. *Chem. Rev.* **2009**, *109*, 6024. (e) Hänni, K. D.; Leigh, D. A. *Chem. Soc. Rev.* **2010**, *39*, 1240. (f) Fang, L.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Goddard, W. A., III; Stoddart, J. F. *Chem. Soc. Rev.* **2010**, *39*, 17. (g) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434. (h) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 1621. (i) Bruns, C. J.; Stoddart, J. F. *Top. Curr. Chem.* **2012**, *323*, 19. (j) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042. (k) Avestro, A.-J.; Belowich, M. E.; Stoddart, J. F. *Chem. Soc. Rev.* **2012**, *41*, 5881. (l) Spruell, J. M.; Coskun, A.; Friedman, D. C.; Forgan, R. S.; Sarjeant, A. A.; Trabolsi, A.; Fahrenbach, A. C.; Barin, G.; Paxton, W. F.; Dey, S. K.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Colvin, M. T.; Carmielli, R.; Caldwell, S. T.; Rosair, G. M.; Hewage, S. G.; Duclairoir, F.; Seymour, J. L.; Slawin, A. M. Z.; Goddard, W. A., III; Wasielewski, M. R.; Cooke, G.; Stoddart, J. F. *Nat. Chem.* **2010**, *2*, 870. (m) Cougnon, F. B. L.; Jenkins, N. A.; Pantoş, G. D.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 1443. (n) Forgan, R. S.; Gassensmith, J. J.; Cordes, D. B.; Boyle, M. M.; Hartlieb, K. J.; Friedman, D. C.; Slawin, A. M. Z.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 17007.

(2) (a) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Top. Curr. Chem.* **2005**, *262*, 29. (b) Durot, S.; Reviriego, F.; Sauvage, J.-P. *Dalton Trans.* **2010**, *39*, 10557. (c) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555. (d) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260.

(3) (a) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532. (b) Kay, E. R.; Leigh, D. A. *Top. Curr. Chem.* **2005**, *262*, 133. (c) Guidry, E. N.; Cantrill, S. J.; Stoddart, J. F.; Grubbs, R. H. *Org. Lett.* **2005**, *7*, 2129. (d) Li, S.; Liu, M.; Zheng, B.; Zhu, K.; Wang, F.; Li, N.; Zhao, X.-L.; Huang, F. *Org. Lett.* **2009**, *11*, 3350. (e) Liu, M.; Li, S.; Hu, M.; Wang, F.; Huang, F. *Org. Lett.* **2010**, *12*, 760. (f) Niu, Z.; Slebodnick, C.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 4616. (g) Chang, C.-F.; Chuang, C.-J.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Angew. Chem., Int. Ed.* **2012**, *51*, 10094.

(4) (a) Vickers, M. S.; Beer, P. D. *Chem. Soc. Rev.* **2007**, *36*, 211. (b) Mullen, K. M.; Beer, P. D. *Chem. Soc. Rev.* **2009**, *38*, 1701. (c) White, N. G.; Beer, P. D. *Chem. Commun.* **2012**, *48*, 8499.

(5) (a) Griffiths, K. E.; Stoddart, J. F. *Pure Appl. Chem.* **2008**, *80*, 485. (b) Au-Yeung, H. Y.; Pantoş, G. D.; Sanders, J. K. M. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 10466. (c) Fang, L.; Basu, S.; Sue, C.-H.; Fahrenbach, A. C.; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 396.

(6) (a) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (b) Lu, J.; Turner, D. R.; Harding, L. P.; Byrne, L. T.; Baker, M. V.; Batten, S. R. *J. Am. Chem. Soc.* **2009**, *131*, 10372.

(7) (a) Coskun, A.; Spruell, J. M.; Barin, G.; Fahrenbach, A. C.; Forgan, R. S.; Colvin, M. T.; Carmielli, R.; Benítez, D.; Tkatchouk, E.; Friedman, D. C.; Sarjeant, A. A.; Wasielewski, M. R.; Goddard, W. A., III; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 4538. (b) Zhu, Z.; Fahrenbach, A. C.; Li, H.; Barnes, J. C.; Liu, Z.; Dyar, S. M.; Zhang, H.; Lei, J.; Carmieli, R.; Sarjeant, A. A.; Stern, C. L.; Wasielewski, M. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 11709.

(8) (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*, 369. (c) Nitschke, J. R. *Acc. Chem. Res.* **2007**, *40*, 103. (d) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618. (e) Northrop, B. H.; Zheng, Y.-R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554. (f) Jin, P.; Dalgarno, S. J.; Atwood, J. L. *Coord. Chem. Rev.* **2010**, *254*, 1760. (g) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (h) Pollock, J. B.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 10607. (i) Chakrabarty, R.; Stang, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 14738. (j) Yoneya, M.; Yamaguchi, T.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2012**, *134*, 14401. (k) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (l) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734.

(9) (a) Ibukuro, F.; Fujita, M.; Yamaguchi, K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 11014. (b) Park, K.-M.; Kim, S.-Y.; Heo, J.; Whang, D.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2002**, *124*, 2140. (c) Hori, A.; Akasaka, A.; Biradha, K.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3269. (d) Dietrich-Buchecker, C.; Colasson, B.; Fujita, M.; Hori, A.; Geum, N.; Sakamoto, S.; Yamaguchi, K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2003**, *125*, 5717. (e) Yamashita, K.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 1850. (f) Liu, Y.; Bruneau, A.; He, J.; Abliz, Z. *Org. Lett.* **2008**, *10*, 765. (g) Westcott, A.; Fisher, J.; Harding, L. P.; Rizkallah, P.; Hardie, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 2950. (h) Henkelis, J. J.; Ronson, T. K.; Harding, L. P.; Hardie, M. J. *Chem. Commun.* **2011**, *47*, 6560.

(10) (a) Chas, M.; Pia, E.; Toba, R.; Peinador, C.; Quintela, J. M. *Inorg. Chem.* **2006**, *45*, 6117. (b) Blanco, V.; Chas, M.; Abella, D.; Peinador, C.; Quintela, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 13978. (c) Blanco, V.; Gutiérrez, A.; Platas-Iglesias, C.; Peinador, C.; Quintela, J. M. *J. Org. Chem.* **2009**, *74*, 6577. (d) Peinador, C.; Blanco, V.; Quintela, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 920. (e) Blanco, V.; García, M. D.; Peinador, C.; Quintela, J. M. *Chem. Sci.* **2011**, *2*, 2407.

(11) Forgan, R. S.; Friedman, D. C.; Stern, C. L.; Bruns, C. J.; Stoddart, J. F. *Chem. Commun.* **2010**, *46*, 5861.

(12) (a) Zheng, Y.-R.; Zhao, Z.; Wang, M.; Ghosh, K.; Pollock, J. B.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 16873. (b) Wang, M.; Zheng, Y.-R.; Cook, T. R.; Stang, P. J. *Inorg. Chem.* **2011**, *50*, 6107. (c) Wang, M.; Lan, W.-J.; Zheng, Y.-R.; Cook, T. R.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 10752. (d) Zheng, Y.-R.; Lan, W.-J.; Wang, M.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 17045.

(13) (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., Part A: 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.

(14) Takeda, Y.; Kudo, Y.; Fujiwara, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1315.

(15) (a) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600. (b) Gibson, H. W.; Wang, H.; Slebodnick, C.; Merola, J.; Kassel, W. S.; Rheingold, A. L. *J. Org. Chem.* **2007**, *72*, 3381.