



Cite this: *Dalton Trans.*, 2018, 47, 2492

Received 19th December 2017,
Accepted 18th January 2018

DOI: 10.1039/c7dt04792d

rsc.li/dalton

Studies towards the synthesis of Pd(II)-containing [2] and [3]catenanes in aqueous media†

E. M. López-Vidal,[†] A. Prokofjevs,^b I. C. Gibbs-Hall,^b E. J. Dale,^b J. M. Quintela^a and C. Peinador[†]

Here is reported the investigation of a synthetic route for the preparation of Pd(II)-containing catenanes in aqueous media. A pseudorotaxane intermediate was prepared, which can potentially be converted into a series of catenanes. From the pseudorotaxane, using a Pd(II)-driven clipping step a dinuclear [3]catenane was obtained in the solid state.

The synthesis of mechanically interlocked molecules (MIMs; *i.e.* rotaxanes, catenanes, and molecular knots)^{1,2} has attracted substantial interest among scientists, not only because of their intrinsic beauty, or the substantial synthetic challenge that they signify, but for other more practical reasons like their prospective use in the development of molecular-scale machinery.^{3,4}

Besides the initial statistical and directed approaches used for the synthesis of MIMs,⁵ template-directed methods have dominated the field since the seminal work by Sauvage *et al.*, who proposed the use of tetrahedral Cu(I) complexes for the preorganization of phenanthroline-based threads and their subsequent conversion into [2]catenanes.^{2,6} To date, all known weak intermolecular interactions have been used for the template-based strategy (*e.g.* hydrogen bonding, π - π interactions, *etc.*).^{1,2} For instance, donor-acceptor π - π interactions have been extensively used for templating the threading of molecular strands through macrocycles, creating pseudorotaxane architectures that can be subsequently converted into the corresponding MIMs by covalent capture (*e.g.* olefin metathesis, alkyne homocoupling, Cu(I)-catalyzed azide-alkyne cycloaddition, *etc.*).⁷ Even though these template-directed

approaches have demonstrated their usefulness, there is still a great need for the development of synthetic strategies capable of producing targeted mechanically interlocked molecules *via* self-assembly of rationally designed components.

In this context, metal-directed self-assembly⁸ has proven to be a very useful tool in those cases where transition metal ions work as templating agents by gathering and organizing ligands around them or as active structural units of the MIM,⁹ serving, for example, as ring closing elements converting pseudorotaxanes into catenanes.¹⁰

Making use of the strategies outlined above, π - π interactions and coordination to metal complexes, we have reported in a previous work the preparation of a [2]catenane in aqueous media by following a stepwise metal-directed strategy.¹¹ As shown in Scheme 1a, this approach consists of the threading of the electron-rich dioxoaryl-based molecular axle **1**²⁺ through the cavity of a preformed electron-deficient metallacycle, yielding the corresponding pseudorotaxane, followed by a kinetically controlled metal-directed cyclization step of the corresponding pseudorotaxane producing the catenane as the main product.

Based on this previous work, we present here the results obtained of our attempted synthesis of [2] and [3]catenanes, as well as the double [2]catenane, which could potentially arise from the substitution of the square-planar complex (en)Pd(NO₃)₂, which has two labile ligands at *cis* positions,⁸ with the complex [Pd(CH₃CN)₄](BF₄)₂. As shown in Scheme 1b, the use of this tetravalent complex, with four labile ligands, would substantially increase the number of potential topologies obtained after the clipping step upon pseudorotaxane formation. The possibility of the ligand coordinating the metal complex in *cis* and/or *trans* would result, potentially, in the formation of 2 isomers of the [2]catenane, 3 isomers of the [3]catenane or a double-[2]catenane. In order to simplify the NMR analysis of the products, we decided to utilise **CBPQT**⁴⁺, a π -deficient receptor,¹² instead of the Pt(II) metallacycle previously used, since **CBPQT**⁴⁺ has a higher symmetry order which would result in simpler NMR spectra.

We began our investigations by studying the interactions concerning the different components of the designed system,

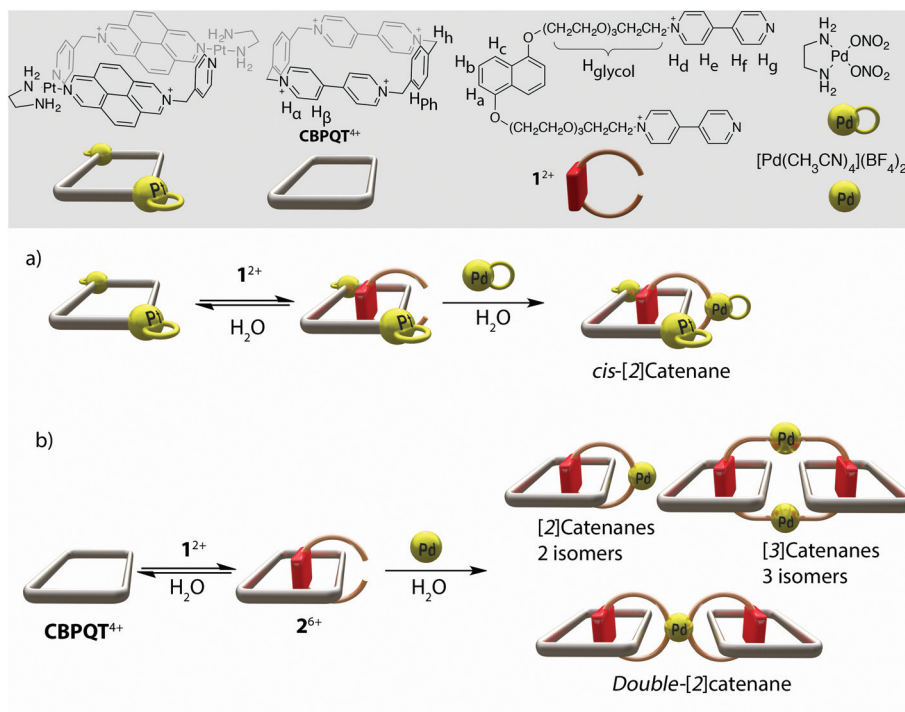
^aDepartamento de Química and Centro de Investigaciones Científicas Avanzadas (CICA). Facultad de Ciencias, Universidade da Coruña, 15071 A Coruña, Spain.
E-mail: E.M.Lopez.Vidal@bath.ac.uk, carlos.peinador@udc.es

^bDepartment of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA

†Electronic supplementary information (ESI) available: Synthetic procedures and NMR, HR-ESI MS and X-ray data (PDF). X-ray crystallographic data in CIF format. CCDC 1812494–1812495. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt04792d

‡Current address: Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.





Scheme 1 Potential topologies arising from a stepwise metal-directed strategy for catenane formation using a Pd(II) square-planar complex with two labile ligands at *cis* positions (a) or with four labile ligands (b).

starting with the first reaction of our intended route, namely, the pseudorotaxane synthesis by self-assembly of CBPQT⁴⁺ with the axle 1²⁺, which contains an electron-rich 1,5-dioxonaphthalene subunit. Thus, addition of 1 equiv. of CBPQT·4Cl to an aqueous solution of 1·2Cl (5 mM) resulted in a prominent colour change, from orange to purple, suggesting that a new charge-transfer interaction between the electron-rich 1,5-dioxonaphthalene subunit in 1²⁺ and the electron-poor regions of CBPQT⁴⁺ had been established, which is a qualitative indication of the formation of the pseudorotaxane 2⁶⁺ (Scheme 1b).

The ¹H NMR spectrum of the reaction mixture in D₂O (Fig. 1) displays signals in good agreement with the expected pseudorotaxane 2⁶⁺. Consequently, the assembly of 2⁶⁺ results in an upfield shift of the naphthalene core protons, suggesting that the electron-rich aromatic system is positioned within the cavity of the tetracationic receptor. Consequently, the donor-acceptor π-π interactions also promote the upfield shift of the nuclei H_α and H_β of the viologen-based box.

Furthermore, both the shielding of H_c (Δδ = -4.73 ppm) and the deshielding (Δδ = 0.22 ppm) of the aromatic protons of the phenylene ring (H_{ph}) can be interpreted as arising from C-H...π interactions between both structural elements, providing further evidence in support of the proposed structure of 2⁶⁺. Moreover, the signals corresponding to the CBPQT⁴⁺ subunit within 2⁶⁺ are duplicated, as compared to those in the free macrocyclic host, which results from the reduced symmetry of the pseudorotaxane. Nevertheless, the ¹H NMR spectrum also displays peaks which are attributable to free

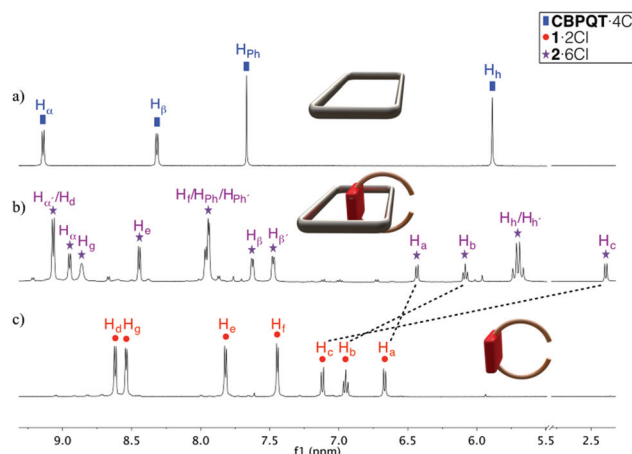


Fig. 1 Partial ¹H NMR spectra (298 K, 500 MHz, D₂O) illustrating salt effects in the formation of 2⁶⁺ from CBPQT⁴⁺ and 1²⁺. (a) CBPQT⁴⁺; (b) equimolar solution of CBPQT⁴⁺ and 1²⁺ in 0.7 M NaCl; (c) 1²⁺.

CBPQT⁴⁺ and 1²⁺, suggesting that all three species exist in equilibrium, which is slow compared to the ¹H NMR timescale (see Fig. S1†).

Based on the integration of the ¹H NMR signals corresponding to 1²⁺, CBPQT⁴⁺, and 2⁶⁺, the equilibrium constant for pseudorotaxane formation in D₂O at 298 K is 2.5 ± 0.5 × 10³ M⁻¹. As could be reasonably anticipated, dissociation of 2⁶⁺ into the starting components can be promoted by raising the temperature of the solution (see Fig. S2†). Conversely,



increasing the ionic strength of the reaction medium by adding NaCl enhances the hydrophobic effect which shifts the equilibrium towards the formation of 2^{6+} (see Fig. 1b and Fig. S3†). This very same effect was obtained using the non-coordinating neutral salt NaNO₃. For instance, the equilibrium constant measured in 0.7 M NaCl solution is $1.6 \pm 0.3 \times 10^4 \text{ M}^{-1}$. Considering these results, it should be noted that addition of a neutral salt is necessary in order to avoid the disentangling of the pseudorotaxane in the envisioned clipping step leading to the targeted catenanes.

Our initial attempts to obtain, by different methods, suitable single crystals of 2^{6+} for XRD, from the solution of the pseudorotaxane in 0.7 M NaCl, were completely unsuccessful. In order to modulate the solubility of the species in water, we decided to precipitate the cation as its tetrachlorozincate salt.¹³ Addition of ZnCl₂ (10 equiv.) to the solution of 2^{6+} , prepared by mixing CBPQT⁴⁺ and 1^{2+} in 0.7 M_(aq) NaCl, resulted in precipitation of a purple solid, substantially reducing the amount of 2^{6+} present in solution. To confirm the identity of this purple precipitate, it was collected and subsequently redissolved in D₂O. A ¹H NMR assay of the resulting solution matched that of the pseudorotaxane 2^{6+} , with no changes in the spectrum resulting from interaction of basic pyridine nitrogens with Zn²⁺. Since addition of an excess of ZnCl₂ to the solution of 1^{2+} also did not result in any significant changes to the ¹H NMR spectrum, neither 2^{6+} nor 1^{2+} appears to engage in strong N...Zn interactions in solution. More significantly, this method allowed us to obtain single crystals suitable for XRD studies. Thus, purple plate-like crystals were produced by storing the liquid fraction of the above-mentioned mixture, prepared by adding 10 equiv. of ZnCl₂ to the solution of CBPQT⁴⁺ and 1^{2+} in 0.7 M_(aq) NaCl, for several days at room temperature. The single crystal structure (Fig. 2) clearly supports the formation of the expected pseudorotaxane, with the electron-rich dioxyaryl moiety of 1^{2+} inserted within the hydrophobic cavity of CBPQT⁴⁺ and the geometrical parameters being in good agreement with the establishment of π - π interactions.

Unexpectedly, the obtained structure has the formula $[2(\text{ZnCl}_3)_2](\text{ZnCl}_4)_2$ instead of $2 \cdot 3(\text{ZnCl}_4)$, with the terminal pyridyl N of the axle 1^{2+} capped with anionic ZnCl₃⁻ moieties.¹⁴ In light of this observation, it is tempting to describe the observed folding of the $[2(\text{ZnCl}_3)_2]^{4+}$ cation as a consequence of an attractive interaction between the bipyridinium rings within CBPQT⁴⁺ and those on the $1(\text{ZnCl}_3)_2$ thread ($\angle_{\text{planes}} = 9.4$ and 4.6° and $d_{\text{cent}} = 4.0$ and 4.0 \AA , respectively, for the two symmetrically independent pseudorotaxanes within the unit cell of the *P* $\bar{1}$ single crystal). Since this coordination-induced folding is also likely to limit the conformational mobility of the supramolecule, it could also explain the facile crystallization of 2·6Cl upon treatment with ZnCl₂.

We then proceeded to explore the products resulting from the self-assembly between 1^{2+} and the Pd(II) complex $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$, which is necessary for the clipping step in our intended synthesis (Scheme 1). Therefore, addition of 1·2Cl (1 equiv.) to an aqueous solution of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (0.5 equiv.) resulted in the self-assembly of the siamese metallacyclophane $3 \cdot (\text{BF}_4)_2\text{Cl}_4$ (Scheme 2). The resulting ¹H NMR

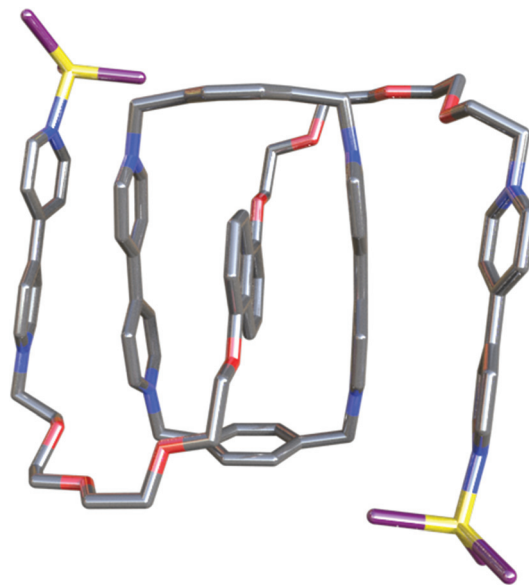
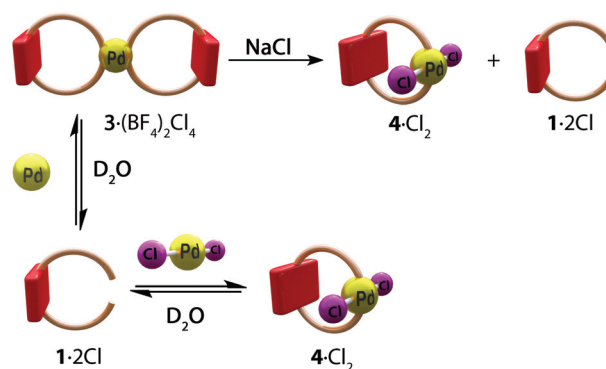


Fig. 2 Projection of one of the two symmetrically independent pseudorotaxanes $[2(\text{ZnCl}_3)_2]^{4+}$ within the unit cell of 2^{6+} , the *P* $\bar{1}$ single crystal of $[2(\text{ZnCl}_3)_2][(\text{ZnCl}_4)_2]$.

spectrum shows all of the bipyridinium signals in 1^{2+} moving downfield as a result of coordination to the metal center ($\Delta\delta_{\text{Hg}} = 1.01 \text{ ppm}$, $\Delta\delta_{\text{Hf}} = 0.60 \text{ ppm}$, $\Delta\delta_{\text{He}} = 0.29 \text{ ppm}$, $\Delta\delta_{\text{Hd}} = 0.28 \text{ ppm}$, see Fig. S9ii†). HR-ESI mass spectrometry further confirmed the identity of 3^{6+} as the self-assembled product (see Fig. S15†).

In order to test the effect of the addition of NaCl and NaNO₃ on the self-assembly of the metallacyclophanes, as this would be a prerequisite for further assembly of the targeted catenanes (*vide supra*), those salts (70 equiv.) were added to solutions of 1^{2+} (1 equiv.) and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (0.5 equiv.) in D₂O.

Whilst the addition of NaNO₃ did not change the outcome of the self-assembly process (Fig. S9viii†), the NMR spectra resulting from the assay with NaCl show the self-assembly of a 1 : 1 mixture of 4^{2+} , along with the free axle 1^{2+} (Fig. S9v†). This



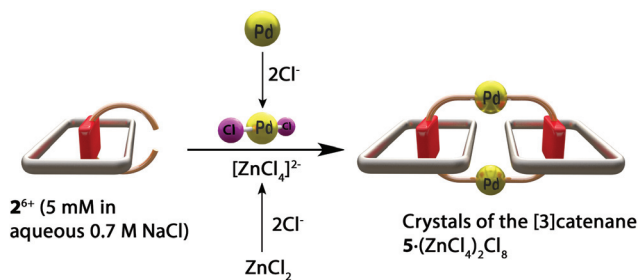
Scheme 2 Self-assembly of the metallacyclophanes 3^{6+} and 4^{2+} from 1^{2+} and the Pd(II) complex $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ in the absence and presence of salts (NaCl or NaNO₃).



situation was also confirmed by HR-ESI mass spectrometry (see Fig. S21 and S22†). These results are in good agreement with the well-known *trans* effect of chloride anions, with the added excess of the halide promoting the blocking of two *trans* positions of the Pd(II) metal center.¹⁵

Further experiments were carried out with the Pd(II) complex Pd(CH₃CN)₂Cl₂ in place of [Pd(CH₃CN)₄](BF₄)₂. The results show that self-assembly does not depend on the complex used, but rather on the salt present in excess in the reaction mixture (see Fig. S9†).

We proceeded with our intended plan for the synthesis of the targeted catenanes by studying the interactions of the pseudorotaxane 2⁶⁺ with the square planar complex [Pd(CH₃CN)₄](BF₄)₂. The ¹H NMR spectrum recorded at room temperature after addition of stoichiometric amounts of the metal center to equimolar solutions of 1·2Cl and CBPQT·4Cl (5 mM) in D₂O, in either 0.7 M NaNO₃ or NaCl, appears to show the formation of very complex reaction mixtures (Fig. S23 and S24i†). Moreover, the identity of the species after addition of the metal center could not be determined by mass spectrometry. Surprisingly, addition of ZnCl₂ (10 equiv.) to an equimolar mixture of the axle 1·2Cl, CBPQT·4Cl and [Pd(CH₃CN)₄](BF₄)₂ (5 mM) in D₂O (0.7 M NaCl) produced changes in the ¹H NMR spectrum (Fig. S24ii†). In order to determine the structure of the self-assembled species, several crystallization experiments were carried out using the previous solution. Fortunately, the slow evaporation of this earlier solution allowed us once again to obtain purple single crystals which were appropriate for XRD. The obtained structure revealed the formation of the [3]catenane 5·(ZnCl₄)₂Cl₈ consisting of two pseudorotaxane subunits of 2⁶⁺ connected by the coordinating bipyridine subunits to two PdCl₂ centers (Fig. 3). The formation and crystallization of the obtained *trans/trans*-[3]catenane can be explained on the basis of two key factors: (i) the



Scheme 3 Reaction conditions for the preparation of single crystals of the [3]catenane 5 (ZnCl₄)₂Cl₈.

in situ blocking of two *trans*-positions on the complex [Pd(CH₃CN)₄](BF₄)₂, and (ii) modulation of the solubility of the resulting catenane by introduction of poorly polarizable [ZnCl₄]²⁻ anions in the reaction media (Scheme 3).

In addition to the expected π - π interactions associated with the CBPQT-dioxyaryl host-guest aggregation, there are also π - π interactions between two viologen-like motifs corresponding to two different CBPQT units. The PdCl₂ centers are also involved in stabilizing the structure by means of Pd-Cl...H-C hydrogen bonds (Fig. 3).¹⁶

Crystals of 5·(ZnCl₄)₂Cl₈ were dissolved in D₂O and dilution experiments performed on this solution resulted in ¹H NMR spectra containing two sets of signals which confirms the existence of two species in solution as one set of signals becomes more intense at decreasing concentrations. We propose that the nature of this second species corresponds to the [2]catenane 6⁶⁺ (Scheme S5†) which consists of a lower number of subcomponents compared to 5¹²⁺, being favored at lower concentrations.

Conclusions

In summary, we have reported herein our studies on the preparation of Pd(II)-containing catenanes in aqueous media using a synthetic route that implies self-assembly of the pseudorotaxane 2⁶⁺ as a synthetic intermediate followed by a Pd(II)-driven clipping step. The self-assembly of 2⁶⁺ takes advantage of donor-acceptor π - π interactions between 1²⁺ and CBPQT⁴⁺ and the hydrophobic effect, with addition of neutral salts to the reaction mixture increasing pseudorotaxane formation by raising the ionic strength of the medium. Coordination of the terminal N atoms of 1²⁺ to ZnCl₃ motifs facilitates pseudorotaxane folding and subsequent crystallization. In order to test the Pd(II)-driven clipping of 1²⁺, this bidentate ligand was reacted with [Pd(CH₃CN)₄](BF₄)₂, which produced the metallocycle 3⁶⁺ or 4²⁺. Remarkably, 3⁶⁺ can be converted into 4²⁺ by *in situ* blocking of the two *trans* positions of [Pd(CH₃CN)₄](BF₄)₂ with chloride anions. Although attempts on the self-assembly of the targeted catenanes led to complex mixtures of products in solution, we were able to crystallize a butterfly-like shaped [3]catenane, 5·(ZnCl₄)₂Cl₈, which is one of the few examples of [3]catenanes self-assembled in aqueous media.¹⁷

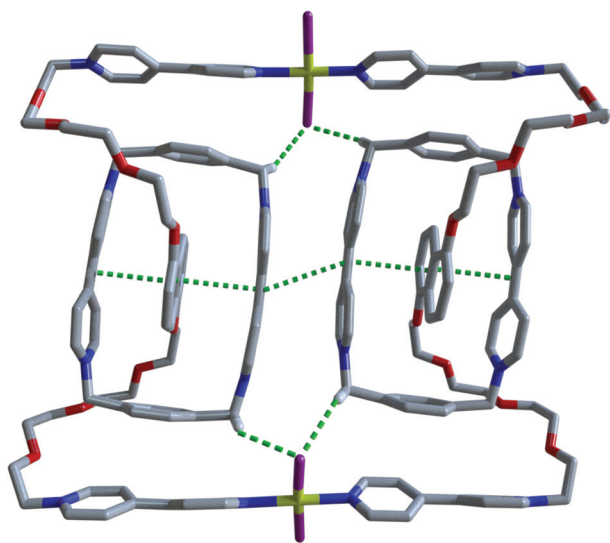


Fig. 3 Crystal structure of the [3]catenane 5¹²⁺. Pd-Cl...H-C hydrogen bonds and π - π interactions are represented as green dotted lines.



Conflicts of interest

There are no conflicts to declare.

Author contributions

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

Funding sources

This research was supported by the Ministerio de Economía, Industria y Competitividad (Ministerio de Economía y Competitividad FEDER, Grant CTQ2016-75629-P).

Acknowledgements

We are enormously grateful to Prof. Sir James Fraser Stoddart (2016 Nobel Laureate in Chemistry) for supervising and hosting part of this research in his laboratory at Northwestern University. We also thank Ms Charlotte Stern (Northwestern University) for the refinement of the crystal structures reported in this work. E. M. L.-V. thanks the Ministerio de Economía, Industria y Competitividad (FPI program).

Notes and references

- J.-P. Sauvage and C. Dietrich-Buchecker, *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, 1999.
- P. D. Beer, M. R. Sambrook and D. Curiel, *Chem. Commun.*, 2006, 2105–2117; J. A. Faiz, V. Heitz and J.-P. Sauvage, *Chem. Soc. Rev.*, 2009, **38**, 422–442; J. D. Crowley, S. M. Goldup, A.-L. Lee, D. A. Leigh and R. T. McBurney, *Chem. Soc. Rev.*, 2009, **38**, 1530–1541; A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.*, 2009, **38**, 875–882; K. D. Hanni and D. A. Leigh, *Chem. Soc. Rev.*, 2010, **39**, 1240–1251; J. E. Beves, B. A. Blight, D. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.*, 2011, **50**, 9260–9327; R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434–5464; V. N. Vukotic and S. J. Loeb, *Chem. Soc. Rev.*, 2012, **41**, 5896–5906; G. T. Spence and P. D. Beer, *Acc. Chem. Res.*, 2012, **46**, 571–586.
- B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, 2001; V. Balzani, M. Venturi and A. Credi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003.
- C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart and J. R. Heath, *Science*, 2000, **289**, 1172–1175; V. Balzani, A. Credi, F. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348–3391; J.-P. Sauvage, *Chem. Commun.*, 2005, 1507–1510; E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191; A. Coskun, J. M. Spruell, G. Barin, W. R. Dichtel, A. H. Flood, Y. Y. Botros and J. F. Stoddart, *Chem. Soc. Rev.*, 2012, **41**, 4827–4859; C. J. Bruns and J. F. Stoddart, *Acc. Chem. Res.*, 2014, **47**, 2186–2199.
- H. L. Frisch and E. Wasserman, *J. Am. Chem. Soc.*, 1961, **83**, 3789–3795; G. Schill, *Catenanes, Rotaxanes and Knots*, Academic Press, New York, 1971; G. Schill and C. Zürcher, *Naturwissenschaften*, 1971, **58**, 40–45.
- C. O. Dietrich-Buchecker and J.-P. Sauvage, *Chem. Rev.*, 1987, **874**, 795–810; B. Champin, P. Mobian and J.-P. Sauvage, *Chem. Soc. Rev.*, 2007, **36**, 358–366.
- 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**, 1750–1761; J. F. Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1802–1820; S. Li, M. Liu, B. Zheng, K. Zhu, F. Wang, N. Li, X.-L. Zhao and F. Huang, *Org. Lett.*, 2009, **11**, 3350–3353.
- P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502–518; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417–425; D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982; B. H. Northrop, Y.-R. Zheng, K.-W. Chi and P. J. Stang, *Acc. Chem. Res.*, 2009, **42**, 1554–1563.
- M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720–723; M. Fujita, N. Fujita, K. Ogura and K. Yamaguchi, *Nature*, 1999, **400**, 52–55; M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53–61; A. Hori, T. Sawada, K. Yamashita and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 4896–4899.
- D. M. Whang, K. M. Park, J. Heo, P. Ashton and K. Kim, *J. Am. Chem. Soc.*, 1998, **120**, 4899–4900; K.-M. Park, S.-Y. Kim, J. Heo, D. Whang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2002, **124**, 2140–2147.
- E. M. López-Vidal, M. D. García, C. Peinador and J. M. Quintela, *Chem. – Eur. J.*, 2015, **21**, 2259–2267.
- B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547–1550.
- C. R. K. Glasson, G. V. Meehan, J. K. Clegg, L. F. Lindoy, P. Turner, M. B. Duriska and R. Willis, *Chem. Commun.*, 2008, **10**, 1190–1192.
- W.-T. Chen, D.-S. Liu, S.-M. Ying, H.-L. Chen and Y.-P. Xu, *Inorg. Chem. Commun.*, 2008, **11**, 1212–1214.
- F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163–179.
- G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653–654.
- A. Hori, K. Kumazawa, T. Kusukawa, D. K. Chand, M. Fujita, S. Sakamoto and K. Yamaguchi, *Chem. – Eur. J.*, 2001, **7**, 4142–4149; F. B. L. Cougnon, N. A. Jenkins, G. D. Pantoş and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2012, **51**, 1443–1447; R. S. Forgan, J. J. Gassensmith, D. B. Cordes, M. M. Boyle, K. J. Hartlieb, D. C. Friedman, A. M. Z. Slawin and J. F. Stoddart, *J. Am. Chem. Soc.*, 2012, **134**, 17007–17010.

