ORGANIC CHEMISTRY







FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue



Cite this: *Org. Chem. Front.*, 2021, **8**, 5280

Efficient one-pot synthesis of [3]catenanes based on Pt(II) metallacycles with a flexible building block†

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Two quadrilateral metallacycles were prepared by coordination-driven self-assembly of a 90° platinum(III) receptor **6** with a flexible donor 1,3-bis(4,4'-bipyridinium)propane **1a** or 1,1-bis(4,4'-bipyridinium)methane **1b**, respectively. Three [3]catenanes (**3**, **4** and **5**) were further prepared by *in situ* addition of crown ethers (DB24C8 or DB30C10) to the yielded metallacycles. By comparing the crystal structures of **1a** and **4**, it was found that the bite angle change of the flexible bidentate donor **1a** (111.0° to 112.3°) is much smaller than that of rigid platinum(III) receptor **6** (90.0° to 83.2°) during metalla-cyclization. The multicomponent [3]catenanes were stabilized by multiple supramolecular interactions, including metal coordination, $\pi - \pi$ stacking, charge transfer, and hydrogen bonding.

Received 17th June 2021, Accepted 21st July 2021 DOI: 10.1039/d1qo00910a rsc.li/frontiers-organic

Introduction

Mechanically interlocked molecules (MIMs) are molecules consisting of subcomponents that are connected by mechanical bonds.1 They have gained much attention from chemists because of not only their unique topological architectures but also their prosperous applications in molecular machines, molecular devices, and smart materials.² Catenanes are a type of MIM composed of two or more mechanically interlocked macrocyclic parts.3 In the past three decades, templatedirected strategies for the synthesis of catenanes and other MIMs, such as rotaxanes, Solomon links, and Borromean rings and knots, have been developed impressively.4 However, the highly efficient preparation of catenanes is still a challenge due to the formation of unexpected polymeric or non-interlocked species during the macrocyclization processes.^{3e-g} In particular, when kinetically controlled reactions are used in the final interlocking step, the thermodynamically favorable but kinetically unfavorable nature of macrocyclization processes will hinder the formation of interlocked products. Instead, the use of dynamic covalent chemistry (DCC, such as imine bond formation, disulfide bond formation, and olefin metathesis) and coordination bonds in the final interlocking step can promote the transformations of unexpected intermediates and byproducts into thermodynamically favored MIMs.⁵ The reversible feature enables product distribution under thermodynamic control, which means that the MIMs with higher thermodynamic stability will be produced with higher efficiency as the reaction reaches an equilibrium.⁶

Coordination-driven self-assembly has great advantages, including various but predictable geometries, high bonding energy, good bond direction and good reversibility. These intrinsic features make it a promising method for the construction of discrete supramolecular coordination complexes (SCCs). A variety of metallacycles, metallacages and other discrete SCCs with fascinating architectures have been prepared through rational design and careful selection of the metal and organic ligands.^{7,8} Because of its modularity and versatility, coordination-driven self-assembly is also a powerful and facile route to provide metal-based macrocyclic supramolecular elements⁹ for the construction of MIMs from simple precursors.10 A number of metal-connected MIMs, including catenanes, rotaxanes, molecular necklaces, Solomon links, and Borromean rings and konts, have been constructed by using this method. 11 The complementary building blocks used in coordination-driven self-assembly are usually structurally rigid conjugated molecules with predefined bite angles. However, the balance of flexibility and rigidity of the ligands also plays a key role in the construction of SCCs. Building blocks with certain flexibility can allow dynamic adaption in the coordination-driven self-assembly, but very flexible linkers are not applicable in most cases. The balance of flexibility and rigidity

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[†] Electronic supplementary information (ESI) available: NMR and mass spectra of the guests, metallacycles and catenanes, host-guest complexation investigation and X-ray analysis data of the guest 1a and catenane 4. CCDC 2079026 and 2079027. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1q000910a

is also significant in the preparation of catenanes. The use of considerably long and highly flexible linkers usually results in the formation of [2]catenanes during the cyclization processes.^{3h} In order to obtain high-order catenanes with more subcomponents, shorter linkers with less flexibility are generally selected. Previously, we have reported the fabrication of metallacycles and metalla-catenanes through Pt(II)-based coordination-driven self-assembly using the 1,2-bis(pyridinium) ethane/dibenzo-24-crown-8 (DB24C8) recognition motif, wherein 1,2-bis(pyridinium)ethane with a slightly flexible ethylene linker acted as a 180° building block. 12 Herein, we want to see whether a more flexible donor with a propylene linker, 1,3-bis(pyridinium)propane, can be used in the construction of SCCs and what bite angle it will have. As monitored by ¹H NMR, ³¹P NMR, and mass spectroscopy and X-ray crystallography analyses, we found that not only quadrilateral metallacycles but also metalla-[3] catenanes can be efficiently prepared by employing this flexible bidentate donor.

From the reported results of Peinador¹³ and us,¹² we knew that the bite angles of 1,1-bis(pyridinium)methane and 1,2-bis (pyridinium)ethane were about 109° and 180°, respectively. We speculated that if the sp³-hybridized propylene carbons are all in stable staggered conformations, the bite angle of 1,3-bis (pyridinium)propane should also be around 109° (Fig. S29†). Therefore, although 1,3-bis(pyridinium)propane is more flexible and has more conformers, it may coordinate with metal acceptors to form metallacycles like 1,1-bis(pyridinium) methane. Herein, both 1,3-bis(4,4'-bipyridinium)propane and 1,1-bis(4,4'-bipyridinium)methane were investigated and compared with each other as the building blocks for the Pt(II)based coordination-driven self-assembly of metallacycles and metalla-catenanes.

Results and discussion

Synthesis of the bis(4,4'-bipyridinium) guests 1a and 1b

As shown in Scheme 1, 1,3-bis(4,4'-bipyridinium)propane 1a and 1,1-bis(4,4'-bipyridinium)methane 1b were conveniently synthesized by N-alkylation of 4,4'-bipyridine and then exchange of anions. Their structures were well characterized by nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass (ESI-MS) spectrometry (Figs. S1-S4†).

The crystals of 1a were obtained by vapor diffusion of isopropyl ether into its acetone solution. The single-crystal X-ray analysis (Fig. 1) indicated that the two bipyridinium units of

Scheme 1 Synthesis of pyridinium-derived guests 1a and 1b.

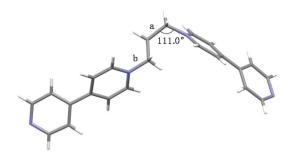


Fig. 1 The crystal structure of 1a. The counterions have been omitted for clarity. Color code: gray = C; white = H; blue = N.

1a are non-coplanar. Because the three propylene carbons on 1a are arranged in the staggered conformations and the C-C bond (Fig. 1a) and N-C bond (Fig. 1b) are basically parallel, the bite angle between the two pyridinium groups should be the same as the C-C-N angle (111.0°), which is a little smaller than that of 1b shown in its crystal structure (112.3°) reported by Peinador and Quintela (Fig. S29†). 13b

Investigation of the host-guest complexation of DB24C8 ⊃ 1a and DB30C10 \supset 1a

Since the host-guest complexation of 1a with crown ethers has never been reported, we firstly investigated their complexation in acetone. The ¹H NMR spectra (Fig. 2) of its mixture solutions with equivalent DB24C8 or DB30C10 (dibenzo-30-crown-10) showed obvious changes on both hosts and 1a. Peaks of H^a, H^b, H^c, H^d and H^e on the guest **1a**, the aromatic protons H^1 and H^2 on DB24C8, and the protons $H^{1'}$, $H^{2'}$, $H^{3'}$ and $H^{4'}$ on DB30C10 all shifted upfield, while H³, H⁴, H⁵, H^{5'} and H^{6'} moved downfield. Only one set of peaks were found in the ¹H NMR spectra of the mixed solutions (Fig. 2b and d), indicating that both of the complexation of DB24C8 \supset 1a and DB30C10 ⊃ 1a are fast-exchange systems on the NMR timescale. The Job plots¹⁴ (Figs. S22 and S24†) based on the ¹H NMR spectro-

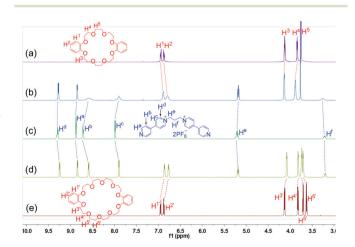


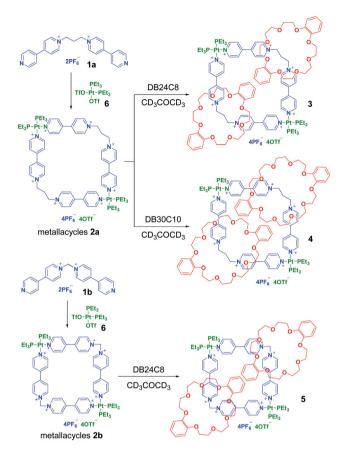
Fig. 2 Partial ¹H NMR spectra (500 MHz, acetone-d₆, 25 °C) of 12.00 mM DB24C8 (a), 12.00 mM 1a + 12.00 mM DB24C8 (b), 12.00 mM 1a (c), 12.00 mM 1a + 12.00 mM DB30C10 (d), and 12.00 mM DB30C10 (e).

scopic data demonstrated that complexes of 1a with both DB24C8 and DB30C10 have 1:1 stoichiometry in solutions.

Furthermore, the 1:1 stoichiometry was confirmed by their ESI-MS spectra. One main peak was observed for [DB24C8 ⊃ $\mathbf{1a} - \mathrm{PF_6}^{\dagger}$: m/z = 947.3587, and one minor peak was found for $[[DB24C8]_2 \supset 1a - PF_6]^+$: m/z = 1395.5655 (Fig. S23†). Nonetheless, the latter is found in very small abundance, indicating that they mainly formed a 1:1 complex in solution. Two relevant peaks were found for the complex of DB30C10 ⊃ 1a with 1:1 stoichiometry, [DB30C10 \supset 1a - PF₆]⁺: m/z = 1035.42387 and [DB30C10 \supset 1a - 2PF₆]²⁺: m/z = 445.2301(Fig. S25†). No peaks were observed for the complexes with other stoichiometries. The association constant (K_a) values of DB24C8 ⊃ 1a and DB30C10 ⊃ 1a were determined to be 2620 (±200) M⁻¹ and 1490 (± 120) M⁻¹, respectively, in CH₃CN by using the UV-vis titration method (Figs. S27 and S28†). Both of them are higher than the previously reported association constant^{13b} of DB24C8 \supset **1b**, 915 \pm 35 M⁻¹, in CH₃CN, probably because the longer propylene linker with higher flexibility is more space-matching and enables better dynamic adaption to be complexed by the crown ethers than the shorter methylene linker.

Preparation of the quadrilateral metallacycles 2a and 2b

As the flexible bis(4,4'-bipyridinium)propane 1a has a similar coordination angle to 1b, it was supposed that it could coordinate with a 90° platinum(II) acceptor to form discrete quadrilateral metallacycles such as 1b. An acetone- d_6 solution of 1aor 1b was stirred with an equimolar 90° Pt(II) receptor (6) at room temperature, which gave rise to the formation of metal assemblies 2a and 2b, respectively (Scheme 2). The ¹H and ³¹P {¹H} NMR spectra of 2a and 2b, together with their ¹H-¹H COSY (correlation spectroscopy) NMR spectra and mass spectrometry, provided solid evidence for the formation of discrete metallacycles. Both the ³¹P{¹H} NMR spectra of 2a and 2b displayed a singlet at -0.30 ppm and -0.23 ppm, respectively, accompanied by a set of symmetrical and uniformed 195Pt satellites, which was consistent with the Pt-N coordination environment (Fig. S6 and S9†). All peaks in their ¹H NMR (Fig. S5 and S8†) and ¹H-¹H COSY NMR spectra (Fig. S7 and S10†) were also clearly assigned. Although the X-ray crystal structure shows a nearly 109° bite angle of 1a in the solid state (Fig. 1), other conformations with slightly different bite angles may exist in solution where the assembly was performed due to its relatively higher flexibility. In the ¹H NMR spectrum of 2a, we observed tiny impure peaks that might belong to the isomeric self-assembly species resulting from the conformational isomerism of the propylene linker. In comparison, no visible impure peaks were found in the ¹H NMR spectrum of 2b, which could be due to the less flexibility of ligand 1b. The ESI-MS measurements further supported the formation of metallacycles 2a and 2b. The ESI-MS spectrum of metallacycle 2a (Fig. S17†) showed two related peaks at m/z = 1224.2068 and 1228.1958, attributed to $[M - 2OTf]^{2+}$ and $[M - 2PF_6]^{2+}$, respectively. For the metallacycle 2b (Fig. S18†), one peak at m/z = 1383.2289 was observed corresponding to $[M + 2K]^{2+}$.



Scheme 2 Synthesis of metallacycles 2a and 2b and [3] catenanes 3, 4,

Synthesis of [3]catenanes 3, 4 and 5

Because of the dynamic nature of the coordination interactions, the in situ addition of crown ethers into the prepared metallacycles 2 resulted in the generation of catenanes. [3] Catenanes 3 and 5 were fabricated by the addition of DB24C8 into the solutions of 2a or 2b (3.0 mM), respectively, at room temperature, while [3]catenane 4 was obtained by the addition of DB30C10 (18.0 mM) into a solution of 2a (3.0 mM). Directly mixing the precursors (1 + 6 + crown ether) in one pot also led to the same results (Fig. S30-35†). After the addition of crown ethers, all the solutions changed from colorless to yellow, which indicated that charge-transfer interactions existed between crown ethers and electron-poor guests.

The dynamic threading processes of metallacycles 2 (2a or 2b) and crown ether (DB24C8 or DB30C10) were observed realtime by ³¹P{¹H} and ¹H NMR spectroscopy. When DB24C8 was added into a 3.0 mM solution of 2a, a new set of peaks corresponding to [3]catenane 3 appeared in the ³¹P{¹H} NMR spectra (Fig. 3). As the amount of DB24C8 increased, 2a gradually converted into 3. Finally, when 18.0 mM DB24C8 was added, the peak related to free metallacycle 2a almost completely disappeared (Fig. 3d). The same trend was also observed in the ¹H NMR spectra (Fig. 4). When 6.0 mM DB24C8 was added into a 3.0 mM solution of 2a, the characteristic peaks indicated

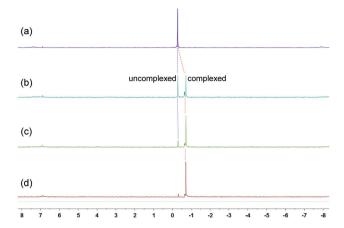


Fig. 3 $^{31}P\{^{1}H\}$ NMR (202 MHz, acetone- d_{6} , 25 °C) spectra of metallacycle 2a (3.0 mM) (a), 2a (3.0 mM) + DB24C8 (6.0 mM) (b), 2a (3.0 mM) + DB24C8 (12.0 mM) (c), and 2a (3.0 mM) + DB24C8 (18.0 mM) (d).

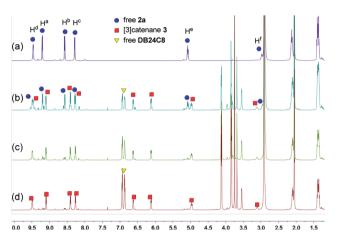


Fig. 4 1 H NMR (500 MHz, acetone- d_{6} , 25 °C) spectra of metallacycle 2a (3.0 mM) (a), 2a (3.0 mM) + DB24C8 (6.0 mM) (b), 2a (3.0 mM) + DB24C8 (12.0 mM) (c), and 2a (3.0 mM) + DB24C8 (18.0 mM) (d).

that the solution mainly contained three different species, the free DB24C8, the free metallacycle 2a and the threaded [3]catenane 3. After more DB24C8 was added, the peaks of 2a decreased gradually. Finally, [3]catenane 3 was formed as the main product (Fig. 4d). Like the host-guest complexation of DB24C8

1a, all aromatic hydrogen signals of the guest moiety 2a shifted upfield, mostly because of the shielding effect and the increase of electron density originated from the charge transfer and CH-O hydrogen bonds, after the formation of 3. The slight upfield shift of the phosphorus signal of 2a should also be attributed to the enrichment of the electron density of 2a after its complexation with the electron-rich crown ethers.

These changes in the ³¹P{¹H} and ¹H NMR spectra all indicated the gradual formation of [3]catenane 3. Similar changes were also observed for 4 (Fig. 5 and 6) and 5 (Fig. 7 and 8). Since there was no great difference in the association constants of DB24C8 \supset 1a, DB30C10 \supset 1a and DB24C8 \supset 1b,

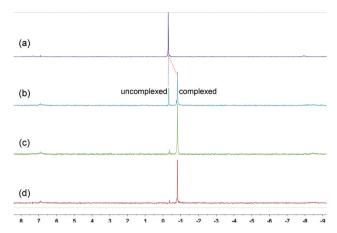


Fig. 5 $^{31}P\{^{1}H\}$ NMR (202 MHz, acetone- d_{6} , 25 °C) spectra of metallacycle 2a (3.0 mM) (a), 2a (3.0 mM) + DB30C10 (6.0 mM) (b), 2a (3.0 mM) + DB30C10 (12.0 mM) (c), and 2a (3.0 mM) + DB30C10 (18.0 mM) (d).

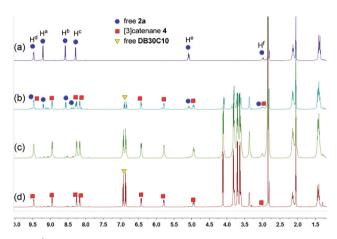


Fig. 6 1 H NMR (500 MHz, acetone- d_{6} , 25 °C) spectra of metallacycle 2a (3.0 mM) (a), 2a (3.0 mM) + DB30C10 (6.0 mM) (b), 2a (3.0 mM) + DB30C10 (12.0 mM) (c), and 2a (3.0 mM) + DB30C10 (18.0 mM) (d).

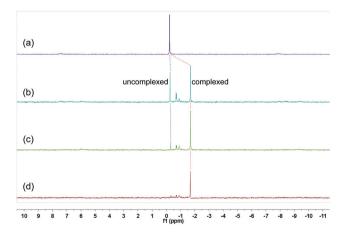


Fig. 7 $^{31}P\{^{1}H\}$ NMR (202 MHz, acetone- d_{6} , 25 °C) spectra of metallacycle 2b (3.0 mM) (a), 2b (3.0 mM) + DB24C8 (6.0 mM) (b), 2b (3.0 mM) + DB24C8 (12.0 mM) (c), 2b (3.0 mM) + DB24C8 (18.0 mM) (d).

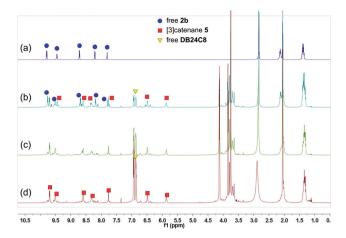


Fig. 8 ¹H NMR (500 MHz, acetone-d₆, 25 °C) spectra of metallacycle 2b (3.0 mM) (a), 2b (3.0 mM) + DB24C8 (6.0 mM) (b), 2b (3.0 mM) + DB24C8 (12.0 mM) (c), and 2b (3.0 mM) + DB24C8 (18.0 mM) (d).

the amounts of crown ethers for complete conversion from free metallacycles to the [3]catenanes 3, 4 and 5 were almost the same.

ESI-MS studies further supported the formation of [3]catenanes. A few peaks belonging to the intact catenanes were found in their MS spectra, but some of them overlapped with their half-fragment peaks (Fig. S19-S21†). Therefore, we further exchanged the mixed counteranions of OTf and PF6to be unified PF6-. The detailed exchange procedures are provided in the ESI.† ¹H and ³¹P{¹H} NMR spectra of the anionexchanged metallacycles (7 and 8) and catenanes (9, 10 and 11) (Fig. S36-S45†) indicated that the exchange of anions did not affect their structures. In the MS spectra of the anionexchanged [3]catenanes, the overlapped half-fragment peaks did not appear. Four related peaks were observed in the MS spectrum of anion-exchanged [3] catenane 9 at m/z =1668.8662, 1064.3447, 1893.1202 and 1533.5529, attributed to $[M - 2PF_6]^{2+}$, $[M - 3PF_6]^{3+}$, $[M + 2MeOH + H_2O + 2K]^{2+}$ and $[M + 2MeOH + H_2O + 2K]^{2+}$ $-4HPF_6 + H + Na]^{2+}$, respectively (Fig. S46†). For [3]catenane 10, three peaks relevant to the intact [3] catenane self-assembly were found at m/z = 1757.0630, 1122.7149 and 1339.5517, corresponding to $[M - 2PF_6]^{2+}$, $[M - 3PF_6]^{3+}$ and $[M - 8HPF_6 +$ Na + NH₄ $]^{2+}$, respectively (Fig. S47†). The ESI-MS spectrum of [3] catenane **11** (Fig. S48†) showed one peak at m/z = 1785.5858, corresponding to $[M + 2H]^{2+}$.

Moreover, the formation of [3]catenanes was unambiguously confirmed by single-crystal X-ray analysis (Fig. 9). The X-ray-quality yellow crystals of [3]catenane 4 were obtained by slow diffusion of methanol into an acetone solution of 2a (3.0 mM) with excess DB30C10 (18.0 mM). The crystal structure of 4 revealed that the bite angle between the two pyridinium groups (112.3°) almost remains the same as that in the free ligand 2a (111.0°, Fig. 1) and the coordination angle of N-Pt-N reduced 6.8° (from the ideal Pt(II) square coordination angle of 90.0° to 83.2°) to meet the demands for the quadrilateral metallacycle with the guest 1a. Two DB30C10 molecules thread

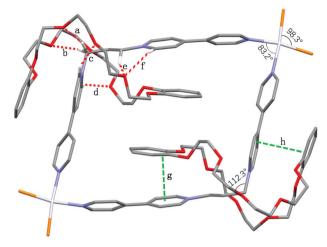


Fig. 9 Single-crystal X-ray structure of [3]catenane 4. The ethyl groups on phosphines, counterions, and H atoms, except for the ones involved in hydrogen bonding, have been omitted for clarity. Hydrogen bond parameters: H···O distance (Å), C-H···O angle (deg); a, 2.314, 161.3; b, 2.396, 159.6; c, 2.400, 158.5; d, 2.403, 137.5; e, 2.549, 133.2; f, 2.541, 141.5. Color code: gray = C; red = O; white = H; blue = N; white = Pt; orange = P.

into the metallacycle 2a with an S-shaped conformation and symmetrically locate on the two diagonal corners of the metallacycle, that is, complex around the propylene groups. The two phenyl rings on the crown ethers are almost parallel to the bipyridine units on the guests inside and outside the metallacycle, and the distances are about 3.5 Å (g and h in Fig. 9), which is a favorable distance for π - π stacking interactions. At the same time, the phenyl rings on the two crown ethers inside the metallacycle are also parallel to each other. Additionally, the ether oxygen atoms of DB30C10 have strong hydrogen bond interactions (a-f in Fig. 9) with some of the hydrogen atoms on the propylene groups or on the pyridinium rings of 1a, which not only stabilize the conformations of the host-guest complex but also strengthen the rigidity of the propylene linker.

Conclusions

In summary, we synthesized a flexible bidentate ligand bis (4,4'-bipyridinium)propane **1a** using bis(4,4'-bipyridinium) methane 1b as a control compound, which could complex with DB24C8 or DB30C10 with high association constants. By coordination-driven self-assembly of these two donors and a 90° platinum(II) receptor, two quadrilateral metallacycles were fabricated efficiently. Taking advantage of the dynamic coordination bonds, three [3]catenanes were obtained quantitatively by the in situ threading of 2 into the crown ethers. By comparing the crystal structures of the free ligand 1a and the coordinated one in [3]catenane 4, it was found that the bite angle between the two pyridinium groups almost remains the same after the formation of the [3]catenane. The bite angle between the two pyridinium groups either in the free ligand 2a

or in the [3]catenane is slightly higher than 109°, while the bite angle of N-Pt-N decreased to 83.2° from the ideal Pt(II) square coordination angle of 90.0° to meet the demands for the formation of the quadrilateral metallacycle. It was believed that the wrapping of crown ethers turns the flexible propylenelinked bidentate ligands 1a rigid and the large bite angle of 1a makes the platinum(II) receptor 6 an adaptable building block in the [3]catenanes. In the future, we will focus on the investigation of ligands with controllable bite angles and their applications in transformable SCCs or molecular machines.

Experimental section

Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed over silica gel (200-300 mesh). NMR spectra were collected on a Bruker AVANCE DMX-500 spectrometer at room temperature. All NMR data are reported in ppm. ³¹P{¹H} NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0), while ¹H NMR and ¹³C ¹H} NMR chemical shifts are reported relative to the residual peak of the deuterated solvents or internal standard tetramethylsilane (TMS). ESI-MS spectra were obtained on an Agilent 1290-6530 UPLC-Q-TOF spectrometer using electrospray ionization. Crystal data were collected on a Bruker D8 Venture (Billerica, Massachusetts, USA). The melting points were measured using a Melting Point M-565 apparatus.

Synthesis of 1,3-bis(4,4'-bipyridinium)propane 1a. A solution of 4,4'-bipyridine (11.60 g, 74.30 mmol) and 1,3-dibromopropane (1.50 g, 7.43 mmol) in DMF (80 mL) was refluxed for 2 days. After cooling to room temperature, the yellow precipitate was filtered and washed with a small amount of DMF to afford a solid which was then re-dissolved in water (15 mL). An excess of NH₄PF₆ was added to the solution until no further precipitation was observed. The resulted residue was purified by flash column chromatography (methanol/2 M NH₄Cl aqueous solution/nitromethane = 20:2:1) and then anion-exchanged by using NH₄PF₆ and dried to afford 1a as a white solid (1.10 g, 23%). M.P. 270–272 °C. ¹H NMR (500 MHz, CD₃CN) δ (ppm) 8.86 (dd, J = 4.5, 1.7 Hz, 4H), 8.80 (d, J = 6.9 Hz, 4H), 8.38 (d, J = 6.9 Hz, = 6.9 Hz, 4H, 7.80 (dd, J = 4.5, 1.7 Hz, 4H), 4.72–4.68 (m, 4H), 2.74–2.68 (m, 2H). $^{13}{\rm C}$ NMR (126 MHz, CD₃CN) δ (ppm) 155.8, 152.3, 146.1, 142.0, 127.4, 122.8, 58.7, 32.7. ESI-TOF-MS (*m/z*): calcd for $C_{23}H_{22}F_6N_4P[M-PF_6]^+$: 499.1481, found: 499.1468.

Synthesis of 1,1-bis(4,4'-bipyridinium)methane 1b. 13b A solution of 4,4'-bipyridine (3.37 g, 21.57 mmol) and dibromomethane (1.50 g, 8.63 mmol) in DMF (50 mL) was refluxed for 2 days. After cooling to room temperature, the yellow precipitate was filtered and washed with a small amount of DMF to afford a solid which was then re-dissolved in water (15 mL). An excess of NH₄PF₆ was added to the solution until no further precipitation was observed. The solid was filtered and washed

with cold water to afford 1b as a white solid (2.40 g, 45%). ¹H NMR (500 MHz, acetone- d_6) δ (ppm) 9.84 (d, J = 7.0 Hz, 4H), 8.90-8.88 (m, 8H), 8.00 (dd, J = 4.5, 1.6 Hz, 4H), 7.90 (s, 2H).

Synthesis of metallacycle 2a. The 90° Pt(II) precursor (6) (4.38 mg, 0.006 mmol) and 1a (3.87 mg, 0.006 mmol) were placed in a 2-dram vial, followed by the addition of acetone- d_6 (0.6 mL). After 5 h of stirring at room temperature, the reaction solution was directly used for characterization. 1H NMR (500 MHz, acetone- d_{6} ,) (Fig. S5†): δ (ppm) 9.47 (d, J = 4.8 Hz, 8H), 9.21 (d, J = 7.0 Hz, 8H), 8.58 (d, J = 7.0 Hz, 8H), 8.29 (d, J =6.6 Hz, 8H), 5.13-5.04 (m, 8H), 3.02-2.95 (m, 4H), 2.18-2.09 (m, 24H), 1.38 (dt, J = 17.5, 7.5 Hz, 36H). ${}^{31}P{}^{1}H{}^{1}$ NMR (202 MHz, acetone- d_6) (Fig. S6†): δ (ppm) -0.30 (s, ¹⁹⁵Pt satellites, $J_{\text{Pt-P}}$ = 3087 Hz). ESI-TOF-MS (m/z): calcd for calcd for [M $-2PF_6^{2+}$: 1228.1934, found: 1228.1958; [M - 2OTf]²⁺: 1224.2094, found: 1224.2068.

Synthesis of metallacycle 2b. The 90° Pt(II) precursor (6) (4.38 mg, 0.006 mmol) and 1b (3.69 mg, 0.006 mmol) were placed in a 2-dram vial, followed by the addition of acetone- d_6 (0.6 mL). After 5 h of stirring at room temperature, the reaction solution was directly used for characterization. ¹H NMR (500 MHz, acetone- d_6) (Fig. S8†): δ (ppm) 9.79 (d, J = 6.9 Hz, 8H), 9.45 (d, J = 4.9 Hz, 8H), 8.72 (d, J = 6.9 Hz, 8H), 8.21 (d, J =6.4 Hz, 8H), 7.81 (s, 4H), 2.20–2.09 (m, 24H), 1.38 (dt, J = 17.3, 7.4 Hz, 36H). ${}^{31}P{}^{1}H}$ NMR (202 MHz, acetone- d_6) (Fig. S9†): δ (ppm) -0.23 (s, ¹⁹⁵Pt satellites, J_{Pt-P} = 3089 Hz). ESI-TOF-MS (m/z): calcd for $[M + 2K]^{2+}$: 1383.1305, found: 1383.2289.

Synthesis of [3]catenane 3. Various equivalents of DB24C8 (see Fig. 3 and 4) were added directly into a solution of metallacycle 2a in acetone- d_6 . The mixture was then stirred for 2 days at room temperature to generate [3]catenane 3. This initial reaction solution was directly used for the following characterization. ¹H NMR (500 MHz, acetone- d_6) (Fig. S11†): δ (ppm) 9.49 (d, J = 5.1 Hz, 8H), 9.10 (d, J = 6.7 Hz, 8H), 8.41 (d,J = 6.7 Hz, 8H), 8.26 (d, J = 6.3 Hz, 8H), 6.63 (dd, J = 5.8, 3.7Hz, 8H), 6.12 (dd, J = 5.9, 3.4 Hz, 8H), 4.99–4.93 (m, 8H), 3.83 (s, 16H), 3.68 (s, 16H), 3.54 (d, J = 5.6 Hz, 16H), 3.10 (br, 4H), 2.15-2.08 (m, 24H), 1.40-1.34 (m, 36H). $^{31}P\{^{1}H\}$ NMR (202 MHz, acetone- d_6) (Fig. S12†): δ (ppm) -0.71 (s, 195 Pt satellites, $J_{\text{Pt-P}}$ = 3101 Hz). ESI-TOF-MS (m/z): calcd for [M - $2PF_6^{2+}$: 1676.4032, found: 1676.4027; calcd for $[M - 2OTf]^{2+}$: 1672.4153, found: 1672.4119.

Synthesis of [3]catenane 4. Various equivalents of DB30C10 (see Fig. 5 and 6) were added directly into a solution of metallacycle 2a in acetone- d_6 . The solution was then stirred for 2 days at room temperature to generate [3]catenane 4. This initial reaction solution was directly used for the following characterization. ¹H NMR (500 MHz, acetone- d_6) (Fig. S13†): δ (ppm) 9.47 (d, J = 4.8 Hz, 8H), 8.95 (d, J = 6.8 Hz, 8H), 8.25 (d, J = 6.8 Hz, 8H, 8.17 (d, J = 6.6 Hz, 8H), 6.48-6.40 (m, 8H),5.84-5.75 (m, 8H), 4.99-4.90 (m, 8H), 3.81-3.78 (m, 16H), 3.68 (dd, J = 5.2, 3.3 Hz, 16H), 3.61 (d, J = 4.6 Hz, 16H), 3.37 (d, J = 4.6 Hz, 16H)2.7 Hz, 16H), 3.04-2.98 (m, 4H), 2.18-2.10 (m, 24H), 1.42 (dt, J = 17.4, 7.5 Hz, 36H). ${}^{31}P{}^{1}H{}$ NMR (202 MHz, acetone- d_6) (Fig. S14†): δ (ppm) -0.81 (s, ¹⁹⁵Pt satellites, $J_{Pt-P} = 3111$ Hz). ESI-TOF-MS (m/z): calcd for $[M - 2OTf]^{2+}$: 1760.4678, found:

1760.4725; calcd for $[M - 2PF_6]^{2+}$: 1764.4556, found: 1764.4629; calcd for [M - 3OTf]³⁺: 1123.9968, found: 1123.9954.

Synthesis of [3]catenane 5. Various equivalents of DB24C8 (see Fig. 7 and 8) were added directly into a solution of metallacycle **2b** in acetone- d_6 . The solution was then stirred for 2 days at room temperature to generate [3]catenane 5. This initial reaction solution was directly used for the following characterization. ¹H NMR (500 MHz, acetone- d_6) (Fig. S15†): δ (ppm) 9.69 (d, J = 6.9 Hz, 8H), 9.51 (s, 8H), 8.59 (d, J = 6.4 Hz, 8H), 8.32 (s, 8H), 7.76 (s, 4H), 6.50-6.46 (m, 8H), 5.86 (s, 8H), 3.80 (s, 16H), 3.69 (d, J = 5.0 Hz, 16H), 3.65 (s, 16H), 2.02-2.00(m, 24H), 1.35-1.30 (m, 36H). ³¹P{¹H} NMR (202 MHz, acetone- d_6) (Fig. S16†): δ (ppm) -1.64 (s, ¹⁹⁵Pt satellites, $J_{\text{Pt-P}}$ = 3141 Hz). ESI-TOF-MS (m/z): calcd for $[M - 2PF_6]^{2+}$: 1648.3718, found: 1648.3750; calcd for $[M - 2OTf]^{2+}$: 1644.3879, found: 1644.3840.

Author contributions

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Investigation, Y. S., L. H., Q. M., T. H., and X. Y.; writing - original draft, Y. S. and Z. Z.; funding acquisition and project administration, S. L.; conceptualization, supervision, validation, and writing - review and editing, S. L. and P. S. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21572042 and 21773052), the Program for Changjiang Scholars and Innovative Research Team in the Chinese University (IRT 1231), and the Science & Technology Innovation Program of Zhejiang Province (2018R52051). The authors thank Jiyong Liu (Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China) for the singlecrystal characterization of 1a and 4.

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