<Electronic Supplementary Information>

Coordinating nature of M_6L_{12} double-stranded macrocycles: co-ligand competition of

perchlorate, water, and acetonitrile depending on metal(II) ions

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	[Mn ₆ (ClO ₄) ₄ (CH ₃ CN 2(H ₂ O) ₆ L ₁₂]8ClO ₄ ·C H ₃ CN·7C ₇ H ₈)[Co ₆ (ClO ₄) ₄ (CH ₃ CN) (H ₂ O)L ₁₂][Co ₆ (ClO ₄). (CH ₃ CN) ₅ (H ₂ O) ₃ L ₁₂] 16ClO ₄ ·6C ₇ H ₈	⁷ 4[Cu ₆ (ClO ₄) ₈ (CH ₃ CN) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN) (H ₂ O) ₆ L ₁₂]8ClO ₄ ·CH ₃ CN·5C ₇ H ₈	² [Cl@Cu ₂ (ClO ₄) ₂ L ₄]Cl O ₄ ·4C ₇ H ₈
Formula	$\begin{array}{c} C_{295}H_{389}Cl_{12}Mn_6N_{27}O_{54}S\\ i_{12}\end{array}$	$SC_{544}H_{713}Cl_{24}Co_{12}N_{60}O_{100}Si_{24}$	$C_{566}H_{728}Cl_{24}Cu_{12}N_{56}O_{96}S_{i_{24}}$	$SC_{281}H_{373}Cl_{12}N_{27}O_{54}Si_{12}Z_{n_6}$	$C_{108}H_{136}Cl_4Cu_2N_8O_{12}Si_4$
$M_{ m w}$	6269.43	11924.82	12139.44	6147.74	2119.48
Cryst. sys.	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P2/n	<i>P</i> 2 ₁	Iba2	P2/n	$P2_{1}/n$
a (Å)	25.370(5)	26.225(5)	35.019(7)	25.489(5)	16.9088(8)
b (Å)	34.527(7)	30.532(6)	45.420(9)	34.525(7)	36.984(2)
<i>c</i> (Å)	43.510(9)	43.614(9)	46.291(9)	43.539(9)	17.1187(7)
$V(Å^3)$	37952(13)	34555(12)	73628(25)	38133(13)	10701.8(8)
Ζ	4	2	4	4	4
ho (g cm ⁻³)	1.097	1.146	1.095	1.071	1.315
μ (mm ⁻¹)	0.359	0.658	0.504	0.759	0.605
R _{int}	0.2017	0.0465	0.0753	0.0498	0.1079
GoF on F^2	1.192	1.022	0.912	1.824	1.081
$R_1 [I > 2\sigma(I)]^a$	0.2040	0.0913	0.0577	0.1910	0.0620
wR_2 (all data) ^b	0.5800	0.2955	0.1731	0.5596	0.1833

Table S1 Crystallographic data

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, {}^{b}wR_{2} = (\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}])^{1/2}$

$\frac{[Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4}{CH_3CN\cdot7C_7H_8}$		$[Co_{6}(ClO_{4})_{4}(CH_{3}CN)_{7}(H_{2}O)L_{12}][Co_{6}(ClO_{4})_{4}(CH_{3}CN)_{5}(H_{2}O)_{3}L_{12}]16ClO_{4}\cdot 6C_{7}H_{8}$				
O(1A)-Mn(1A)	2.155(10)	Co(1A)-N(1)	2.16(1)	Co(1B)-N(37)	2.129(8)	
N(1)-Mn(1A)	2.119(7)	Co(1A)-N(2)	2.162(9)	Co(1B)-N(39)	2.171(9)	
O(1)-Mn(2A)	2.427(7)	Co(2A)-O(53)	2.106(8)	Co(2B)-O(81)	2.128(7)	
O(2A)-Mn(2A)	2.319(13)	Co(2A)-O(1A)	2.187(8)	Co(2B)-O(1B)	2.216(7)	
O(5)-Mn(3A)	2.307(15)	Co(3A)-O(82)	2.075(7)	Co(3B)-N(58)	2.131(9)	
O(3A)-Mn(3A)	2.478(13)	Co(3A)-O(5A)	2.221(7)	Co(3B)-O(5B)	2.217(7)	
O(4A)-Mn(1B)	2.222(7)	Co(4A)-N(4)	2.150(10)	Co(4B)-N(56)	2.117(8)	
Mn(1B)-N(2)	2.188(9)	Co(4A)-N(3)	2.162(9)	Co(4B)-N(38)	2.170(8)	
O(9)-Mn(2B)	2.233(6)	O(9A)-Co(5A)	2.262(8)	Co(5B)-N(61)	2.128(9)	
O(5A)-Mn(2B)	2.198(6)	Co(5A)-O(83)	2.101(9)	Co(5B)-O(9B)	2.182(8)	
O(13)-Mn(3B)	2.261(6)	Co(6A)-N(59)	2.15(1)	Co(6B)-N(57)	2.128(8)	
O(6A)-Mn(3B)	2.132(6)	Co(6A)-O(13A)	2.234(7)	Co(6B)-O(13B)	2.183(7)	
N(1)-Mn(1A)-O(1A)	173.3(5)	N(1)-Co(1A)-N(2)	174.5(4)	N(37)-Co(1B)-N(39)	179.2(4)	
O(2A)-Mn(2A)-O(1)	174.5(4)	O(53)-Co(2A)-O(1A)	176.1(4)	O(81)-Co(2B)-O(1B)	171.3(3)	
O(5)-Mn(3A)-O(3A)	162.3(5)	O(82)-Co(3A)-O(5A)	179.2(3)	N(58)-Co(3B)-O(5B)	177.5(4)	
N(2)-Mn(1B)-O(4A)	178.3(3)	N(4)-Co(4A)-N(3)	178.2(4)	N(56)-Co(4B)-N(38)	179.3(4)	
O(5A)-Mn(2B)-O(9)	173.9(3)	O(83)-Co(5A)-O(9A)	175.7(4)	N(61)-Co(5B)-O(9B)	173.7(4)	
O(6A)-Mn(3B)-O(13)	171.5(3)	N(59)-Co(6A)-O(13A))177.5(4)	N(57)-Co(6B)-O(13B)	179.2(4)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN	N)4L12]4ClO4·5C7H8	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈	N)2(H2O)6L12]8ClO4.	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C	10 ₄ ·4C ₇ H ₈	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1)	$(N)_4 L_{12}] 4 C I O_4 \cdot 5 C_7 H_8$ 2.361(8)	$\frac{[Zn_6(ClO_4)_4(CH_3CN_5C_7H_8)}{CH_3CN\cdot 5C_7H_8}$	N ₂ (H ₂ O) ₆ L ₁₂]8ClO ₄ · 2.15(2)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C)	IO ₄ · 4C ₇ H ₈ 2.026(4)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17)	N) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A)	₹) 2(H2O)6L12]8ClO4 . 2.15(2) 2.196(9)	[Cl@Cu₂(ClO₄)₂L₄]C Cu(1)-N(1C) Cu(1)-N(1D)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1)	N) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A)	112 (H ₂ O) ₆ L ₁₂]8ClO₄· 2.15(2) 2.196(9) 2.29(1)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B)	10 ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21)	N ₄ L ₁₂] 4ClO ₄ · 5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A)	₹,15(2) 2.15(2) 2.296(9) 2.29(1) 2.29(2)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3)	N ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8)	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN)]$ $CH_{3}CN \cdot 5C_{7}H_{8}$ $O(1A)-Zn(1A)$ $N(1)-Zn(1A)$ $O(1)-Zn(2A)$ $Zn(2A)-O(2A)$ $O(5)-Zn(3A)$	3.15(2) 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5)	N ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7)	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN)\\CH_{3}CN \cdot 5C_{7}H_{8}$ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A)	3)2(H2O)6L12]8ClO4. 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3) 2.661(1)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5) N(3)-Cu(4)	X) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B)	₹) ₂ (H ₂ O) ₆ L ₁₂]8ClO ₄ . 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cl(2)	2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3) 2.661(1) 2.672(1)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5) N(3)-Cu(4) Cu(4)-O(25)	v) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B) Zn(1B)-N(2)	₹2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3) 2.661(1) 2.672(1) 2.037(4)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5) N(3)-Cu(4) Cu(4)-O(25) Cu(5)-O(29)	x) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B) Zn(1B)-N(2) O(9)-Zn(2B)	₹ 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2D)	IO ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3) 2.661(1) 2.672(1) 2.037(4) 2.038(3)	
$[Cu_6(ClO_4)_8(CH_3CN_6)(Cu_1)-N(1)-(1)-(1)-(1)-(1)-(1)-(1)-(1)-(1)-(1)-$	x) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B) Zn(1B)-N(2) O(9)-Zn(2B) Zn(2B)-O(2B)	3.15(2) 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C)	$\begin{array}{c} \textbf{IO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \end{array}$	
$\begin{tabular}{ c c c c c } \hline & [Cu_6(ClO_4)_8(CH_3CN_6)] \\ \hline & Cu(1)-N(1) \\ Cu(1)-O(17) \\ Cu(2)-O(1) \\ Cu(2)-O(21) \\ N(2)-Cu(3) \\ Cu(2)-Cu(3) \\ Cu(3)-O(5) \\ N(3)-Cu(4) \\ Cu(4)-O(25) \\ Cu(4)-O(25) \\ Cu(5)-O(29) \\ Cu(5)-O(9) \\ N(4)-Cu(6) \end{tabular}$	A) ₄ L ₁₂]4ClO ₄ ·5C ₇ H ₈ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8) 2.449(8)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B) Zn(1B)-N(2) O(9)-Zn(2B) Zn(2B)-O(2B) O(13)-Zn(3B)	3.15(2) 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cl(2) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C) Cu(2)-N(2A)	ID ₄ · 4C ₇ H ₈ 2.026(4) 2.030(3) 2.042(3) 2.047(3) 2.379(3) 2.661(1) 2.672(1) 2.037(4) 2.038(3) 2.040(3) 2.045(4)	
[Cu ₆ (ClO ₄) ₈ (CH ₃ CN Cu(1)-N(1) Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5) N(3)-Cu(4) Cu(4)-O(25) Cu(5)-O(29) Cu(5)-O(9) N(4)-Cu(6) Cu(6)-O(13)	$(3)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8) 2.449(8) 2.495(6)	[Zn ₆ (ClO ₄) ₄ (CH ₃ CN CH ₃ CN·5C ₇ H ₈ O(1A)-Zn(1A) N(1)-Zn(1A) O(1)-Zn(2A) Zn(2A)-O(2A) O(5)-Zn(3A) Zn(3A)-O(3A) Zn(1B)-O(1B) Zn(1B)-N(2) O(9)-Zn(2B) Zn(2B)-O(2B) O(13)-Zn(3B) Zn(3B)-O(3B)	3.15(2) 2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-O(5)	$\begin{array}{c} \mathbf{IO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \end{array}$	
$[Cu_{6}(ClO_{4})_{8}(CH_{3}CN)]$ $Cu(1)-N(1)$ $Cu(2)-O(1)$ $Cu(2)-O(1)$ $Cu(2)-O(21)$ $N(2)-Cu(3)$ $Cu(3)-O(5)$ $N(3)-Cu(4)$ $Cu(4)-O(25)$ $Cu(5)-O(29)$ $Cu(5)-O(29)$ $Cu(5)-O(9)$ $N(4)-Cu(6)$ $Cu(6)-O(13)$ $N(1)-Cu(1)-O17$	$(3)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8) 2.449(8) 2.449(8) 2.495(6) 176.27(3)	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN CH_{3}CN CH_{3}C$	2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.15(1) 2.15(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cl(2) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-N(2A) Cu(2)-O(5) N(1D)-Cu(1)-N(1B)	$\begin{array}{c} \mathbf{HO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \\ \hline 179.3(2) \end{array}$	
$\begin{tabular}{ c c c c c } \hline & [Cu_6(ClO_4)_8(CH_3CN_5)] \\ \hline & Cu(1)-N(1) \\ Cu(1)-O(17) \\ Cu(2)-O(1) \\ Cu(2)-O(21) \\ N(2)-Cu(3) \\ Cu(3)-O(5) \\ N(3)-Cu(4) \\ Cu(3)-O(5) \\ N(3)-Cu(4) \\ Cu(4)-O(25) \\ Cu(5)-O(29) \\ Cu(5)-O(29) \\ Cu(5)-O(9) \\ N(4)-Cu(6) \\ Cu(6)-O(13) \\ \hline & N(1)-Cu(1)-O17 \\ O(1)-Cu(2)-O(21) \\ \hline \end{tabular}$	$(3)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8) 2.449(8) 2.449(8) 2.495(6) 176.27(3) 178.58(4)	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN) CH_{3}CN SC_{7}H_{8}$ $O(1A)-Zn(1A)$ $N(1)-Zn(1A)$ $O(1)-Zn(2A)$ $Zn(2A)-O(2A)$ $O(5)-Zn(3A)$ $Zn(1B)-O(1B)$ $Zn(1B)-O(1B)$ $Zn(1B)-N(2)$ $O(9)-Zn(2B)$ $Zn(2B)-O(2B)$ $O(13)-Zn(3B)$ $Zn(3B)-O(3B)$ $O(1A)-Zn(1A)-N(1)$ $O(2A)-Zn(2A)-O(1)$	2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7) 177.7(6) 167.1(6)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-N(2A) Cu(2)-O(5) N(1D)-Cu(1)-N(1B) N(1C)-Cu(1)-N(1A)	$\begin{array}{c} \mathbf{IO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \\ \hline 179.3(2) \\ 178.2(1) \end{array}$	
$\frac{[Cu_6(ClO_4)_8(CH_3CN)]}{Cu(1)-N(1)}$ Cu(1)-O(17) Cu(2)-O(1) Cu(2)-O(21) N(2)-Cu(3) Cu(3)-O(5) N(3)-Cu(4) Cu(4)-O(25) Cu(5)-O(29) Cu(5)-O(9) N(4)-Cu(6) Cu(6)-O(13) N(1)-Cu(1)-O17 O(1)-Cu(2)-O(21) N(2)-Cu(3)-O(5)	$(3)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ 2.361(8) 2.595(6) 2.469(7) 2.379(6) 2.401(8) 2.544(7) 2.343(7) 2.611(8) 2.405(7) 2.451(8) 2.495(6) 176.27(3) 178.58(4) 170.94(4)	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN)$ $CH_{3}CN \cdot 5C_{7}H_{8}$ $O(1A) - Zn(1A)$ $N(1) - Zn(1A)$ $O(1) - Zn(2A)$ $Zn(2A) - O(2A)$ $O(5) - Zn(3A)$ $Zn(1B) - O(1B)$ $Zn(1B) - O(1B)$ $Zn(1B) - N(2)$ $O(9) - Zn(2B)$ $Zn(2B) - O(2B)$ $O(13) - Zn(3B)$ $Zn(3B) - O(3B)$ $O(1A) - Zn(1A) - N(1)$ $O(2A) - Zn(2A) - O(1)$ $O(3A) - Zn(3A) - O(5)$	2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7) 177.7(6) 167.1(6) 175.6(4)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2C) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-O(5) N(1D)-Cu(1)-N(1B) N(1C)-Cu(1)-N(1A) O(1)-Cu(1)-Cl(1)	$ \begin{array}{r} IO_4 \cdot 4C_7H_8 \\ 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \\ 179.3(2) \\ 178.2(1) \\ 174.0(1) \\ \end{array} $	
$\frac{ Cu_{6}(ClO_{4})_{8}(CH_{3}CN) }{Cu(1)-N(1)}$ $Cu(1)-O(17)$ $Cu(2)-O(1)$ $Cu(2)-O(21)$ $N(2)-Cu(3)$ $Cu(3)-O(5)$ $N(3)-Cu(4)$ $Cu(4)-O(25)$ $Cu(5)-O(29)$ $Cu(5)-O(9)$ $N(4)-Cu(6)$ $Cu(6)-O(13)$ $N(1)-Cu(1)-O17$ $O(1)-Cu(2)-O(21)$ $N(2)-Cu(3)-O(5)$ $N(3)-Cu(4)-O(25)$	$\begin{aligned} \mathbf{\hat{N}_{4}L_{12}} \mathbf{ 4ClO_{4} \cdot 5C_{7}H_{8}} \\ \hline 2.361(8) \\ 2.595(6) \\ 2.469(7) \\ 2.379(6) \\ 2.401(8) \\ 2.544(7) \\ 2.343(7) \\ 2.611(8) \\ 2.405(7) \\ 2.451(8) \\ 2.495(7) \\ 2.495(6) \\ \hline 176.27(3) \\ 178.58(4) \\ 170.94(4) \\ 176.11(3) \end{aligned}$	$[Zn_{6}(ClO_{4})_{4}(CH_{3}CN)$ $CH_{3}CN \cdot 5C_{7}H_{8}$ $O(1A) - Zn(1A)$ $O(1) - Zn(2A)$ $O(1) - Zn(2A)$ $O(5) - Zn(3A)$ $Zn(2A) - O(2A)$ $O(5) - Zn(3A)$ $Zn(1B) - O(1B)$ $Zn(1B) - O(1B)$ $Zn(1B) - N(2)$ $O(9) - Zn(2B)$ $O(13) - Zn(3B)$ $Zn(2B) - O(2B)$ $O(13) - Zn(3B)$ $Zn(3B) - O(3B)$ $O(1A) - Zn(1A) - N(1)$ $O(2A) - Zn(2A) - O(1)$ $O(3A) - Zn(3A) - O(5)$ $O(1B) - Zn(1B) - N(2)$	2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7) 177.7(6) 167.1(6) 175.6(4) 178.0(3)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2B) Cu(2)-N(2C) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-O(5) N(1D)-Cu(1)-N(1B) N(1C)-Cu(1)-N(1A) O(1)-Cu(1)-Cl(1) N(2B)-Cu(2)-N(2D)	$\begin{array}{c} \mathbf{IO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \\ \hline 179.3(2) \\ 178.2(1) \\ 174.0(1) \\ 177.8(1) \end{array}$	
$\frac{ Cu_6(ClO_4)_8(CH_3CN) }{ Cu(1)-N(1) }$ $Cu(1)-O(17) $ $Cu(2)-O(1) $ $Cu(2)-O(21) $ $N(2)-Cu(3) $ $Cu(3)-O(5) $ $N(3)-Cu(4) $ $Cu(4)-O(25) $ $Cu(5)-O(29) $ $Cu(5)-O(9) $ $N(4)-Cu(6) $ $Cu(6)-O(13) $ $N(1)-Cu(1)-O17 $ $O(1)-Cu(2)-O(21) $ $N(2)-Cu(3)-O(5) $ $N(3)-Cu(4)-O(25) $ $O(9)-Cu(5)-O(29) $	$\begin{aligned} \mathbf{\hat{N}_{4}L_{12}} \mathbf{ 4ClO_{4} \cdot 5C_{7}H_{8}} \\ \hline 2.361(8) \\ 2.595(6) \\ 2.469(7) \\ 2.379(6) \\ 2.401(8) \\ 2.544(7) \\ 2.343(7) \\ 2.611(8) \\ 2.405(7) \\ 2.451(8) \\ 2.495(7) \\ 2.451(8) \\ 2.495(6) \\ \hline 176.27(3) \\ 178.58(4) \\ 170.94(4) \\ 176.11(3) \\ 178.62(4) \end{aligned}$	$[Zn_6(ClO_4)_4(CH_3CN)CH_3CN·5C_7H_8O(1A)-Zn(1A)N(1)-Zn(1A)O(1)-Zn(2A)Zn(2A)-O(2A)O(5)-Zn(3A)Zn(3A)-O(3A)Zn(1B)-O(1B)Zn(1B)-N(2)O(9)-Zn(2B)Zn(2B)-O(2B)O(13)-Zn(3B)Zn(3B)-O(3B)O(1A)-Zn(1A)-N(1)O(2A)-Zn(2A)-O(1)O(3A)-Zn(2A)-O(5)O(1B)-Zn(1B)-N(2)O(2B)-Zn(2B)-O(9)$	2.15(2) 2.196(9) 2.29(1) 2.29(2) 2.38(1) 2.15(1) 2.111(6) 2.239(8) 2.251(6) 2.148(6) 2.272(6) 2.135(7) 177.7(6) 167.1(6) 175.6(4) 178.0(3) 178.2(3)	[Cl@Cu ₂ (ClO ₄) ₂ L ₄]C Cu(1)-N(1C) Cu(1)-N(1D) Cu(1)-N(1B) Cu(1)-N(1A) Cu(1)-O(1) Cu(1)-Cl(1) Cl(1)-Cu(2) Cu(2)-N(2B) Cu(2)-N(2B) Cu(2)-N(2D) Cu(2)-N(2C) Cu(2)-N(2C) Cu(2)-N(2A) Cu(2)-O(5) N(1D)-Cu(1)-N(1B) N(1C)-Cu(1)-N(1A) O(1)-Cu(1)-Cl(1) N(2B)-Cu(2)-N(2D) N(2C)-Cu(2)-N(2A)	$\begin{array}{r} \mathbf{IO_4 \cdot 4C_7H_8} \\ \hline 2.026(4) \\ 2.030(3) \\ 2.042(3) \\ 2.047(3) \\ 2.379(3) \\ 2.661(1) \\ 2.672(1) \\ 2.037(4) \\ 2.038(3) \\ 2.040(3) \\ 2.040(3) \\ 2.045(4) \\ 2.409(4) \\ \hline 179.3(2) \\ 178.2(1) \\ 174.0(1) \\ 177.8(1) \\ 178.6(1) \end{array}$	

Table S2 Selected bond length (Å) and angle (°)



Fig. S1 IR spectra of L (a), $[Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 7C_7H_8$ (b), $[Co_6(ClO_4)_4(CH_3CN)_7(H_2O)L_{12}][Co_6(ClO_4)_4(CH_3CN)_5(H_2O)_3L_{12}]16ClO_4 \cdot 6C_7H_8$ (c), $[Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ (d), and $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 5C_7H_8$ (e).



Fig. S2 ¹H NMR spectra of L (a, f), $[Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 7C_7H_8$ (b, g), $[Co_6(ClO_4)_4(CH_3CN)_7(H_2O)L_{12}][Co_6(ClO_4)_4(CH_3CN)_5(H_2O)_3L_{12}]16ClO_4 \cdot 6C_7H_8$ (c, h), $[Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ (d, i), and $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 5C_7H_8$ (e, j) in Me₂SO-*d*₆ (dissociated; a - f) and CD₃CN (dissolved; g - j). Square and triangle indicate toluene and acetonitrile, respectively.



Fig. S3 PXRD patterns obtained through calculations (top) and experiments (bottom) in $[Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 7C_7H_8$ (a), $[Co_6(ClO_4)_4(CH_3CN)_7(H_2O)L_{12}][Co_6(ClO_4)_4(CH_3CN)_5(H_2O)_3L_{12}]16ClO_4 \cdot 6C_7H_8$ (b), $[Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ (c), and $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 5C_7H_8$ (d).











Fig. S4 The ellipsoidal model of $[Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 7C_7H_8$ (a), $[Co_6(ClO_4)_4(CH_3CN)_7(H_2O)L_{12}][Co_6(ClO_4)_4(CH_3CN)_5(H_2O)_3L_{12}]16ClO_4 \cdot 6C_7H_8$ (b), $[Cu_6-(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ (c), $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 5C_7H_8$ (d), and $[Cl@Cu_2(ClO_4)_2L_4]ClO_4 \cdot 4C_7H_8$ (e).



 $\begin{array}{l} \label{eq:Fig. S5} \mbox{The packing modes(top view) for} \\ [Mn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4\cdot CH_3CN\cdot 7C_7H_8\ (a), \\ [Co_6(ClO_4)_4(CH_3CN)_7(H_2O)L_{12}][Co_6(ClO_4)_4(CH_3CN)_5(H_2O)_3L_{12}]16ClO_4\cdot 6C_7H_8\ (b), \\ [Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4\cdot 5C_7H_8\ (c), \ and \\ [Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4\cdot CH_3CN\cdot 5C_7H_8\ (d). \end{array}$



Fig. S6 ¹H NMR spectra of L (a), $[Mn(ClO_4)_2L_2]_n$ (b), $[Co(ClO_4)_2L_2]_n$ (c), $[Cu(ClO_4)_2L_2]_n$ (d), and $[Zn(ClO_4)_2L_2]_n$ (e) after heating up to 170 °C.



Fig. S7 PXRD patterns of $[Mn(ClO_4)_2L_2]_n$, $[Co(ClO_4)_2L_2]_n$, $[Cu(ClO_4)_2L_2]_n$, and $[Zn(ClO_4)_2L_2]_n$ after heating up to 170 °C.



Fig. S8 IR spectra of L (a), $[Mn(ClO_4)_2L_2]_n$ (b), $[Co(ClO_4)_2L_2]_n$ (c), $[Cu(ClO_4)_2L_2]_n$ (d), and $[Zn(ClO_4)_2L_2]_n$ (e) after heating up to 170 °C.



Fig. S9 The homogeneous catalysis rates of 3,5-di-*tert*-butylcatechol using $[Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ in dichloromethane (black line), acetone (red line), and acetonitrile (blue line) at 40 °C (square) and RT (triangle).



Fig. S10 ¹H NMR spectral procedure on catalytic oxidation 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylorthoquinone using $[Cu_6(ClO_4)_8(CH_3CN)_4L_{12}]4ClO_4 \cdot 5C_7H_8$ in dichoromethaned₂.



Fig. S11 Plot showing catalytic yields of transesterification of phenyl acetate using $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]$ 8ClO₄·CH₃CN·5C₇H₈ (black line), $[Zn(ClO_4)_2L_2]$ (red line), and $Zn(ClO_4)_2 + L$ (blue line) in methanol at 50 °C.



Fig. S12 ¹H NMR spectral procedure on transesterification of phenyl acetate using $[Zn_6(ClO_4)_4(CH_3CN)_2(H_2O)_6L_{12}]8ClO_4 \cdot CH_3CN \cdot 5C_7H_8$ in methanol at 50 °C.