Binding of anions in triply interlocked coordination catenanes and dynamic allostery for dehalogenation reactions†

Linlin Yang,‡ Xu Jing,‡ Bowen An, Cheng He,✉* Yang Yang and Chunying Duan✉*

By synergistic combination of multicomponent self-assembly and template-directed approaches, triply interconnected metal organic catenanes that consist of two isolated chirally identical tetrahedrons were constructed and stabilized as thermodynamic minima. In the presence of suitable template anions, the structural conversion from the isolated tetrahedral conformers into locked catenanes occurred via the cleavage of an intrinsically reversible coordination bond in each of the tetrahedrons, followed by the reengineering and interlocking of two fragments with the regeneration of the broken coordination bonds. The presence of several kinds of individual pocket that were attributed to the triply interlocked patterns enabled the possibility of encapsulating different anions, allowing the dynamic allostery between the unlocked/locked conformers to promote the dehalogenation reaction of 3-bromo-cyclohexene efficiently, as with the use of dehalogenase enzymes. The interlocked structures could be unlocked into two individual tetrahedrons through removal of the well-matched anion templates. The stability and reversibility of the locked/unlocked structures were further confirmed by the catching/releasing process that accompanied emission switching, providing opportunities for the system to be a dynamic molecular logic system.

A template-directed approach that preorganizes building blocks into entwined or threaded systems by non-covalent interactions was developed to precisely control the architectures and topologies of the mechanically interlocked molecules.† The presence of several kinds of individual pocket that were attributed to the triply interlocked patterns enabled the possibility of encapsulating different anions, allowing the dynamic allostery between the unlocked/locked conformers to promote the dehalogenation reaction of 3-bromo-cyclohexene efficiently, as with the use of dehalogenase enzymes. The interlocked structures could be unlocked into two individual tetrahedrons through removal of the well-matched anion templates. The stability and reversibility of the locked/unlocked structures were further confirmed by the catching/releasing process that accompanied emission switching, providing opportunities for the system to be a dynamic molecular logic system.

Introduction

Biomolecular machines are fascinating systems in which integrated functions are controlled in a synergistic manner. The constitution of the individual components within the interconnected networks governs their capacity to perform specific functions and to interact with other relevant species in the recognition mediated systems.1–5 Inspired by sophisticated structures and mechanisms in biological systems, molecular recognition and self-assembly have been exploited as efficient driving forces for the fabrication of artificial molecular systems that operate far from equilibrium in a preorganized manner through well-controlled molecular design.6,7 Of these reported artificial systems, molecules containing mechanical bonds, such as catenanes,8–10 knots11 and rotaxanes,12–14 have captured the attention of the scientific community because of their intriguing architectures and topologies as well as the ability of their components to undergo controllable intra-molecular movements.

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bonds. The pathway involving substrate capture surmounts the kinetic barriers of the reaction through a “mild” equilibrium control method. Multiply interlocked catenanes exhibit high stabilities and have the potential to form different kinds of pocket that encapsulate several kinds of guest with different sizes and shapes. In these cases, positively charged, multiply coordinated interlocked structures are promising promoters to selectively and simultaneously bind a large number of guest anions. Inspired by these systems, a new approach based on interlocked catenane was developed to realize the dehalogenation process, simulating the mechanism in dehalogenation enzymes.

Herein, through the synergistic combination of multi-component self-assembly with a template-directed approach, we report a new approach to construct triply interlocked coordination catenanes from 40 components. The one-pot assembly reaction was well controlled from several types of commercially available fragment including a tris(4-amino phenyl)amine (TPA) group extended by a 2,2'-bipyridine-5-carbaldehyde chelator and the dynamics active zinc(II) ions. These triply interlocked catenanes could also be formed and unlocked into individual tetrahedrons upon the addition or removal of an anion template with a well-matched size and conformational structure. Additionally, the large inner pocket and the multiply interlocked fashion lead to a cavity that is divided into several individual pockets, enabling the encapsulation of different kinds of anion and promoting the dehalogenation reaction of 3-bromo-cyclohexene (Scheme 1).

Results and discussion

The reaction of tris(4-aminophenyl)amine (TPA, 8 equiv.) with 2,2'-bipyridine-5-carbaldehyde (24 equiv.) and Zn(BF_4)_2 (8 equiv.) provided the complex Cat-BF_4 with a 60% yield. The ESI-MS spectrum revealed a series of m/z species corresponding to [Zn_nL_3][BF_4]_n (16–37) (where L is the postulated Schiff-base ligand derived from the condensation of TPA and 2,2'-bipyridine-5-carbaldehyde, Scheme S1; †n = 7–10, Fig. S25†). The splitting of the signals in the 19F-NMR spectrum of the BF_4^- anions revealed the encapsulation of BF_4^- anions within the molecular architecture (Fig. S3†). The fact that the one-pot self-assembly from 40 individual pieces led to the metal-organic catenane suggested the high thermodynamic stability of Cat-BF_4 in the solution.

X-ray crystallographic analysis of Cat-BF_4 confirmed the formation of the metal-organic catenane and revealed that the triply locked identical cages feature seven pockets, each filled with a BF_4^- anion (Fig. 1). In the asymmetrical unit, four zinc centers with identical Δ or Δ stereochemistries of one tetrahedron are positioned at the terminal apical sites and are bridged by four tripod ligands that cap the four faces. Within one tetrahedron, the average Zn⋯Zn separation is 19.1 Å, and a tetrahedron has an approximate volume of 820 Å³. Two chirally identical tetrahedrons interlocked in C_2 symmetry with one Zn(bipy)_3 node situated at the center of the internal cavity of the counterpart. Three bidentate chelating arms coordinated to one catenane-coordinated zinc center inter-penetrate across three of the four openings of the counterpart to form a triply interlocked cage.

MS spectrum revealed a series of m/z species corresponding to [Zn_nL_3][BF_4]_n (16–37) (where L is the postulated Schiff-base ligand derived from the condensation of TPA and 2,2'-bipyridine-5-carbaldehyde, Scheme S1; †n = 7–10, Fig. S25†). The splitting of the signals in the 19F-NMR spectrum of the BF_4^- anions revealed the encapsulation of BF_4^- anions within the molecular architecture (Fig. S3†). The fact that the one-pot self-assembly from 40 individual pieces led to the metal-organic catenane suggested the high thermodynamic stability of Cat-BF_4 in the solution.

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Scheme 1 The illustration of the reversible assembly and dehalogenation reaction of triply interlocked catenanes via anion template and subcomponent self-assembly.
The six locked arms face one another to create an inner core—a molecular bowl that is similar to an ‘egg cup’.

One of the BF₄⁻ anions occupies the center of the molecular bowl. Abundant C–H···F interactions, which stabilize the interlocked structure, are found between the CH=N groups and BF₄⁻ anions (Fig. S21†). It should also be noted that the large inner pocket and the multiply interlocked fashion lead to a cavity that is divided into 7 individual pockets. Beside the center pocket (inner pocket) that is filled by a BF₄⁻ anion, the other six pockets (outer pockets) formed each encapsulate a BF₄⁻ anion. These anions occupy the middle point of the seven shortest separated zinc pairs of the catenane zinc(u) nodes to adhere the charged zinc(u) nodes together through electrostatic interactions and to partly balance the positive charges of the catenane tetrahedrons. These cooperative weak interactions allow the subcomponents of Cat-BF₄ to recognize each other well and to finely compact in an interlocked nature, benefiting the construction of complicated systems using the same constituent fragments.⁸⁸

Replacing Zn[BF₄]₂ with Zn(CF₃SO₃)₂ under the same assembly conditions gave an isolated tetrahedron Tet-1. ESI-MS analysis of the resulting solution of Tet-1 revealed a family of prominent signals at m/z = 619.15, 772.77, 1003.2 and 1387.25 that are assigned to [Zn₄L₄(CF₃SO₃)₂]^{[8–n]+} (n = 2, 3, 4 and 5, Fig. S27†) species based on a comparison with simulated and natural isotopic abundances (Fig. 4a). The presence of one set of ligand signals in the ¹H NMR (Fig. 2b) and ¹⁹F-NMR (Fig. S10†) spectra suggests that the four ligands and eight CF₃SO₃⁻ anions in Tet-1 are identical. Important evidence for the interlocked structure of Cat-BF₄ is provided in the NOESY spectrum (Fig. S5†), where H–H interactions between the bipyridyl protons (Hₙ) and the TPA protons were found. However, no relevant signals were observed for Tet-1 because of the long distance of these interactions (Fig. S9†).

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Meanwhile, with BF$_4^-$ as the template anion (Fig. S51†), both the rate and conversion of Tet-1 to catenate were quite low compared to those in the presence of ClO$_4^-$, whereas the addition of the PF$_6^-$ anion could not lead to the formation of the interlocked structure (Fig. S47†), further confirming that the size and shape of the template anions were essential to the interlocked system.

The formation of interlocked Cat-Clo$_4^-$ was dynamically active, and the well-fitted linear relationship of 1/[Tet-1] with the reaction time at a fixed temperature suggested a second-order kinetic behaviour (Fig. 3b). The efficient collision between the two tetrahedrons was assumed to be the rate-determining step, which agreed well with the aforementioned thermodynamics assumption for the interlocked transformation. From the determination of kinetic constants at different temperatures, the activation energy of the catenate construction reaction from two isolated tetrahedrons was calculated to be 59.5 kJ mol$^{-1}$, according to the Arrhenius equation (Table S3†). Generally, the interlocked transformation involves the breaking of at least two of the interacting bonds followed by the recovery of these bonds to interlock together. The fact that the activation energy is lower than the cleavage energy of one set of the chelating Zn(II) coordination bonds suggests that the structural conversion likely occurs through the random cleavage of one high-probability coordination bond out of the twelve active positions of each tetrahedron, followed by the reengineering of the two colloidal activated tetrahedrons with the formation of new chelating coordination bonds (Fig. 3c). Control experiments involving the use of more inert metal ions, with Fe(u) or Co(u) replacing Zn(u) in the subcomponent assembly, gave only the isolated tetrahedron (Fig. S31–S34†). The inactivity of the interlocked transformation with the kinetically inert metal ions confirmed that the structural formation was controlled by the partial dissociation dynamics of the Werner-type interactions and the suitable metal–lignid interactions.

The kinetic study suggested that the addition of anions with a similar size which could weakly coordinate to the Zn centers would lower the reaction energy barrier and accelerate the conversion. In this case, the addition of halide anions as NBu$_4$ or Bu$_4$NI and as the template anion (Fig. S51†) with the (a) Bu$_4$NBr, (b) Bu$_4$NI and (c) Bu$_4$NPF$_6$ salts to the solution of Tet-1 resulted in the quickly exclusive formation of Cat-Br, showing the formation of interlocked structures with a 7Br$^- <$ Zn$_8$L$_8$ core, 7I$^- <$ Zn$_8$L$_8$ core and host–guest DSA < Tet-1 species, respectively.

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Fig. 4. ESI-MS spectra of the solution containing the isolated tetrahedron Tet-1 (a). The aforementioned solution upon the addition of (b) Bu$_4$NBr, (c) Bu$_4$NI and (d) Bu$_4$NPSA, showing the formation of interlocked structures with a 7Br$^- <$ Zn$_8$L$_8$ core, 7I$^- <$ Zn$_8$L$_8$ core and host–guest DSA < Tet-1 species, respectively.

structure, the I$^-$ anion in the central cavity was strongly fixed, while the outer six I$^-$ anions could be randomly exchanged with the added BF$_4^-$ anions. The results showed that there are two kinds of micro-environment in this catenate. The central cavity can bind anions more powerfully than the other six “outer” cavities, which is likely due to the presence of more hydrogen bonding interaction sites (Fig. 1f).

To elucidate the driving force for dimerization and the origin of the thermodynamic stability of the interlocked tetrahedrons, we evaluated the thermodynamic parameters using isothermal titration calorimetry (ITC). A typical titration curve is shown in Fig. 5a. The observed inclusion number between Tet-1 and Br$^-$ anions was 3.5, which is in good agreement with the seven Br$^-$ anions in the ESI-MS spectra of Cat-Br. Curve fitting by the computer simulation using an “independent” model reveals the activation enthalpy $\Delta H = 8.1$ kJ mol$^{-1}$, the activation entropy $\Delta S = 123.8$ J mol$^{-1}$, and the Gibbs free energy $\Delta G = -28.77$ kJ mol$^{-1}$ (Fig. S69†). These results demonstrate that the dimerization of Tet-1 is an entropy-driven endothermic reaction, which is attributed to the increase of molecular disorder and release of solvents. Similarly, the $\Delta G$ between the dimerization of Tet-1 with I$^-$ anions is $-30.15$ kJ mol$^{-1}$ (Fig. S70†). The sequence of the Gibbs free energy in the dimerization process seems to be ranked as BF$_4^-$ < ClO$_4^-$ < Br$^-$ < I$^-$. Since silver salts can remove halide anions from solution via the formation of an insoluble AgX precipitate, we identified that the bound halide anions in Cat-X could also be precipitated by the addition of AgCF$_3$SO$_3$ with the catenate unlocked. As shown in Fig. 2d, the $^1$H-NMR titration of AgCF$_3$SO$_3$ into a solution containing Cat-Br resulted in the deterioration of the splitting of the signals of the interlocked structure. The simple NMR pattern is attributed to the tetrahedron Tet-1, and the ESI-MS
Fig. 5 (a) The isothermal titration calorimetry (ITC) data for sequential injections (10 µL per injection) of Br− solution (5 mM) into Tet-1 solution (0.125 mM). (b) The apparent reaction heat obtained from the integration of calorimetric traces. (c) The fluorescence of DSA C Tet-1 species with the addition of 10 equiv. of different template ions (PF6−, Br− and I−, cyan column) followed by titration of 20 equiv. of AgCF3SO3− (red column) to the aforementioned solution (F0 corresponds to the fluorescence of DSA C Tet-1). (d) The reversible Br−/Ag+ controlled uptake and release of DSA monitored by fluorescence.

Fig. 6 The kinetics study of the dehalogenation reaction of 3-bromocyclohexene. (a) The variation in turnover number (per mole of the catalyst Tet-1) with the concentration of the substrate 3-bromocyclohexene varies in the system containing 2,4,6-collidine (20 mM), MeOTf (20 mM), and Tet-1 (1 mM), and (b) the conversion of the substrate 3-bromocyclohexene (10.0 mM) with the concentration of Tet-1 varies in the system containing 2,4,6-collidine (20 mM) and MeOTf (20 mM).
concentration of Tet-1. When the concentration of Tet-1 was fixed, the initial turnover frequency of the reaction hardly changed with the concentration of the substrate. It seems that the rate of the reaction only depends on the concentration of the bromide encapsulated interlocked complex. The formation of the bromide encapsulated interlocked complex was possibly the rate-limited step and the dehalogenation reaction took place through the direct SN1 cleavage of the C-Br bond.

Conclusions

In summary, we report a new approach to construct triply interlocked coordination catenanes that consist of two chirally identical tetrahedrons. The new approach included the synergic combination of multi-component self-assembly and molecular recognition, and at the same time also involved seeking the thermodynamic minima of the interlocked/unlocked equilibrium based on the intrinsic dynamic active nature of the coordination assembly. The presence of several kinds of individual pocket that were attributed to the triply interlocked patterns provided the possibility to encapsulate different kinds of anion, allowing the dynamic allosteroy between the locked/unlocked conformers to efficiently promote the elimination of 3-bromo-cyclohexene.

Experimental

Preparation of the interlocked tetrahedron Cat-BF4 [Zn8L8] [BF4]16

TPA (29 mg, 0.1 mmol, 4 equiv.), 2,2′-bipyridine-5-carbaldehyde (56 mg, 0.3 mmol, 12 equiv.), Zn(BF4)2 (34 mg, 0.1 mmol, 4 equiv.), and dry acetonitrile (30 mL) were added to a Schlenk tube. The solution was degassed for three evacuation/nitrogen fill cycles. The tube was kept at 343 K for 24 h. Diethyl ether was diffused into an acetonitrile solution and the desired product Cat-BF4 was isolated by filtration as red square crystals in 60% yield. 1H NMR (500 MHz, 298 K, CD3CN): δ = 9.00 (6H, d), 8.86 (24H, m), 8.59–8.70 (36H, m), 8.56 (12H, s), 8.27–8.42 (36H, m), 8.15 (12H, s), 7.9–8.1 (18H, d), 7.76 (6H, s), 7.6–7.7 (24H, m), 7.45 (12H, d), 7.37 (12H, d), 7.29 (6H, d), 7.0 (6H, d), 6.65–6.79 (24H, dd), 6.66 (12H, d), 6.25–6.36 (24H, dd), 5.7 (12H, d), ESI-MS: m/z [Zn8L8(BF4)16]+ 826.8, [Zn8L8(BF4)15]16+ 941.0, [Zn8L8(BF4)14]17+ 1087.9, [Zn8L8(BF4)13]18+ 1283.7, [Zn8L8(BF4)12]19+ 1557.8. Elemental analysis [Zn4C10H19N16O14Br2F14·H2O] (C, H, N, Br) calcld (%): C 56.8, H 3.65, N 13.42; found (%): C 56.8, H 3.7, N 13.3; found (%): C 56.8, H 3.65, N 13.42. IR (KBr, cm⁻¹): ν 3547, 3076, 1609, 1487, 1497, 1317, 1280, 1084, 834, 795, 750, 624.

Preparation of the interlocked tetrahedron Cat-ClO4 [Zn8L8] [ClO4]16

TPA (29 mg, 0.1 mmol, 4 equiv.), 2,2′-bipyridine-5-carbaldehyde (56 mg, 0.3 mmol, 12 equiv.), Zn(ClO4)2 (37 mg, 0.1 mmol, 4 equiv.), and dry acetonitrile (30 mL) were added to a Schlenk tube. The solution was degassed by three evacuation/nitrogen fill cycles. The tube was kept at 343 K for 24 h. Diethyl ether was diffused into an acetonitrile solution and the desired product Cat-ClO4 was isolated by filtration as red square crystals in 65% yield (based on the product dried under vacuum). 1H NMR (500 MHz, 298 K, CD3CN): δ = 8.88 (24H, m), 8.60–8.64 (6H, m), 8.52 (6H, s), 8.37 (6H, s), 8.28 (36H, m), 8.19 (12H, m), 8.06–7.97 (24H, d), 7.62 (36H, m), 7.47 (12H, d), 7.38 (12H, d), 6.8 (12H, d), 6.67 (12H, d), 6.6 (12H, d), 6.31–6.36 (24H, dd), 5.9 (12H, d), ESI-MS: m/z [Zn8L8(ClO4)16]+ 836.8, [Zn8L8(ClO4)15]16+ 953.9, [Zn8L8(ClO4)14]17+ 1104.3, [Zn8L8(ClO4)13]18+ 1304.9, [Zn8L8(ClO4)12]19+ 1585.2. Elemental analysis: [Zn4C48H38N28O48Cl16]·O4·2CH3CN·7H2O calcld (%): C 57.3, H 3.59, N 13.3; found (%): C 56.8, H 3.65, N 13.42. IR (KBr, cm⁻¹): ν 3520, 3065, 1604, 1498, 1474, 1439, 1317, 1280, 1088, 834, 795, 750, 624.

Preparation of the discrete tetrahedron Tet-1

TPA (29 mg, 0.1 mmol, 4 equiv.), 2,2′-bipyridine-5-carbaldehyde (56 mg, 0.3 mmol, 12 equiv.), Zn(CF3SO3)2 (36 mg, 0.1 mmol, 4 equiv.), and dry acetonitrile (30 mL) were added to a Schlenk tube. The solution was degassed by three evacuation/nitrogen fill cycles. The tube was kept at 343 K for 24 h. Then BuNX (X = Br or I) was added to give a solution containing the interlocked cage [Zn8L8] with X⁻ inclusion.

Preparation of Cat-UBF4 [Zn8L8(BF4)14]

TPA (29 mg, 0.1 mmol, 4 equiv.), 2,2′-bipyridine-5-carbaldehyde (56 mg, 0.3 mmol, 12 equiv.), Zn(CF3SO3)2 (36 mg, 0.1 mmol, 4 equiv.), and dry acetonitrile (30 mL) were added to a Schlenk tube. The solution was degassed by three evacuation/nitrogen fill cycles. The tube was kept at 343 K for 24 h. BuNX (X = Br or I) was added to give a solution containing the interlocked cage [Zn8L8] with X⁻ inclusion.

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X-ray crystallography

Crystals of the interlocked Cat-BF$_4^-$ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex over a few days. Crystals of the interlocked Cat-BF$_4^-$ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution of complex Cat-I in the presence of 10 equivalents of BF$_4^-$ over a few days. The crystals were very susceptible to loss of solvent. Despite rapid handling times and a low temperature collection, the quality of data was less than ideal.

X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å) using the SMART and SAINT programs.$^{60,67}$ The crystal data was solved by direct methods and further refined by full-matrix least-squares refinements on $F^2$ using the SHELXL-97 software.$^{68}$ Non-H atoms were refined with anisotropic displacement parameters. The hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms.

Crystal data for Cat-BF$_4^-$: $\text{Zn}_2\text{C}_3\text{O}_{16}\text{N}_{46}\text{O}_2\text{BF}_3\text{I}_2$, $M = 4237.66$, monoclinic, space group $C2/c$, red block, $a = 47.616(2)$ Å, $b = 31.748(1)$ Å, $c = 56.289(2)$ Å, $\alpha = 111.304(2)^\circ$, $V = 79.279(5)$ Å$^3$, $Z = 8$, $\rho_{\text{calc}} = 0.712$ g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 0.289 mm$^{-1}$, $T = 100(2)$ K. $R_{\text{int}} = 0.1629$. Final $R_1$ with $I > 2\sigma(I)$ = 0.0985, $wR_2$ (all data) = 0.2896. CCDC number 1515722.

Crystal data for Cat-I/BF$_4^-$: $\text{Zn}_2\text{C}_2\text{O}_{16}\text{N}_{46}\text{O}_2\text{BF}_3\text{I}_2\text{BF}_4$, $M = 4477.14$, monoclinic, space group $C2/c$, red block, $a = 47.061(2)$ Å, $b = 32.042(1)$ Å, $c = 55.568(3)$ Å, $\alpha = 110.4(1)^\circ$, $V = 78.535(7)$ Å$^3$, $Z = 8$, $\rho_{\text{calc}} = 0.757$ g cm$^{-3}$, $\mu$(Mo-K$_\alpha$) = 0.637 mm$^{-1}$, $T = 150(2)$ K. $R_{\text{int}} = 0.1617$. Final $R_1$ with $I > 2\sigma(I)$ = 0.0885, $wR_2$ (all data) = 0.2659. CCDC number 1515723.

For the refinement of Cat-BF$_4^-$, several atoms on some pyridine rings of the ligands were disordered into two parts, with the site occupancy factors (s.o.f.) of each part being fixed at 0.5. Several fluorine atoms in the BF$_4^-$ anions were disordered into two parts with the s.o.f. of each part being refined with a fixed value. Except for the disordered parts, the partially occupied solvent molecules and the partially occupied anions, the other non-hydrogen atoms were refined anisotropically. The hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The bond distance in some of the pyridine and benzene rings, as well as in several BF$_4^-$ anions, was confined as idealized values. The thermal parameters of adjacent atoms of the disordered parts of the ligand backbone and the particularly occupied BF$_4^-$ groups were confined to be similar. The SQUEEZE subroutine in PLATON was used.

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Conflicts of interest

The authors declare no competing financial interests.

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