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

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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)<sup>1,2</sup> 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.<sup>3,4</sup>

Besides the initial statistical and directed approaches used for the synthesis of MIMs,<sup>5</sup> 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.<sup>2,6</sup> To date, all known weak intermolecular interactions have been used for the template-based strategy (*e.g.* hydrogen bonding,  $\pi$ - $\pi$  interactions, *etc.*).<sup>1,2</sup> For instance, donor-acceptor  $\pi$ - $\pi$  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.*).<sup>7</sup> 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-assembly<sup>8</sup> 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,<sup>9</sup> serving, for example, as ring closing elements converting pseudorotaxanes into catenanes.<sup>10</sup>

Making use of the strategies outlined above,  $\pi$ - $\pi$  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.<sup>11</sup> As shown in Scheme 1a, this approach consists of the threading of the electron-rich dioxoaryl-based molecular axle **1**<sup>2+</sup> 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(NO<sub>3</sub>)<sub>2</sub>, which has two labile ligands at *cis* positions,<sup>8</sup> with the complex [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>. 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**<sup>4+</sup>, a  $\pi$ -deficient receptor,<sup>12</sup> instead of the Pt(II) metallacycle previously used, since **CBPQT**<sup>4+</sup> 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,

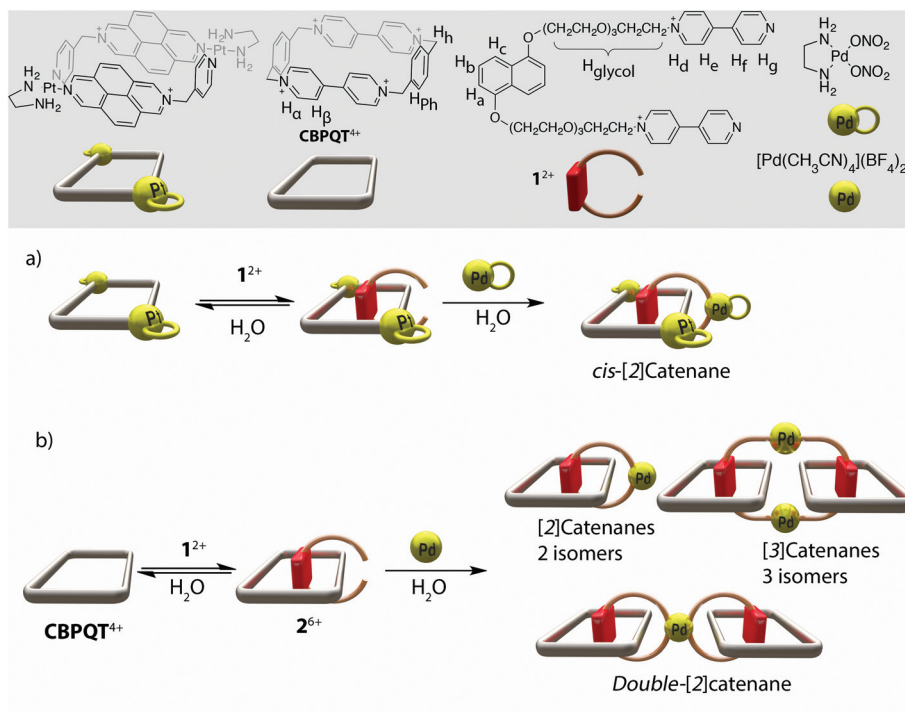
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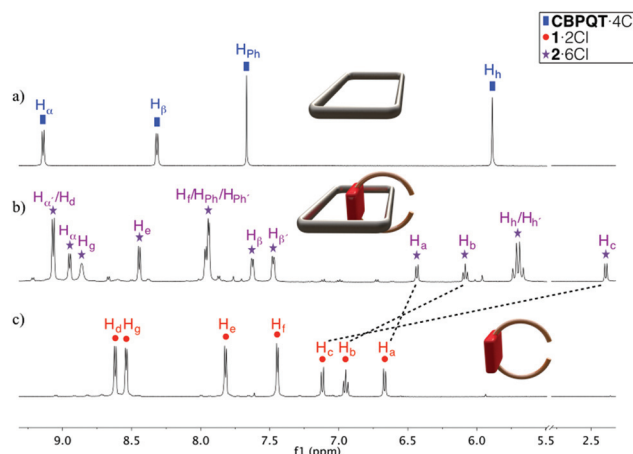


**Scheme 1** Potential topologies arising from a stepwise metal-directed strategy for catenane formation using a Pd(II) square-planar complex with two labile ligands at *cis* positions (a) or with four labile ligands (b).

starting with the first reaction of our intended route, namely, the pseudorotaxane synthesis by self-assembly of  $\text{CBPQT}^{4+}$  with the axle  $1^{2+}$ , which contains an electron-rich 1,5-dioxonaphthalene subunit. Thus, addition of 1 equiv. of  $\text{CBPQT} \cdot 4\text{Cl}$  to an aqueous solution of  $1 \cdot 2\text{Cl}$  (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  $1^{2+}$  and the electron-poor regions of  $\text{CBPQT}^{4+}$  had been established, which is a qualitative indication of the formation of the pseudorotaxane  $2^{6+}$  (Scheme 1b).

The  $^1\text{H}$  NMR spectrum of the reaction mixture in  $\text{D}_2\text{O}$  (Fig. 1) displays signals in good agreement with the expected pseudorotaxane  $2^{6+}$ . Consequently, the assembly of  $2^{6+}$  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  $\pi$ - $\pi$  interactions also promote the upfield shift of the nuclei  $\text{H}_\alpha$  and  $\text{H}_\beta$  of the viologen-based box.

Furthermore, both the shielding of  $\text{H}_c$  ( $\Delta\delta = -4.73$  ppm) and the deshielding ( $\Delta\delta = 0.22$  ppm) of the aromatic protons of the phenylene ring ( $\text{H}_{\text{Ph}}$ ) can be interpreted as arising from C-H $\cdots$  $\pi$  interactions between both structural elements, providing further evidence in support of the proposed structure of  $2^{6+}$ . Moreover, the signals corresponding to the  $\text{CBPQT}^{4+}$  subunit within  $2^{6+}$  are duplicated, as compared to those in the free macrocyclic host, which results from the reduced symmetry of the pseudorotaxane. Nevertheless, the  $^1\text{H}$  NMR spectrum also displays peaks which are attributable to free



**Fig. 1** Partial  $^1\text{H}$  NMR spectra (298 K, 500 MHz,  $\text{D}_2\text{O}$ ) illustrating salt effects in the formation of  $2^{6+}$  from  $\text{CBPQT}^{4+}$  and  $1^{2+}$ . (a)  $\text{CBPQT}^{4+}$ ; (b) equimolar solution of  $\text{CBPQT}^{4+}$  and  $1^{2+}$  in 0.7 M NaCl; (c)  $1^{2+}$ .

$\text{CBPQT}^{4+}$  and  $1^{2+}$ , suggesting that all three species exist in equilibrium, which is slow compared to the  $^1\text{H}$  NMR timescale (see Fig. S1 $\dagger$ ).

Based on the integration of the  $^1\text{H}$  NMR signals corresponding to  $1^{2+}$ ,  $\text{CBPQT}^{4+}$ , and  $2^{6+}$ , the equilibrium constant for pseudorotaxane formation in  $\text{D}_2\text{O}$  at 298 K is  $2.5 \pm 0.5 \times 10^3 \text{ M}^{-1}$ . As could be reasonably anticipated, dissociation of  $2^{6+}$  into the starting components can be promoted by raising the temperature of the solution (see Fig. S2 $\dagger$ ). 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 NaNO<sub>3</sub>. 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.<sup>13</sup> Addition of ZnCl<sub>2</sub> (10 equiv.) to the solution of  $2^{6+}$ , prepared by mixing CBPQT<sup>4+</sup> and  $1^{2+}$  in 0.7 M<sub>(aq)</sub> 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 D<sub>2</sub>O. A <sup>1</sup>H 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 Zn<sup>2+</sup>. Since addition of an excess of ZnCl<sub>2</sub> to the solution of  $1^{2+}$  also did not result in any significant changes to the <sup>1</sup>H 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 ZnCl<sub>2</sub> to the solution of CBPQT<sup>4+</sup> and  $1^{2+}$  in 0.7 M<sub>(aq)</sub> 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 CBPQT<sup>4+</sup> and the geometrical parameters being in good agreement with the establishment of  $\pi$ - $\pi$  interactions.

Unexpectedly, the obtained structure has the formula [2(ZnCl<sub>3</sub>)<sub>2</sub>](ZnCl<sub>4</sub>)<sub>2</sub> instead of 2·3(ZnCl<sub>4</sub>), with the terminal pyridyl N of the axle  $1^{2+}$  capped with anionic ZnCl<sub>3</sub><sup>-</sup> moieties.<sup>14</sup> In light of this observation, it is tempting to describe the observed folding of the [2(ZnCl<sub>3</sub>)<sub>2</sub>]<sup>4+</sup> cation as a consequence of an attractive interaction between the bipyridinium rings within CBPQT<sup>4+</sup> and those on the 1(ZnCl<sub>3</sub>)<sub>2</sub> thread ( $\angle_{\text{planes}} = 9.4$  and  $4.6^\circ$  and  $d_{\text{cent}} = 4.0$  and  $4.0 \text{ \AA}$ , 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 ZnCl<sub>2</sub>.

We then proceeded to explore the products resulting from the self-assembly between  $1^{2+}$  and the Pd(II) complex [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, 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 [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.5 equiv.) resulted in the self-assembly of the siamese metallacyclophane 3·(BF<sub>4</sub>)<sub>2</sub>Cl<sub>4</sub> (Scheme 2). The resulting <sup>1</sup>H NMR

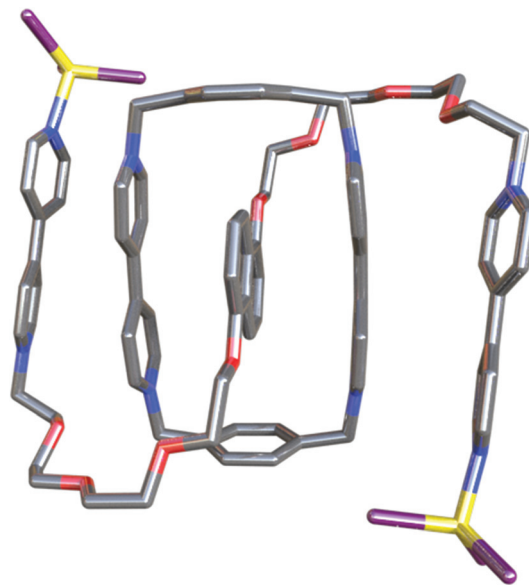
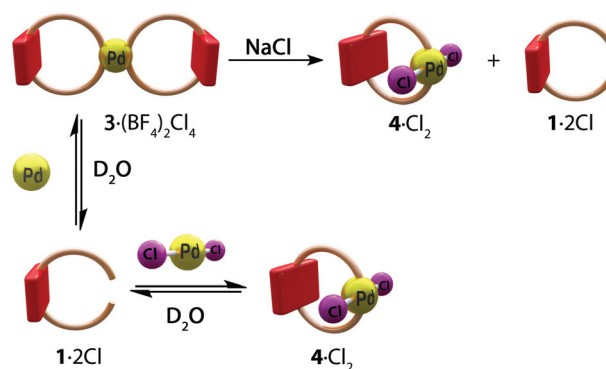


Fig. 2 Projection of one of the two symmetrically independent pseudorotaxanes [2(ZnCl<sub>3</sub>)<sub>2</sub>]<sup>4+</sup> within the unit cell of  $2^{6+}$ , the *P* $\bar{1}$  single crystal of [2(ZnCl<sub>3</sub>)<sub>2</sub>](ZnCl<sub>4</sub>)<sub>2</sub>.

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 NaNO<sub>3</sub> 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 [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (0.5 equiv.) in D<sub>2</sub>O.

Whilst the addition of NaNO<sub>3</sub> 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 [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> in the absence and presence of salts (NaCl or NaNO<sub>3</sub>).

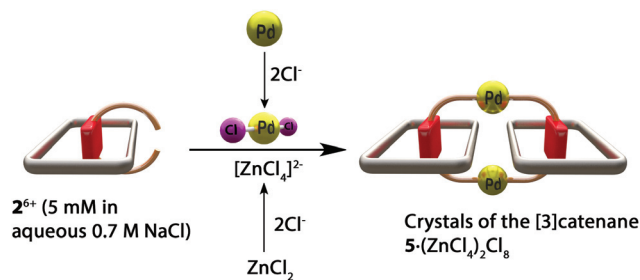




situation was also confirmed by HR-ESI mass spectrometry (see Fig. S21 and S22†). These results are in good agreement with the well-known *trans* effect of chloride anions, with the added excess of the halide promoting the blocking of two *trans* positions of the Pd(II) metal center.<sup>15</sup>

Further experiments were carried out with the Pd(II) complex Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> in place of [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>. 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 2<sup>6+</sup> with the square planar complex [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>. The <sup>1</sup>H 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 D<sub>2</sub>O, in either 0.7 M NaNO<sub>3</sub> 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 ZnCl<sub>2</sub> (10 equiv.) to an equimolar mixture of the axle 1·2Cl, CBPQT·4Cl and [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (5 mM) in D<sub>2</sub>O (0.7 M NaCl) produced changes in the <sup>1</sup>H 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·(ZnCl<sub>4</sub>)<sub>2</sub>Cl<sub>8</sub> consisting of two pseudorotaxane subunits of 2<sup>6+</sup> connected by the coordinating bipyridine subunits to two PdCl<sub>2</sub> 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 (ZnCl<sub>4</sub>)<sub>2</sub>Cl<sub>8</sub>.

*in situ* blocking of two *trans*-positions on the complex [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, and (ii) modulation of the solubility of the resulting catenane by introduction of poorly polarizable [ZnCl<sub>4</sub>]<sup>2-</sup> anions in the reaction media (Scheme 3).

In addition to the expected  $\pi$ - $\pi$  interactions associated with the CBPQT-dioxyaryl host-guest aggregation, there are also  $\pi$ - $\pi$  interactions between two viologen-like motifs corresponding to two different CBPQT units. The PdCl<sub>2</sub> centers are also involved in stabilizing the structure by means of Pd-Cl...H-C hydrogen bonds (Fig. 3).<sup>16</sup>

Crystals of 5·(ZnCl<sub>4</sub>)<sub>2</sub>Cl<sub>8</sub> were dissolved in D<sub>2</sub>O and dilution experiments performed on this solution resulted in <sup>1</sup>H 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 6<sup>6+</sup> (Scheme S5†) which consists of a lower number of subcomponents compared to 5<sup>12+</sup>, 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 2<sup>6+</sup> as a synthetic intermediate followed by a Pd(II)-driven clipping step. The self-assembly of 2<sup>6+</sup> takes advantage of donor-acceptor  $\pi$ - $\pi$  interactions between 1<sup>2+</sup> and CBPQT<sup>4+</sup> 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 1<sup>2+</sup> to ZnCl<sub>3</sub> motifs facilitates pseudorotaxane folding and subsequent crystallization. In order to test the Pd(II)-driven clipping of 1<sup>2+</sup>, this bidentate ligand was reacted with [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>, which produced the metallocycle 3<sup>6+</sup> or 4<sup>2+</sup>. Remarkably, 3<sup>6+</sup> can be converted into 4<sup>2+</sup> by *in situ* blocking of the two *trans* positions of [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> 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·(ZnCl<sub>4</sub>)<sub>2</sub>Cl<sub>8</sub>, which is one of the few examples of [3]catenanes self-assembled in aqueous media.<sup>17</sup>

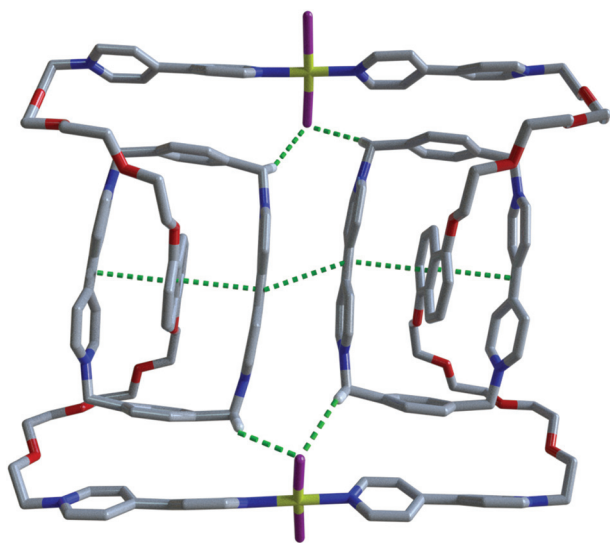


Fig. 3 Crystal structure of the [3]catenane 5<sup>12+</sup>. Pd-Cl...H-C hydrogen bonds and  $\pi$ - $\pi$  interactions are represented as green dotted lines.



## 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.

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