Electronic Supplementary Material (ESI) for Dalton Transactions

Looking for the origin of the switch between coordination-captured helicates and catenates.

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Supporting Information (13 pages)

Table S1 Summary of crystal data, intensity measurement and structure refinement for $[Zn_2(\mathbf{L6})Cl](CF_3SO_3)_3(H_2O)_2(CH_3CN)_4$ (**1**).

Compound	**1**
Formula	$Zn_2C_{62}H_{59}N_{15}Cl_1O_{11}F_9S_3$
fw	1623.7
Crystal system	triclinic
Space Group	$P\bar{1}$
a (Å)	12.4234(8)
b (Å)	17.5344(12)
c (Å)	18.8655(13)
α (deg)	68.137(8)
β (deg)	71.102(7)
γ (deg)	73.688(8)
V (Å^3)	3547.8(5)
Z	2
Crystal Size (mm)	0.054 x 0.13 x 0.25
d_{calcd} (Mg m^{-3})	1.520
μ(MoKα) (mm^{-1})	0.894
*T*min, *T*max	0.8203 , 0.9495
2θmax (deg)	51.2
No. of reflns collected	26547
No. of independent reflns	12893
No. of obsd [a] (used[b]) reflns	5709 (5816)
No. of variables	1000
Weighting scheme *p* [c]	0.00025
Max and min $\Delta\rho$ (e Å^{-3})	1.15 , -1.02
GOF (*F*) [d] (all data)	1.01(1)
R [e], ωR [f]	0.051 , 0.046

[a] $|Fo| > 4\sigma(Fo)$; [b] Used in the refinements (including reflns with $|Fo| \le 4\sigma(Fo)$ if $|Fc| > |Fo|$); [c] $\omega = 1/[\sigma^2 (F_o) + p (F_o)^2]$; [d] $S = [\Sigma \{((F_o-F_c) / \sigma(F_o))^2 \} / (N_{ref} - N_{var})]^{1/2}$; [e] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [f] $\omega R = [\Sigma (\omega|Fo|-|Fc|)^2 / \Sigma \omega|Fo|^2]^{1/2}$.

Table S2 Distances and angles between H-bond donors and acceptors in the crystal structure of $[Zn_2(\mathbf{L6})(Cl)(H_2O)_2(CF_3SO_3)](CF_3SO_3)_2(CH_3CN)_4$ (**1**). (numbering scheme is given in Fig. 6 and a pictorial illustration in Fig. S5).

D-H···A	*d* (D-H)/ Å	*d* (H···A)/ Å	d (D···A)/ Å	∠ (D-H···A)/ °
O(1w)-H(11w)···O(1b)	0.96	1.77	2.692(8)	160
O(1w)-H(12w)···O(3a)	0.98	1.68	2.640(7)	164
O(2w)-H(21w)···Cl(1)	0.98	2.17	3.115(5)	163
O(2w)-H(22w)···O(2c)	0.97	1.70	2.66(3)	170

Table S3 Bond distances [Å] and bond angles [°] in the molecular structure of the cation $[Zn_2(\mathbf{L6})(Cl)(H_2O)_2(CF_3SO_3)]^{2+}$ (numbering scheme is given in Fig. 6).

Bond distances / Å

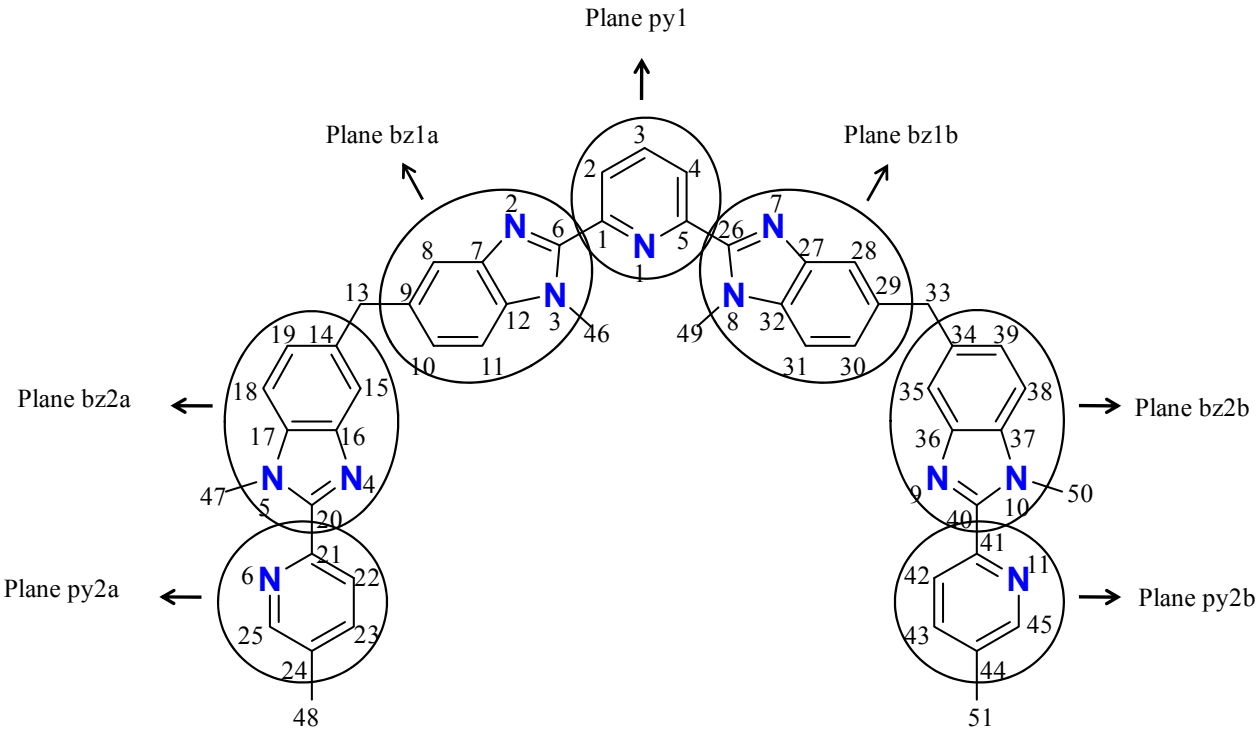
Zn1-N1	2.113(6)	Zn1-N2	2.131(5)
Zn1-N7	2.137(6)	Zn1-Cl1	2.252(3)
Zn1-O1w	2.004(6)		
Zn2-N4	2.087(5)	Zn2-N6	2.144(6)
Zn2-N9	2.077(6)	Zn2-N11	2.157(9)
Zn2-O2w	2.067(5)	Zn2-O1a	2.340(7)

Bond Angles / °

N1-Zn1-N2	75.1(2)	N2-Zn1-N7	150.2(3)
N1-Zn1-N7	75.2(2)	N2-Zn1-O1w	92.1(3)
N1-Zn1-O1w	107.7(3)	N2-Zn1-Cl1	100.7(2)
N1-Zn1-Cl1	133.9(2)	N7-Zn1-O1w	99.0(3)
O1w-Zn1-Cl1	118.4(2)	N7-Zn1-Cl1	98.1(2)
N4-Zn2-N6	78.4(2)	N6-Zn2-N9	94.9(3)
N4-Zn2-N9	171.8(2)	N6-Zn2-N11	98.1(3)
N4-Zn2-N11	98.7(3)	N6-Zn2-O1a	86.4(3)
N4-Zn2-O1a	89.7(3)	N6-Zn2-O2w	166.3(3)
N4-Zn2-O2w	94.4(2)	N9-Zn2-N11	77.5(3)
N11-Zn2-O1a	171.1(2)	N9-Zn2-O1a	94.6(3)
N11-Zn2-O2w	94.5(2)	N9-Zn2-O2w	93.1(2)
O1a-Zn2-O2w	81.9(3)		

Table S4 Selected Least-Squares Planes Data for **1**.

Least-squares planes description	Abbreviation	Max. deviation/Å	Atom
Pyridine, N1	py1	0.005	C5
Benzimidazole, N2, N3	bz1a	0.008	C6
Benzimidazole, N4, N5	bz2a	0.017	C19
Pyridine, N6	py2a	0.023	C24
Benzimidazole, N7, N8	bz1b	0.010	C29
Benzimidazole, N9, N10	bz2b	0.016	C34
Pyridine, N11	py2b	0.013	C42

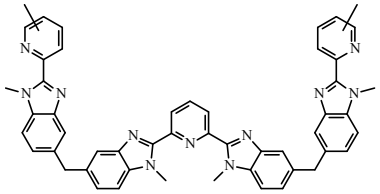


Intramolecular interplanar angles /°

	py1	bz1a	bz2a	py2a	bz1b	bz2b
bz1a	4.6(2)					
bz2a	65.3(2)	65.9(2)				
py2a	48.9(2)	50.4(2)	18.5(2)			
bz1b	7.6(2)	9.6(2)	57.7(2)	41.4(2)		
bz2b	56.2(2)	51.8(2)	84.9(1)	90.0(2)	60.1(2)	
py2b	52.4(3)	48.4(2)	80.7(2)	88.4(2)	57.4(2)	9.1(2)

Intermolecular interplanar distances and angles involved in stacking interactions (°)

Plane 1 - plane 2#	Symmetry operation for plane 2#	$\bar{d}$ /Å	∠ (plane 1, plane 2#) /°
py1 - bz1a #	(1-x, 1-y, 1-z)	3.52(8)	4.6(2)
bz2a – bz2a #	(1-x, 2-y, -z)	3.413(10)	0
bz1b - bz1b #	(-x, 1-y, 1-z)	3.717(6)	0
bz2b – bz2b #	(-x, 2-y, 1-z)	3.308(8)	0



$$2\,\mathbf{L}\boldsymbol{k} + [Fe(CH_3CN)_6]^{2+} + 2\,[Ag(CH_3CN)_4]^{+} \underset{}{\overset{\beta_{1,2,2}^{Fe,Ag,\mathbf{L}\boldsymbol{k}}}{\rightleftharpoons}} [FeAg_2(\mathbf{L}\boldsymbol{k})_2]^{4+} + 14\,CH_3CN \quad (3)$$

				helicate	catenate		
					PP/*MM*	*MP*	
Point groups:	C_{2v}	O_h	T_d	D_2	D_2	S_4	C_{3v}
σ^{ext}:	2	24	12	4	4	2	3
σ^{int}:	3^6	3^6	3^4	3^{12}	3^{12}	3^{12}	1
σ^{chiral}:	1	1	1	1/2	1/2	1	1

$$\omega_{1,2,2}^{Fe,Ag,\mathbf{L}\boldsymbol{k}}(D_2) = \frac{\left(2\cdot 3^6\right)^2\left(24\cdot 3^6\right)\left(12\cdot 3^4\right)^2}{\left(4\cdot 3^{12}\right)3^{14}} = 3456 \qquad \omega_{1,2,2}^{chiral}(D_2) = \frac{1^2\cdot 1\cdot 1^2}{(1/2)\cdot 1^{14}} = 2$$

$$\Rightarrow \omega_{1,2,2}^{Fe,Ag,\mathbf{L}\boldsymbol{k}}\omega_{1,2,2}^{chiral}(D_2) = 3456\cdot 2 = 6912$$

$$\omega_{1,2,2}^{Fe,Ag,\mathbf{L}\boldsymbol{k}}(S_4) = \frac{\left(2\cdot 3^6\right)^2\left(24\cdot 3^6\right)\left(12\cdot 3^4\right)^2}{\left(2\cdot 3^{12}\right)3^{14}} = 6912 \qquad \omega_{1,2,2}^{chiral}(S_4) = \frac{1^2\cdot 1\cdot 1^2}{1\cdot 1^{14}} = 1$$

$$\Rightarrow \omega_{1,2,2}^{Fe,Ag,\mathbf{L}\boldsymbol{k}}\omega_{1,2,2}^{chiral}(S_4) = 6912\cdot 1 = 6912$$

Figure S1 Symmetry numbers (σ) and statistical factors (ω) for the complexation of $[Fe(CH_3CN)_6]^{2+}$ and $[Ag(CH_3CN)_4]^{+}$ to **L5** or **L6** in acetonitrile. The two diastereomeric [2]catenates with D_2 (*PP*/*MM* enantiomers) and S_4 (meso-*PM* isomer) symmetries are considered.

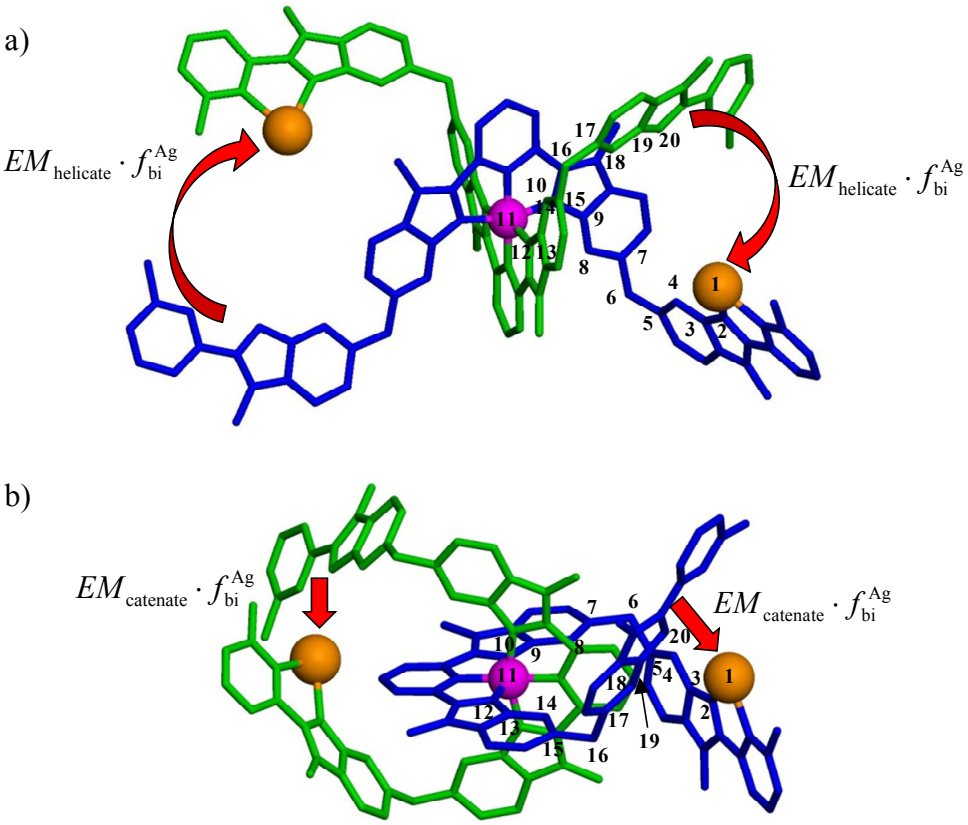


Figure S2 Schematic illustration of the intramolecular macrocyclization processes responsible for the formation of $[AgFeAg(\mathbf{L5})_2]^{4+}$ as a) a double-stranded helicate and b) a [2]catenate. The twenty atoms of the crooked chains connecting the interacting groups are highlighted.

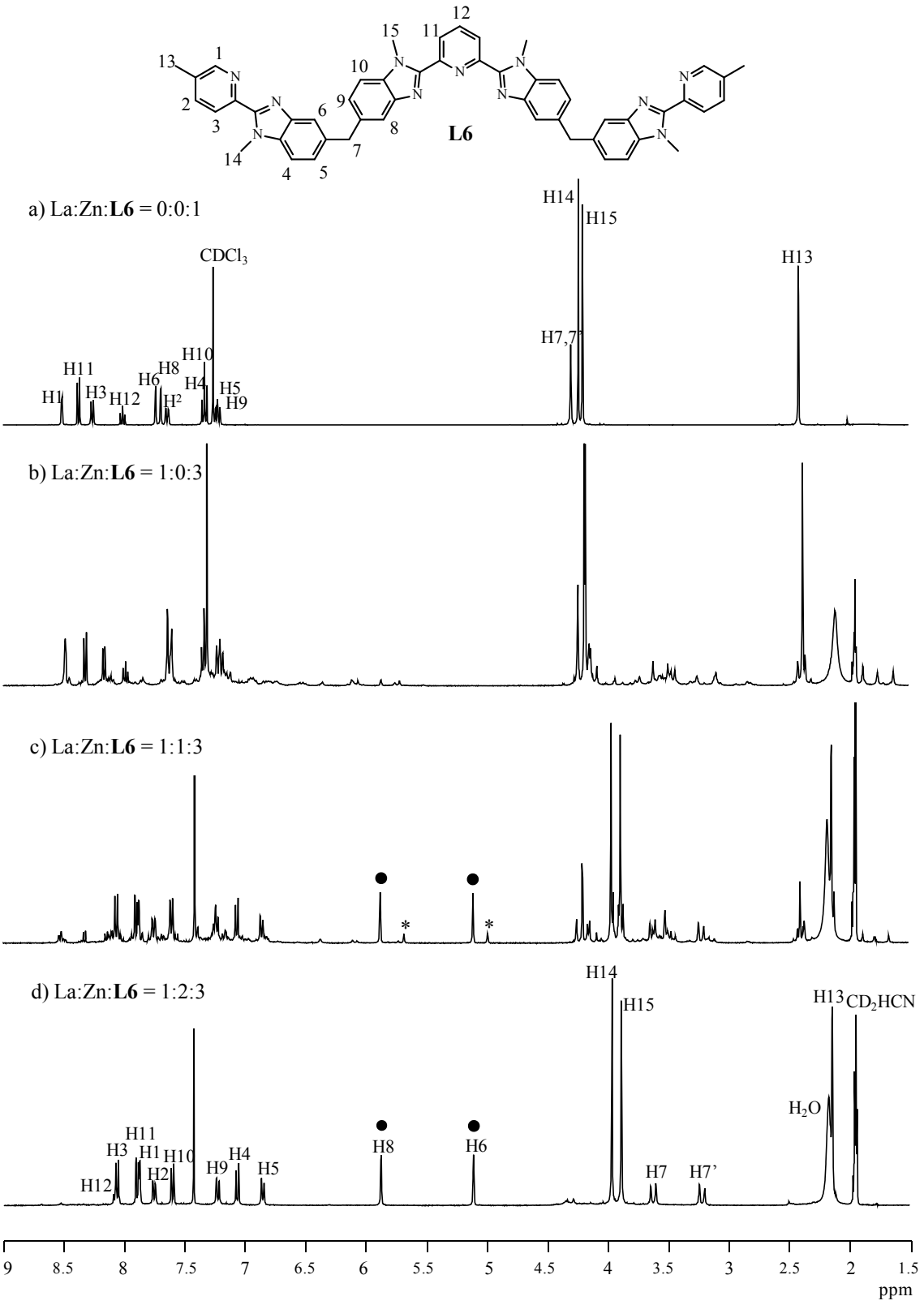


Figure S3 ^{1}H NMR titration of **L6** (10^{-2} M) with La(III) and Zn(II) in $CDCl_3/CD_3CN$ = 1:1 at 293 K with numbering scheme and highlighting the chemical shifts for H6 and H8 during the successive formation of $[LaZn(\mathbf{L6})_3]^{5+}$ (*) and $[ZnLaZn(\mathbf{L6})_3]^{7+}$ (•) . Adapted from ref. 24.

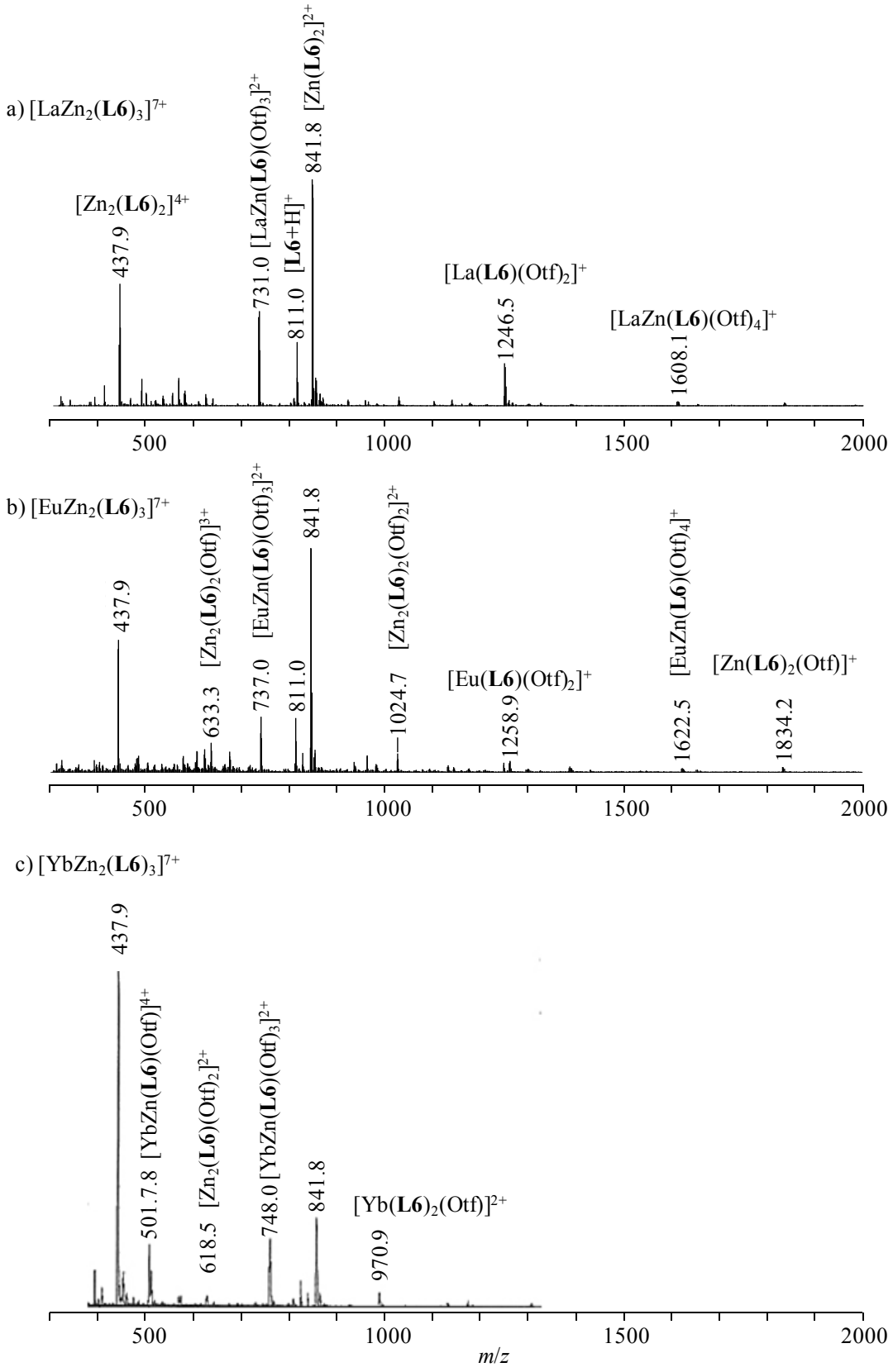


Figure S4 ESI-MS spectra of $[LnZn_2(\mathbf{L6})_3]^{7+}$ with a) Ln = La (10^{-4} M), b) Ln = Eu (10^{-4} M) and c) Ln = Yb ($5 \cdot 10^{-4}$ M) in CH_3CN:$CHCl_3$ (1:1) at 298 K ($Otf^- = CF_3SO_3^-$).

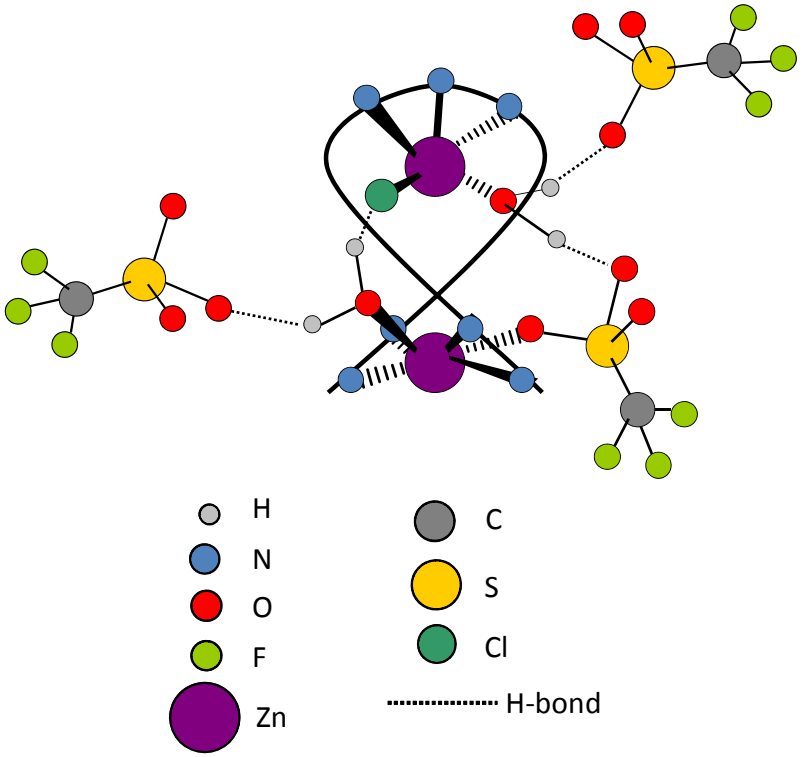


Figure S5 Schematic view of the hydrogen bonding network in the crystal structure of $[Zn_2(\mathbf{L6})(Cl)(H_2O)_2(CF_3SO_3)](CF_3SO_3)_2(CH_3CN)_4$ (**1**). The acetonitrile molecules are not involved in hydrogen bonding and are thus omitted for clarity.

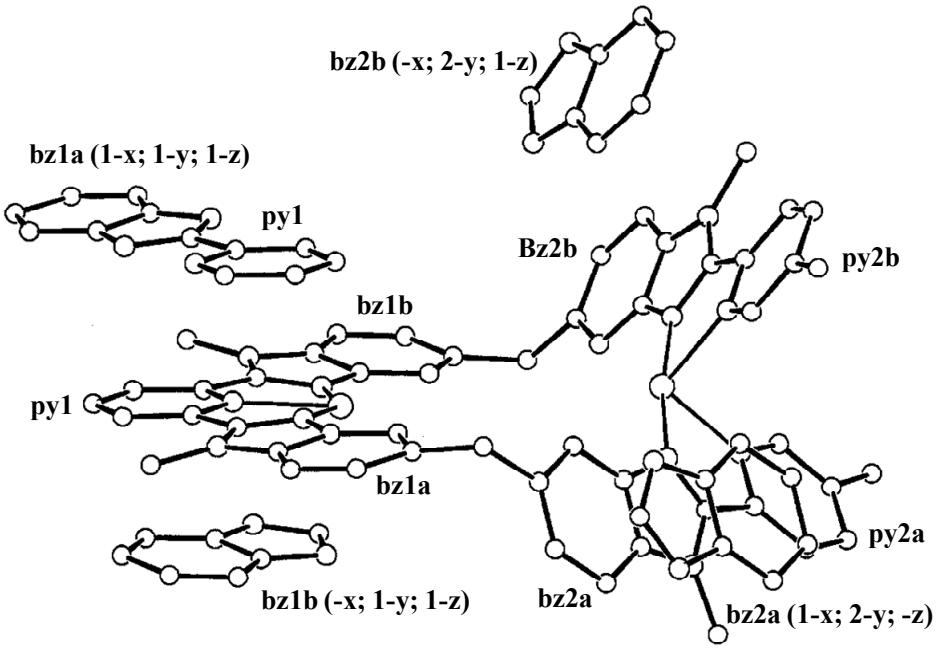
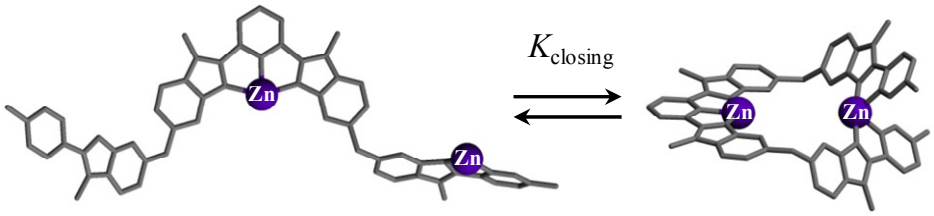


Figure S6 Aromatic rings involved in intermolecular π-stacking interactions in the crystal structure of $[Zn_2(\mathbf{L6})(Cl)(H_2O)_2(CF_3SO_3)](CF_3SO_3)_2(CH_3CN)_4$ (**1**). The symmetry operations relating the various molecules are given between parentheses. Interplanar angles and distances are collected in Table S4.



(7)

Acyclic-$[Zn_2(\mathbf{L6})]^{4+}$ cyclic-$[Zn_2(\mathbf{L6})]^{4+}$

Point groups:	C_s	C_2
σ^{ext}:	1	2
σ^{int}:	3^6	3^6
σ^{chiral}:	1	1/2

$$\omega_{closing}^{geometry} = \frac{\left(1 \cdot 3^6\right)}{\left(2 \cdot 3^6\right)} = 1/2 \qquad \omega_{closing}^{chiral} = \frac{1}{(1/2)} = 2$$

$$\Rightarrow \omega_{closing} = \omega_{closing}^{geometry} \cdot \omega_{closing}^{chiral} = \frac{1}{2} \cdot 2 = 1$$

Figure S7 Symmetry numbers (σ) and statistical factors (ω) for the macrocyclization of $[Zn_2(\mathbf{L6})]^{4+}$ in acetonitrile.

Appendix 1. Experimental speciation obtained by ^{1}H NMR for equilibrium 9.

For a given stoichiometric $|Zn|_{tot} / |\mathbf{L6}|_{tot}$ ratio, the integrated intensities of the ^{1}H NMR signals recorded for the same proton in $[Zn_2(\mathbf{L6})]^{4+}$ (I_{Zn2L}), $[Zn(\mathbf{L6})_2]^{2+}$ (I_{ZnL2}) and $[Zn_3(\mathbf{L6})_2]^{6+}$ (I_{Zn3L2}) can be compared according to equilibrium 9 (eq. S1) and scaled with respect to $|Zn_2(\mathbf{L6})|$ (eq. S2).

$$\frac{|Zn(\mathbf{L6})_2|}{|Zn_3(\mathbf{L6})_2|} = \left(\frac{I_{ZnL2}}{I_{Zn3L2}}\right) = 1 \qquad \text{(S1)}$$

$$\frac{|Zn(\mathbf{L6})_2|}{|Zn_2(\mathbf{L6})|} = \left(\frac{I_{ZnL2}}{2I_{Zn2L}}\right) \qquad \text{(S2)}$$

Introducing eqs (S1) and (S2) into the mass balance eq. (S3) yields eq. (S4) after straightforward algebraic transformations.

$$|\mathbf{L6}|_{tot} = |Zn_2(\mathbf{L6})| + 2|Zn(\mathbf{L6})_2| + 2|Zn_3(\mathbf{L6})_2| \qquad \text{(S3)}$$

$$|Zn_2(\mathbf{L6})| = |\mathbf{L6}|_{tot}\left(\frac{I_{Zn2L}}{I_{Zn2L} + 2I_{ZnL2}}\right) \qquad \text{(S4)}$$

Introducing eq. (S4) into eqs (S1) and (S2) gives the remaining complex speciation

$$|Zn(\mathbf{L6})_2| = |Zn_3(\mathbf{L6})_2| = |\mathbf{L6}|_{tot}\left(\frac{I_{ZnL2}}{2\left(I_{Zn2L} + 2I_{ZnL2}\right)}\right) \qquad \text{(S5)}$$

The missing concentration $|Zn|$ shown in eq. (S7) can be deduced from the mass balance written for the metal concentration (eq. S6).

$$|Zn| = |Zn|_{tot} - |Zn(\mathbf{L6})_2| - 2|Zn_2(\mathbf{L6})| - 3|Zn_3(\mathbf{L6})_2| \qquad \text{(S6)}$$

$$|Zn| = |Zn|_{tot} - 2|\mathbf{L6}|_{tot}\left(\frac{I_{Zn2L} + I_{ZnL2}}{I_{Zn2L} + 2I_{ZnL2}}\right) \qquad \text{(S7)}$$

The final introduction of the various concentrations expressed in eqs (S4)-(S7) into the law of mass action associated with equilibrium (9) yields eq. (S8) for $|Zn|_{tot} = 2|\mathbf{L6}|_{tot}$ (the standard concentration of the reference state is set at c^{θ} =1 M).

$$K_{exch} = \frac{|Zn(\mathbf{L6})_2| \cdot |Zn_3(\mathbf{L6})_2| \cdot |Zn|^4}{|Zn_2(\mathbf{L6})|^4} = 4\left(|\mathbf{L6}|_{tot}\right)^2 \frac{\left(I_{ZnL2}\right)^6}{\left(I_{Zn2L}\right)^4\left(I_{Zn2L} + 2I_{ZnL2}\right)^2} \qquad \text{(S8)}$$

Integration of the signals for H8 in the ^{1}H NMR spectrum of $[Zn_2(\mathbf{L6})Cl(CF_3SO_3)(H_2O)_2](CF_3SO_3)_2$ ($|\mathbf{L6}|_{tot}$ = 2.5 mM, CD_3CN, 293 K, Fig. 9) gave I_{Zn2L} = 5 and I_{ZnL2} = 1, from which we calculated $|Zn_2(\mathbf{L6})|$ = $1.79\cdot10^{-3}$ M (eq S4), $|Zn(\mathbf{L6})_2| = |Zn_3(\mathbf{L6})_2|$ = $1.79\cdot10^{-4}$ M (eq. S5), $|Zn|$ = $7.14\cdot10^{-4}$ M (eq. S7) and K_{exch} = $8.16\cdot10^{-10}$.

Appendix 2. **Thermodynamic model for equilibrium 9**.

$$4\,[Zn_2(\mathbf{L6})]^{4+} \underset{}{\overset{K_{exch}}{\rightleftharpoons}} [Zn(\mathbf{L6})_2]^{2+} + [Zn_3(\mathbf{L6})_2]^{6+} + 4\,[Zn]^{2+} \quad (9)$$

Point groups:	C_2	D_{2d}	S_4	O_h
σ^{ext}:	2	4	2	24
σ^{int}:	3^6	3^{12}	3^{12}	1
σ^{chiral}:	1/2	1	1	1

$$\omega_{exch} = \frac{\left(2\cdot 3^6\cdot\left(\tfrac{1}{2}\right)\right)^4}{\left(4\cdot 3^{12}\right)\left(2\cdot 3^{12}\right)(24)^4} = \frac{1}{2654208}$$

$$\Rightarrow K_{exch} = \omega_{exch}\frac{\left[\left(f_{tri}^{Zn}\right)^2 u_{tri}^{\mathbf{L6},\mathbf{L6}}\right]\cdot\left[\left(f_{tri}^{Zn}\right)^2\left(f_{bi}^{Zn}\right)^4\left(EM_{catenate}\right)^2 u_{tri}^{\mathbf{L6},\mathbf{L6}}\left(u_{bi}^{\mathbf{L6},\mathbf{L6}}\right)^2\left(u^{Zn,Zn}\right)^2\right]}{\left[\left(f_{tri}^{Zn}\right)\left(f_{bi}^{Zn}\right)^2\left(EM_{catenate}\right)\left(u_{bi}^{\mathbf{L6},\mathbf{L6}}\right)\left(u^{Zn,Zn}\right)\right]^4}$$

$$\Rightarrow K_{exch} = \omega_{exch}\left(\frac{u_{tri}^{\mathbf{L6},\mathbf{L6}}}{u_{bi}^{\mathbf{L6},\mathbf{L6}}}\frac{1}{EM_{catenate}\cdot\left(f_{bi}^{Zn}\right)^2\cdot u^{Zn,Zn}}\right)^2 \quad (10)$$