

RESEARCH ARTICLE

View Article Online
View Journal | View IssueCite this: *Mater. Chem. Front.*,
2019, 3, 2397

Facile synthesis of diverse rotaxanes via successive supramolecular transformations†

Yang Hu,^a Wei Wang,^{*a} Rui Yao,^a Xu-Qing Wang,^a Yu-Xuan Wang,^a Bin Sun,^a Li-Jun Chen,^a Ying Zhang,^b Xiao-Li Zhao,^{id a} Lin Xu,^{id a} Hong-Wei Tan,^{id b} Yihua Yu,^c Xiaopeng Li^{id d} and Hai-Bo Yang^{id *a}Received 1st July 2019,
Accepted 5th September 2019

DOI: 10.1039/c9qm00430k

rsc.li/frontiers-materials

Facile synthesis of diverse rotaxanes was successfully realized through a simple and efficient supramolecular transformation strategy. Starting from an organometallic [3]rotaxane with a platinum-acetylide moiety as the bridge moiety and transformation site, employing a simple phosphine ligand exchange and sequential reductive elimination reactions resulted in the successful preparation of various rotaxanes with diverse structures and properties.

Rotaxanes, as a fundamental class of mechanically interlocked molecules (MIMs), have proven to be crucial candidates for the construction of artificial molecular machinery and electronic devices due to their shuttling and switching properties.¹ For instance, the pioneering work on rotaxane-based molecular shuttles by 2016 Nobel laureate, J. Fraser Stoddart, initiated a new era of the design and synthesis of molecular machines.² Relying on concepts such as molecular recognition and non-covalent synthesis, template-directed protocols have led to a great evolution in rotaxane synthesis.³ A number of templates, such as transition metal ions, anions, hydrogen bonding, and donor-acceptor interactions, have been employed in the highly efficient synthesis of rotaxanes and the related higher-order interlocked molecules. However, most of the current reports mainly focus on either one rotaxane with a specific structure or a family of rotaxanes with similar structural characteristics. The construction of diverse rotaxanes composed of a family of rotaxanes with varied structures and properties has rarely been explored, which might be due to the lack of efficient approaches towards the high throughput synthesis of diverse rotaxanes.⁴ Very few examples of the end-cap exchange of rotaxanes using suitable reactions such as the transesterification grafting reaction,⁴ condensation reaction,⁵ Wittig reaction,⁶ and Tsuji-Trost

allylation reaction⁷ allowed for the successful structural derivations of rotaxanes. However, in these reports, the modifications were only limited to the stopper replacements, while the modification of the structure or properties of the main skeleton has not been realized. Since diverse rotaxane structures branched up from one principal structure would lead to attractive properties and potential applications in wide areas, the development of new synthetic protocols for the synthesis of rotaxanes with adequate diversity in both structures and properties remains an attractive proposition.

Inspired by biological transformation processes of fundamental biomacromolecules such as proteins, DNA, RNA *etc.*, in which stimuli-induced structural changes lead to specific functions as the outputs,⁸ we envisaged that such a supramolecular transformation strategy could be employed for the synthesis of rotaxanes with adequate diversity in structures, properties, and applications. In order to realize such a strategy, a given rotaxane with a specific transformation site should be firstly prepared. Sequential supramolecular transformations derived from this reactive site under specific conditions could afford the formation of diverse rotaxanes with varied structures and properties. Based on our ongoing interest in organoplatinum chemistry,⁹ a *trans*-platinum-acetylide moiety with PPh₃ ligands was chosen as the key transformation site. Under mild conditions, the *trans*-platinum-acetylide moiety could transform into its *cis*-analogue and further into a butadiyne moiety without the platinum atom, thus resulting in structural and property modification (Scheme 1).¹⁰ In addition, in this study, a pillar[5]arene/alkyl chain host-guest complex was selected as the key rotaxane moiety.¹¹ The low polarity and good solubility of such a neutral rotaxane system would allow for convenient transformation and purification processes.

According to above-mentioned design strategy, pillar[5]-arene-based organometallic [3]rotaxane **1** containing a *trans*-platinum-acetylide moiety with PPh₃ ligands was prepared as

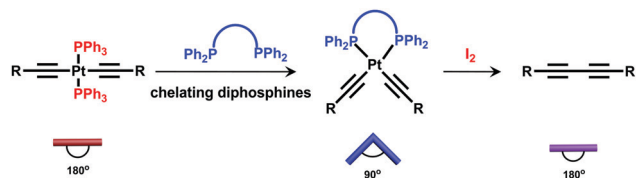
^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, Chang-Kung Chuang Institute, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062, P. R. China.
E-mail: hbyang@chem.ecnu.edu.cn, weiwang@stu.ecnu.edu.cn

^b College of Chemistry, Beijing Normal University, Beijing, 100875, P. R. China

^c Shanghai Key Laboratory of Magnetic Resonance, East China Normal University, Shanghai 200062, P. R. China

^d Department of Chemistry, University of South Florida, East Fowler Ave., Florida 4202, USA

† Electronic supplementary information (ESI) available: CCDC 1938209. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9qm00430k



Scheme 1 Schematic representation of the successive transformations of the platinum-acetylide moiety with PPh_3 ligands.

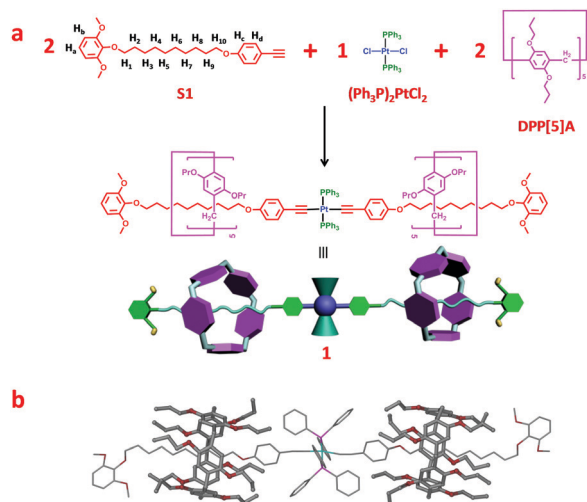


Fig. 1 Synthesis of the key [3]rotaxane precursor **1** (a) and its single-crystal X-ray structure (b).

the key rotaxane precursor through an efficient one-pot multi-component reaction (“from five to one”), as shown in Fig. 1a. The ^{31}P NMR spectrum of [3]rotaxane **1** revealed a single peak at 18.7 ppm, indicating the formation of only one dominant platinum containing species (Fig. S3, ESI †). In addition, in the ^1H spectrum (Fig. 2a and e), the methylene peaks in the alkyl chain displayed an obvious upfield shift to even below 0 ppm due to the shielding effects. These changes were in accordance with previous reports on mechanically interlocked structures derived from pillar[5]arene with neutral alkyl chains,¹² thus strongly supporting the existence of rotaxane structures.

Furthermore, the formation of rotaxane was further confirmed by a two-dimensional (2-D) NOESY NMR study (Fig. S4, ESI †), in which correlation signals between protons on the pillar[5]arene unit and methylene protons on the alkyl chain were observed. Finally, the structure of organometallic [3]rotaxane **1** was unambiguously confirmed by means of single-crystal X-ray diffraction (Fig. 1b). Slow diffusion of ethyl acetate (EtOAc) into a CH_2Cl_2 solution of **1** afforded pale yellow single crystals suitable for crystallographic analysis. The single crystal structure of [3]rotaxane **1** disclosed that two pillar[5]arene rings encircled two alkyl chain moieties on the dumbbell component. The platinum-acetylide moiety located in the center of the rotaxane and the acetylenic π -ligand displayed a coplanar geometry.

With the “reactive” rotaxane precursor **1** in hand, the investigation on the synthesis of diverse rotaxanes through supramolecular transformations of the platinum-acetylide

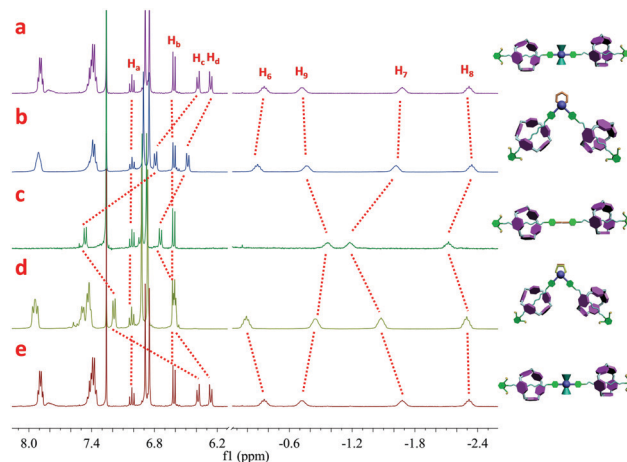
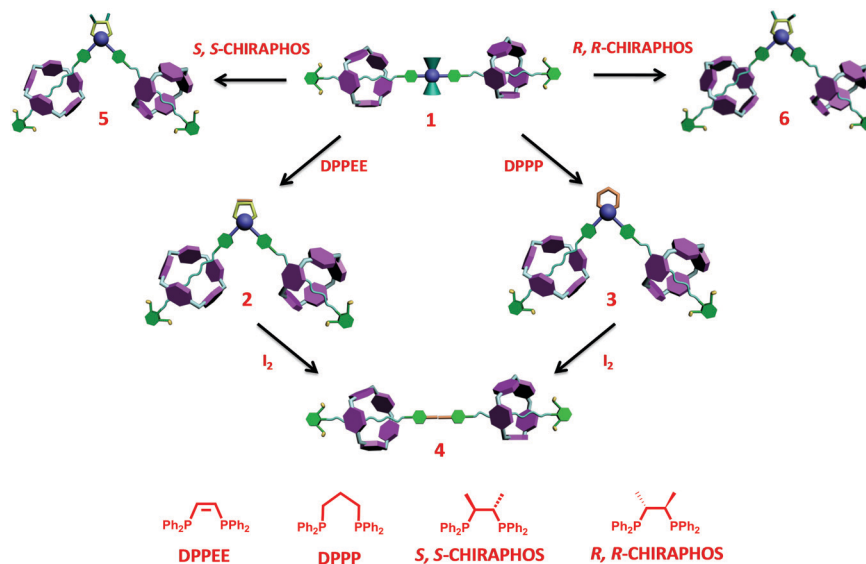


Fig. 2 Partial ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of the organo-metallic [3]rotaxane **1** (a and e), **2** (d), **3** (b) and organic [3]rotaxane **4** (c).

moiety was then carried out. Four chelating diphosphines, including *cis*-bis(diphenylphosphino)ethylene (**DPPEE**), 1,3-bis(diphenylphosphino)propane (**DPPP**), (2*S*,3*S*)-bis(diphenylphosphino)butane (**S,S-CHIRAPHOS**), and (2*R*,3*R*)-bis(diphenylphosphino)butane (**R,R-CHIRAPHOS**), were chosen to replace the PPh_3 ligands, thus leading to the transformation processes (Scheme 2). All the transformations proceeded under mild conditions (see general procedures in ESI †) and the details are shown below.

For the achiral chelating ligands **DPPEE** and **DPPP**, the transformation from the *trans*-platinum acetylide moiety in [3]rotaxane **1** to its *cis*-analogue proceeded efficiently under mild conditions, thus allowing for the formation of corresponding V-shaped [3]rotaxanes **2** and **3** in 95% and 90% yield, respectively. As shown in Fig. 2, after the transformation process, the ^1H NMR spectra exhibited an obvious change of the peaks (H_c and H_d) attributed to phenyl rings near the platinum-acetylide moiety, while the peaks below 0 ppm that belonged to the rotaxane moiety remained intact. These results clearly indicated the maintenance of the threaded structures upon the ligand exchange processes. In addition, the shifts in the ^{31}P NMR spectra from 18.7 ppm (**1**) to 52.2 ppm (**2**) and -5.5 ppm (**3**), respectively, with the decrease of the coupling constant (2671 Hz for **1**, 2283 Hz for **2**, and 2202 Hz for **3**) further supported the formation of the corresponding V-shaped [3]rotaxanes. For both V-shaped rotaxanes, isotopically resolved peaks attributed to the targeted structures were observed in their MALDI-TOF MS spectra (*i.e.* $m/z = 3471.47$ for $[\mathbf{2} + \text{H}]^+$ and $m/z = 3487.40$ for $[\mathbf{3} + \text{H}]^+$, respectively), thus supporting the successful synthesis of the desired rotaxanes through supramolecular transformation.

In order to gain an in-depth understanding of such efficient supramolecular transformations between rotaxanes of different shapes, NMR titration was carried out. As shown in Fig. 3, with the increase of the amount of **DPPEE** from 0.33 to 1.00 equiv., the peaks corresponding to the original organometallic [3]rotaxane **1** gradually disappeared accompanied by an increase of the new peaks attributed to V-shaped [3]rotaxane **2**. In $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Fig. S22, ESI †), with the addition of **DPPEE**, the phosphine peak at



Scheme 2 Construction of diverse rotaxanes **1–6** via a successive supramolecular transformation approach.

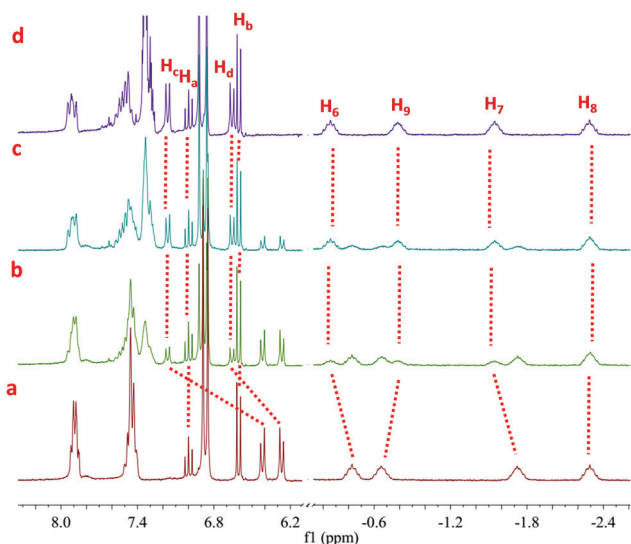


Fig. 3 Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K) of the supramolecular transformation from linear [3]rotaxane **1** to V-shaped [3]rotaxane **2** with the addition of different amounts of **DPPEE**: (a) [3]rotaxane **1**; (b) 0.33 equiv.; (c) 0.66 equiv.; (d) 1.00 equiv.

18.5 ppm, attributed to the PPh_3 ligands on the platinum-acetylide moiety in the original [3]rotaxane **1**, dramatically decreased along with the appearance of two new peaks at 51.6 and -5.5 ppm, which were ascribed to the **DPPEE** ligand in the newly-formed *cis*-platinum-acetylide moiety and the released free PPh_3 ligand, respectively. Through the NMR titration study, supramolecular transformation from linear [3]rotaxane **1** to V-shaped [3]rotaxane **2** through the simple and highly efficient ligand exchange was undoubtedly confirmed.

Interestingly, the resultant V-shaped [3]rotaxanes **2** and **3** could undergo further transformations to afford the corresponding organic [3]rotaxane **4** with a linear butadiyne link. In order to realize the de-platinum process, [3]rotaxanes **2** and **3**

were treated with I_2 (4.0 eq.) at room temperature in CHCl_3 . TLC analysis revealed that such a reductive elimination reaction proceeded efficiently with complete conversion within 12 hours. Purification by flash column chromatography afforded the de-platinum [3]rotaxane **4** in 64% (from **2**) and 59% (from **3**) yield as well as the corresponding Pt complexes $\text{Pt}(\text{DPPEE})\text{I}_2$ (from **2**) or $\text{Pt}(\text{DPPP})\text{I}_2$ (from **3**), respectively, thus suggesting an oxidatively induced reductive elimination mechanism. As revealed by the ^1H NMR spectrum, in the resultant organic [3]rotaxane, no peaks attributed to phosphine ligands were observed, while the peaks ascribed to the threaded structure were retained (Fig. 2c). As expected, no peaks were observed in the ^{31}P NMR spectrum. Furthermore, the MALDI-TOF-MS spectrum of **4** clearly displayed a single peak at $m/z = 2880.36$, which was attributed to the species $[\mathbf{4} + \text{H}]^+$ (Fig. S27, ESI †). All these data strongly indicated the generation of de-platinum [3]rotaxane **4**. It is worth noting that by the successive supramolecular transformations shown above, we successfully realized a “three-station” shape transformation of [3]rotaxanes, *i.e.* from “linear” for **1** to “V-shaped” for **2** or **3** and further back to “linear” for **4**. More importantly, along with such multiple structural interconversions, obvious changes in the length of rotaxane skeletons were achieved. For instance, according to the simulated structures (Fig. S28, ESI †), such successive structural transformation led to a contraction ratio of 0.17 from **1** to **2** and an extension ratio of 0.12 from **2** to **4** (Table S1, ESI †), respectively, thus making them excellent candidates for the construction of rotaxane-based dynamic materials.¹³

Inspired by an emerging asymmetric catalytic investigation with chiral rotaxanes,¹⁴ we envisioned that the employment of chiral chelating ligands would afford the corresponding chiral V-shaped [3]rotaxane upon similar supramolecular transformation processes. More importantly, if it works, from the same rotaxane precursor, both enantiomers of the rotaxane could be prepared by using enantiomeric chelating ligands,



Fig. 4 CD spectra of the chiral [3]rotaxane **5** derived from **S,S-CHIRAPHOS** (red line) and its enantiomer, *i.e.*, the chiral [3]rotaxane **6** derived from **R,R-CHIRAPHOS** (black line).

thus highlighting the feasibility of this supramolecular transformation strategy for the generation of diverse chiral rotaxanes.

To test our hypothesis, two types of classical chiral chelating diphosphine ligands, *i.e.* **S,S-CHIRAPHOS** and **R,R-CHIRAPHOS**, were employed in the ligand exchange reactions with **1**. Treatment of **1** with **S,S-CHIRAPHOS** and **R,R-CHIRAPHOS** in CH_2Cl_2 at room temperature for 18 h resulted in the successful synthesis of the corresponding chiral V-shaped [3]rotaxanes **5** and **6** in 55% and 65% yield, respectively. As shown in Fig. S14 and S18 (ESI[†]), respectively, enantiomers **5** and **6** displayed the same ^1H NMR spectra, in which the peaks attributed to the chiral ligands and interlocked structures were observed. Furthermore, a single peak at 44.7 ppm with a coupling constant of $^1J_{\text{P-Pt}} = 2234$ Hz was also observed in the ^{31}P NMR spectra of both enantiomers (Fig. S16 and S20, ESI[†]). The investigation of the chirality of chiral [3]rotaxanes **5** and **6** was performed by using circular dichroism (CD) spectra as shown in Fig. 4. The CD spectra of both **5** and **6** exhibited two major bands at approximately 240 nm and 260 nm, respectively. In addition, as expected, these two spectra mirrored each other in both form and intensity, which is consistent with an enantiomeric relationship.

In summary, a simple yet efficient supramolecular transformation approach for the facile construction of diverse rotaxanes was successfully developed. By inserting a platinum-acetylide moiety as the transformation site in the rotaxane precursor, a simple ligand exchange and sequential reductive elimination reactions afforded the synthesis of rotaxanes with diversity in both structures and properties. Notably, successive “three-station” supramolecular transformations from linear organometallic [3]rotaxane **1** to V-shaped [3]rotaxanes **2** or **3** and back to linear organic [3]rotaxane **4** led to obvious changes in the length of rotaxane skeletons, thus making them excellent candidates for the construction of rotaxane-based dynamic materials. In addition, starting from the same [3]rotaxane **1**, both enantiomeric rotaxanes **5** and **6** were prepared in a divergent way. Due to the diversity in both structures and properties, these resultant rotaxanes feature potential applications in many fields ranging from molecular devices to dynamic materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the NSFC/China (No. 21625202 and 21572066), the Innovation Program of Shanghai Municipal Education Commission (No. 2019-01-07-00-05-E00012), and the Program for Changjiang Scholars and Innovative Research Team in University.

Notes and references

- (a) J. F. Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1802; (b) X. Ma and H. Tian, *Chem. Soc. Rev.*, 2010, **39**, 70; (c) R. S. Forgan, J. P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434; (d) E. A. Neal and S. M. Goldup, *Chem. Commun.*, 2014, **50**, 5128; (e) S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan and A. L. Nussbaumer, *Chem. Rev.*, 2015, **115**, 10081; (f) C. J. Bruns and J. F. Stoddart, *The Nature of the Mechanical Bond: From Molecules to Machines*, John Wiley and Sons, Hoboken, 2016; (g) J. E. M. Lewis, M. Galli and S. M. Goldup, *Chem. Commun.*, 2017, **53**, 298; (h) M. Denis and S. M. Goldup, *Nat. Rev. Chem.*, 2017, 0061; (i) X.-Q. Wang, W.-J. Li, W. Wang and H.-B. Yang, *Chem. Commun.*, 2018, **54**, 13303; (j) J. P. Sauvage, *Eur. J. Org. Chem.*, 2019, 3287; (k) Z. Meng, J.-F. Xiang and C.-F. Chen, *J. Am. Chem. Soc.*, 2016, **138**, 5652; (l) Z. Meng, J.-F. Xiang and C.-F. Chen, *Chem. Sci.*, 2014, **5**, 1520; (m) Q. Shi and C.-F. Chen, *Chem. Sci.*, 2019, **10**, 2529; (n) X. Fu, Q. Zhang, S.-J. Rao, D.-H. Qu and H. Tian, *Chem. Sci.*, 2016, **7**, 1696; (o) S.-J. Rao, Q. Zhang, J. Mei, X.-H. Ye, C. Gao, Q.-C. Wang, D.-H. Qu and H. Tian, *Chem. Sci.*, 2017, **8**, 6777; (p) D.-H. Qu, Q.-C. Wang, Q.-W. Zhang, X. Ma and H. Tian, *Chem. Rev.*, 2015, **115**, 7543; (q) Q. Zhang, S.-J. Rao, T. Xie, X. Li, T.-Y. Xu, D. W. Li, D.-H. Qu, Y.-T. Long and H. Tian, *Chem*, 2018, **4**, 2670; (r) Q. Jiang, H.-Y. Zhang, M. Han, Z.-J. Ding and Y. Liu, *Org. Lett.*, 2010, **12**, 1728; (s) Z.-J. Zhang, H.-Y. Zhang, H. Wang and Y. Liu, *Angew. Chem., Int. Ed.*, 2011, **50**, 10834.
- (a) P. L. Anelli, N. Spencer and J. F. Stoddart, *J. Am. Chem. Soc.*, 1991, **113**, 5131; (b) P. R. Ashton, D. Philp, N. Spencer and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1992, **16**, 1124; (c) P. R. Ashton, R. A. Bissell, N. Spencer, J. F. Stoddart and M. S. Tolley, *Synlett*, 1992, 914; (d) P. R. Ashton, R. A. Bissell, R. Górski, D. Philp, N. Spencer, J. F. Stoddart and M. S. Tolley, *Synlett*, 1992, 919; (e) P. R. Ashton, R. A. Bissell, N. Spencer, J. F. Stoddart and M. S. Tolley, *Synlett*, 1992, 923; (f) R. A. Bissell, E. Córdova, A. E. Kaifer and J. F. Stoddart, *Nature*, 1994, **369**, 133; (g) K. Zhu, C. A. O’Keefe, V. N. Vukotic, R. W. Schurko and S. J. Loeb, *Nat. Chem.*, 2015, **7**, 514; (h) K. Zhu, G. Baggi and S. J. Loeb, *Nat. Chem.*, 2018, **10**, 625.
- (a) J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh and R. T. McBurney, *Chem. Soc. Rev.*, 2009, **38**, 1530; (b) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.*, 2011, **50**, 9260;

- (c) W. R. Dichtel, O. S. Miljanić, W. Zhang, J. M. Spruell, K. Patel, I. Aprahamian, J. R. Heath and J. F. Stoddart, *Acc. Chem. Res.*, 2008, **41**, 1750; (d) P. D. Beer, M. R. Sambrook and D. Curiel, *Chem. Commun.*, 2006, 2105; (e) J. A. Faiz, V. Heitz and J.-P. Sauvage, *Chem. Soc. Rev.*, 2009, **38**, 422; (f) D.-H. Qu and H. Tian, *Chem. Sci.*, 2011, **2**, 1011; (g) G. T. Spence and P. D. Beer, *Acc. Chem. Res.*, 2012, **46**, 571; (h) M. Xue, Y. Yang, X. Chi, X. Yan and F. Huang, *Chem. Rev.*, 2015, **115**, 7398; (i) J. E. M. Lewis, P. D. Beer, S. J. Loeb and S. M. Goldup, *Chem. Soc. Rev.*, 2017, **46**, 2577; (j) J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2017, **56**, 11094; (k) J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2017, **56**, 11080.
- 4 J. S. Hannam, S. M. Lacy, D. A. Leigh, C. G. Saiz, A. M. Z. Slawin and S. G. Stutchell, *Angew. Chem., Int. Ed.*, 2004, **43**, 3260.
- 5 D. W. Zehnder II and D. B. Smithrud, *Org. Lett.*, 2001, **3**, 2485.
- 6 (a) S. J. Rowan and J. F. Stoddart, *J. Am. Chem. Soc.*, 2000, **122**, 164; (b) S.-H. Chiu, S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White and D. J. Williams, *Chem. – Eur. J.*, 2002, **8**, 5170.
- 7 N. Kihara, S. Motoda, T. Yokozawa and T. Takata, *Org. Lett.*, 2005, **7**, 1199.
- 8 (a) J. Monod, J. P. Changeux and F. Jacob, *J. Mol. Biol.*, 1963, **6**, 306; (b) M. F. Perutz, *Nature*, 1970, **228**, 726; (c) H. R. Saibil, W. A. Fenton, D. K. Clare and A. L. Horwich, *J. Mol. Biol.*, 2013, **425**, 1476; (d) W. Wang, Y.-X. Wang and H.-B. Yang, *Chem. Soc. Rev.*, 2016, **45**, 2656.
- 9 (a) S. Chen, L.-J. Chen, H.-B. Yang, H. Tian and W. Zhu, *J. Am. Chem. Soc.*, 2012, **134**, 13596; (b) L. Xu, L.-J. Chen and H.-B. Yang, *Chem. Commun.*, 2014, **50**, 5156; (c) W. Wang and H.-B. Yang, *Chem. Commun.*, 2014, **50**, 5171; (d) Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 8577; (e) L.-J. Chen, G.-Z. Zhao, B. Jiang, B. Sun, M. Wang, L. Xu, J. He, Z. Abliz, H. Tan, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 5993; (f) W. Wang, Y. Zhang, B. Sun, L.-J. Chen, X.-D. Xu, M. Wang, X. Li, Y. Yu, W. Jiang and H.-B. Yang, *Chem. Sci.*, 2014, **5**, 4554; (g) B. Sun, M. Wang, Z. Lou, M. Huang, C. Xu, X. Li, L.-J. Chen, Y. Yu, G. L. Davis, B. Xu, H.-B. Yang and X. Li, *J. Am. Chem. Soc.*, 2015, **137**, 1556; (h) W. Wang, L.-J. Chen, X.-Q. Wang, B. Sun, X. Li, Y. Zhang, J. Shi, Y. Yu, L. Zhang, M. Liu and H.-B. Yang, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 5597; (i) L.-J. Chen, Y.-Y. Ren, N.-W. Wu, B. Sun, J.-Q. Ma, L. Zhang, H. Tan, M. Liu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 11725; (j) X.-Q. Wang, W. Wang, G.-Q. Yin, Y.-X. Wang, C.-W. Zhang, J.-M. Shi, Y. Yu and H.-B. Yang, *Chem. Commun.*, 2015, **51**, 16813; (k) L. Xu and H.-B. Yang, *Chem. Rec.*, 2016, **16**, 1274; (l) W. Zheng, L.-J. Chen, G. Yang, B. Sun, X. Wang, B. Jiang, G.-Q. Yin, L. Zhang, X. Li, M. Liu, G. Chen and H.-B. Yang, *J. Am. Chem. Soc.*, 2016, **138**, 4927; (m) B. Jiang, J. Zhang, J.-Q. Ma, W. Zheng, L.-J. Chen, B. Sun, C. Li, B.-W. Hu, H. Tan, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2016, **138**, 738; (n) W. Zheng, G. Yang, N. Shao, L.-J. Chen, B. Ou, S.-T. Jiang, G. Chen and H.-B. Yang, *J. Am. Chem. Soc.*, 2017, **139**, 13811; (o) Y.-X. Wang, Q.-F. Zhou, L.-J. Chen, L. Xu, C.-H. Wang, X. Li and H.-B. Yang, *Chem. Commun.*, 2018, **54**, 2224; (p) W. Zheng, W. Wang, S.-T. Jiang, G. Yang, Z. Li, X.-Q. Wang, G.-Q. Yin, Y. Zhang, H. Tan, X. Li, H. Ding, G. Chen and H.-B. Yang, *J. Am. Chem. Soc.*, 2019, **141**, 583; (q) X.-Q. Wang, W.-J. Li, W. Wang, J. Wen, Y. Zhang, H. Tan and H.-B. Yang, *J. Am. Chem. Soc.*, 2019, **141**, 13923.
- 10 (a) C.-K. Hui, B. W.-K. Chu, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2002, **41**, 6178; (b) V. W.-W. Yam, C.-K. Hui, K. M.-C. Wong, N. Zhu and K.-K. Cheung, *Organometallics*, 2002, **21**, 4326; (c) K. Campbell, R. McDonald, M. J. Ferguson and R. R. Tykwinski, *J. Organomet. Chem.*, 2003, **683**, 379; (d) T. Hasegawa, H. Goto, Y. Furusho, H. Katagiri and E. Yashima, *Angew. Chem., Int. Ed.*, 2007, **46**, 5885; (e) S. Y.-L. Leung, W. H. Lam, N. Zhu and V. W.-W. Yam, *Organometallics*, 2010, **29**, 5558; (f) J. Stahl, W. Mohr, L. de Quadras, T. B. Peters, J. C. Bohling, J. M. Martín-Alvarez, G. R. Owen, F. Hampel and J. A. Gladysz, *J. Am. Chem. Soc.*, 2007, **129**, 8282; (g) G. Fuhrmann, T. Debaerdemaeker and P. Bäuerle, *Chem. Commun.*, 2003, 948; (h) P. Bäuerle, M. Ammann, M. Wilde, G. Götz, E. Mena-Osteritz, A. Rang and C. A. Schalley, *Angew. Chem., Int. Ed.*, 2007, **46**, 363; (i) V. W.-W. Yam, *Acc. Chem. Res.*, 2002, **35**, 55; (j) K. M.-C. Wong and V. W.-W. Yam, *Acc. Chem. Res.*, 2011, **44**, 424; (k) V. W.-W. Yam, V. K.-M. Au and S. Y.-L. Leung, *Chem. Rev.*, 2015, **115**, 7589; (l) A. K.-W. Chan and V. W.-W. Yam, *Acc. Chem. Res.*, 2018, **51**, 3041.
- 11 (a) T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022; (b) W. Wang, B. Sun, X.-Q. Wang, Y.-Y. Ren, L.-J. Chen, J. Ma, Y. Zhang, X. Li, Y. Yu, H. Tan and H.-B. Yang, *Chem. – Eur. J.*, 2015, **21**, 6286; (c) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294; (d) T. Ogoshi and T. Yamagishi, *Chem. Commun.*, 2014, **50**, 4776; (e) C. Li, *Chem. Commun.*, 2014, **50**, 12420; (f) N. L. Strutt, H. Zhang, S. T. Schneebeli and J. F. Stoddart, *Acc. Chem. Res.*, 2014, **47**, 2631; (g) W. Si, P. Xin, Z.-T. Li and J.-L. Hou, *Acc. Chem. Res.*, 2015, **48**, 1612; (h) T. Ogoshi, T.-a. Yamagishi and Y. Nakamoto, *Chem. Rev.*, 2016, **116**, 7937; (i) B. Jiang, W. Wang, Y. Zhang, Y. Lu, C.-W. Zhang, G.-Q. Yin, X.-L. Zhao, L. Xu, H. Tan, X. Li, G.-X. Jin and H.-B. Yang, *Angew. Chem., Int. Ed.*, 2017, **56**, 14438; (j) X.-Q. Wang, W. Wang, W.-J. Li, L.-J. Chen, R. Yao, G.-Q. Yin, Y.-X. Wang, Y. Zhang, J. Huang, H. Tan, Y. Yu, X. Li, L. Xu and H.-B. Yang, *Nat. Commun.*, 2018, **9**, 3190; (k) S. Fa, T. Kakuta, T.-A. Yamagishi and T. Ogoshi, *CCS Chem.*, 2019, **1**, 50; (l) X.-Q. Wang, W. Wang, W.-J. Li, Y. Qin, G.-Q. Yin, W.-L. Jiang, X. Li, S. Wu and H.-B. Yang, *Org. Chem. Front.*, 2019, **6**, 1686.
- 12 (a) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668; (b) T. Ogoshi, T. Aoki, R. Shiga, R. Iizuka, S. Ueda, K. Demachi, D. Yamafuji, H. Kayama and T.-A. Yamagishi, *J. Am. Chem. Soc.*, 2012, **134**, 20322; (c) T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T.-A. Yamagishi, Y. Hayashi and S. Kawachi, *Chem. – Eur. J.*, 2012, **18**, 7493; (d) S. Dong, J. Yuan and F. Huang, *Chem. Sci.*,

- 2014, **5**, 247; (e) S.-H. Li, H.-Y. Zhang, X. Xu and Y. Liu, *Nat. Commun.*, 2015, **6**, 7590; (f) G. Yu, D. Wu, Y. Li, Z. Zhang, L. Shao, J. Zhou, Q. Hu, G. Tang and F. Huang, *Chem. Sci.*, 2016, **7**, 3017.
- 13 (a) C. J. Bruns and J. F. Stoddart, *Acc. Chem. Res.*, 2014, **47**, 2186, and references therein; (b) A. Goujon, E. bMoulin, G. Fuks and N. Giuseppone, *CCS Chem.*, 2019, **1**, 83.
- 14 (a) D. A. Leigh, V. Marcos and M. R. Wilson, *ACS Catal.*, 2014, **4**, 4490; (b) R. Bordolli and S. M. Goldup, *J. Am. Chem. Soc.*, 2014, **136**, 4817; (c) S. Hoekman, M. O. Kitching, D. A. Leigh, M. Pappmeyer and D. Roke, *J. Am. Chem. Soc.*, 2015, **137**, 7656; (d) M. Galli, J. E. M. Lewis and S. M. Goldup, *Angew. Chem., Int. Ed.*, 2015, **54**, 13545; (e) Y. Cakmak, S. Erbas-Cakmak and D. A. Leigh, *J. Am. Chem. Soc.*, 2016, **138**, 1749; (f) E. M. G. Jamieson, F. Modicom and S. M. Goldup, *Chem. Soc. Rev.*, 2018, **47**, 5266; (g) M. A. Jinks, A. de Juan, M. Denis, C. J. Fletcher, M. Galli, E. M. G. Jamieson, F. Modicom, Z. Zhang and S. M. Goldup, *Angew. Chem., Int. Ed.*, 2018, **57**, 14806; (h) N. H. Evans, *Chem. – Eur. J.*, 2018, **24**, 3101; (i) N. Pairault and J. Niemeyer, *Synlett*, 2018, 689.