<Electronic Supplementary Information>

Construction and catalytic effects of solvent- and metal(II)-dependent crystal structures: transformation of process of 0D into 3D structures

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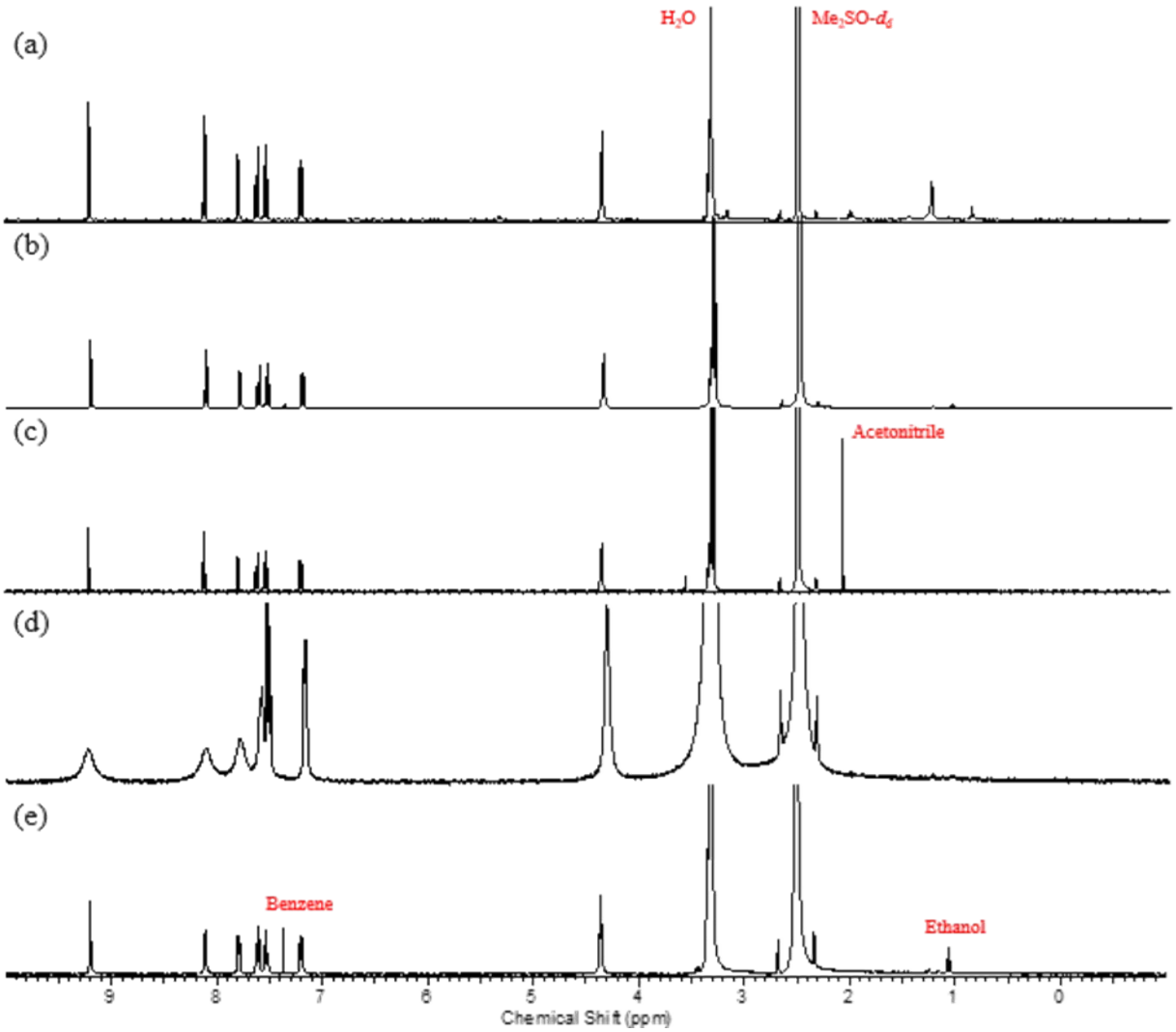

Fig. S1 ^{1}H NMR spectra of L (a), $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (b), $[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$ (c), $[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (d), and $[NO_3@Ni_3(NO_3)_3L_2(H_2O)_6]2NO_3\cdot C_2H_5OH\cdot C_6H_6$ (e) in Me_2SO-d_6.

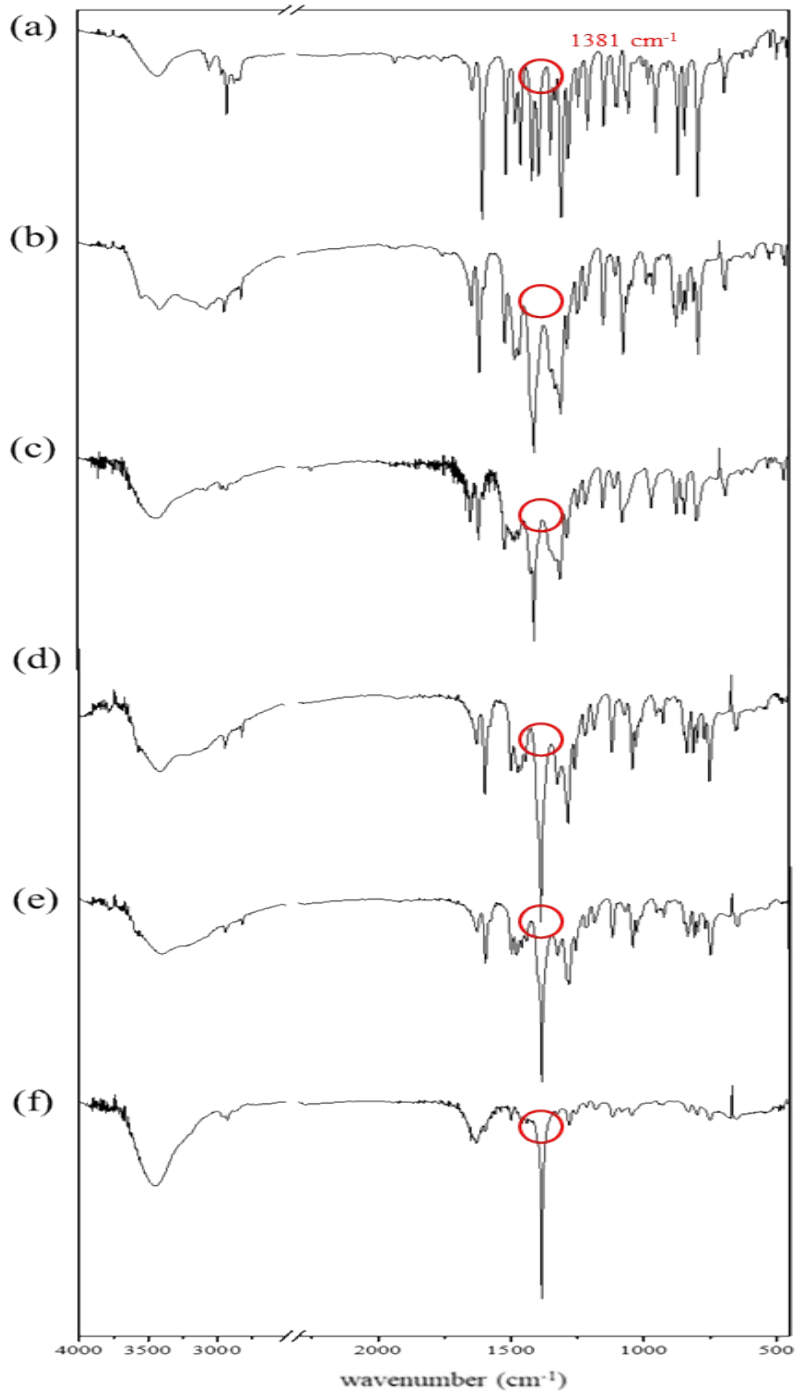

Fig. S2 IR spectra of L (a), $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (b), $[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$ (c), $[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (d), $[NO_3@Ni_3(NO_3)_3L_2(H_2O)_6]2NO_3\cdot C_2H_5OH\cdot C_6H_6$ (e), and $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$ (f).

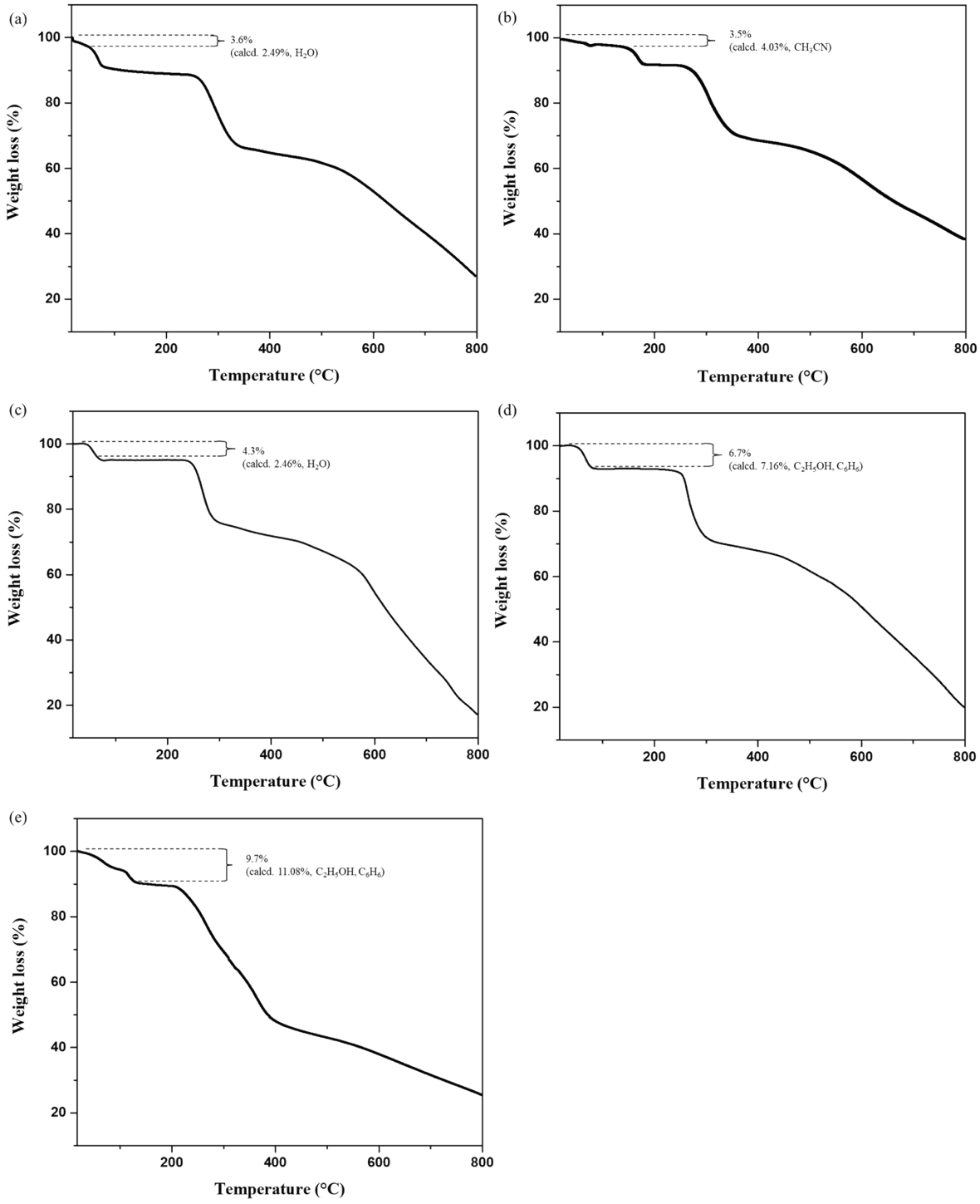

Fig. S3 TGA curves for $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (a), $[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$ (b), $[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (c), $[NO_3@Ni_3(NO_3)_3L_2(H_2O)_6]2NO_3\cdot C_2H_5OH\cdot C_6H_6$ (d), and $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$ (e).

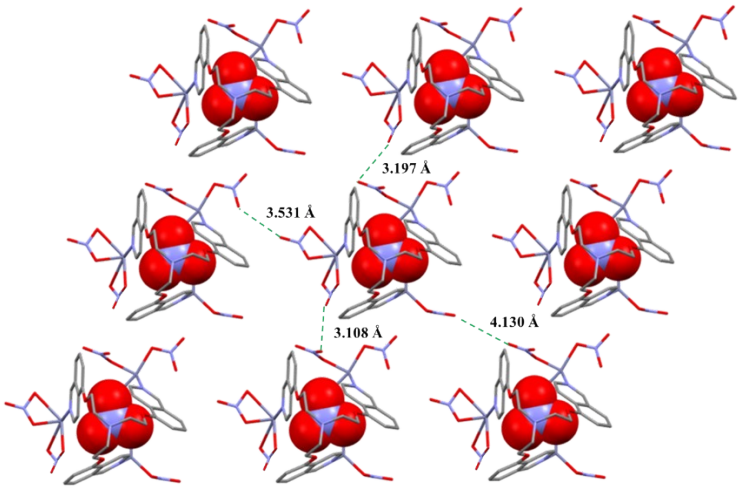

Fig. S4 Packing mode of $[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$.

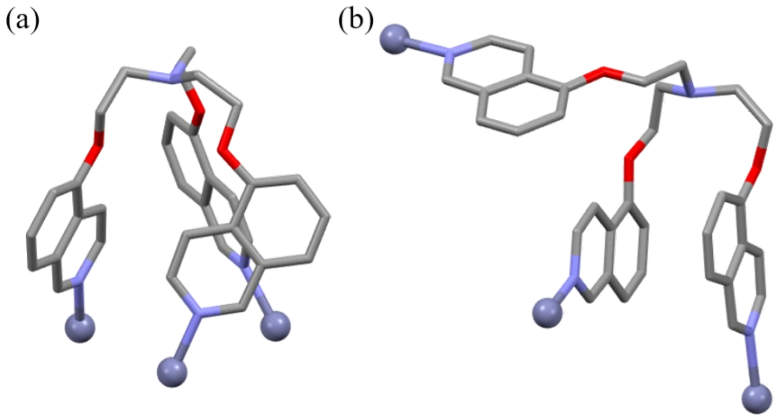

Fig. S5 L conformation of the cage and the 3D networks.

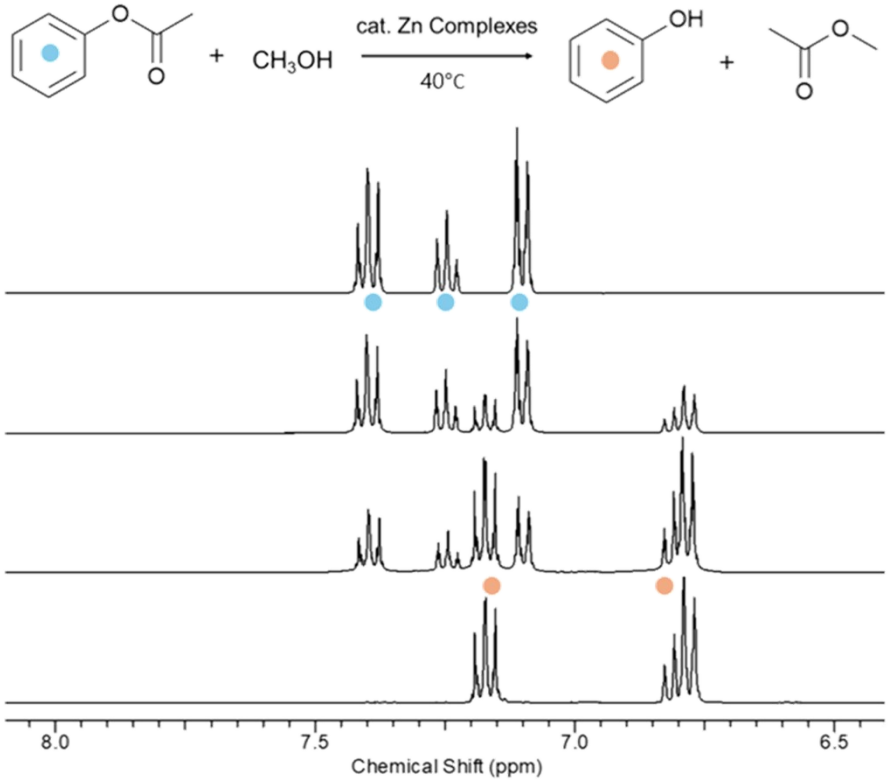

Fig. S6 ^{1}H-NMR spectra of $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ transesterification catalysis at 40°C in MeOD.

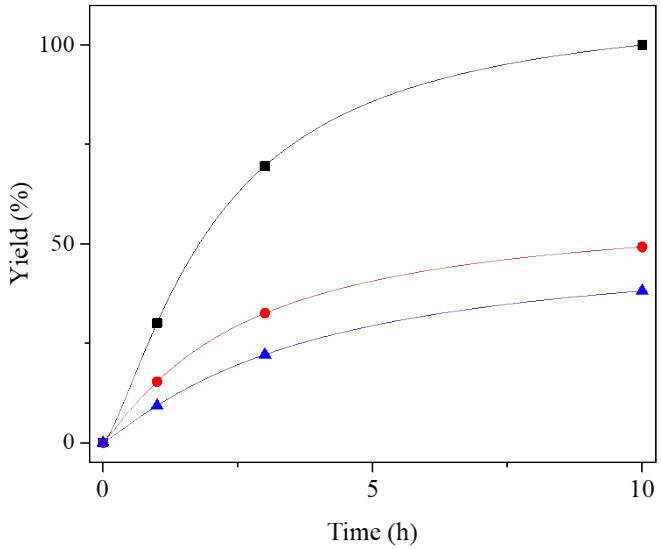

Fig. S7 Plot showing transesterification catalysis of phenyl acetate with dried methanol using $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (black line), mixture of $Zn(NO_3)_2$: L (1 : 1) (red line), and $[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$ (blue) at 40°C.

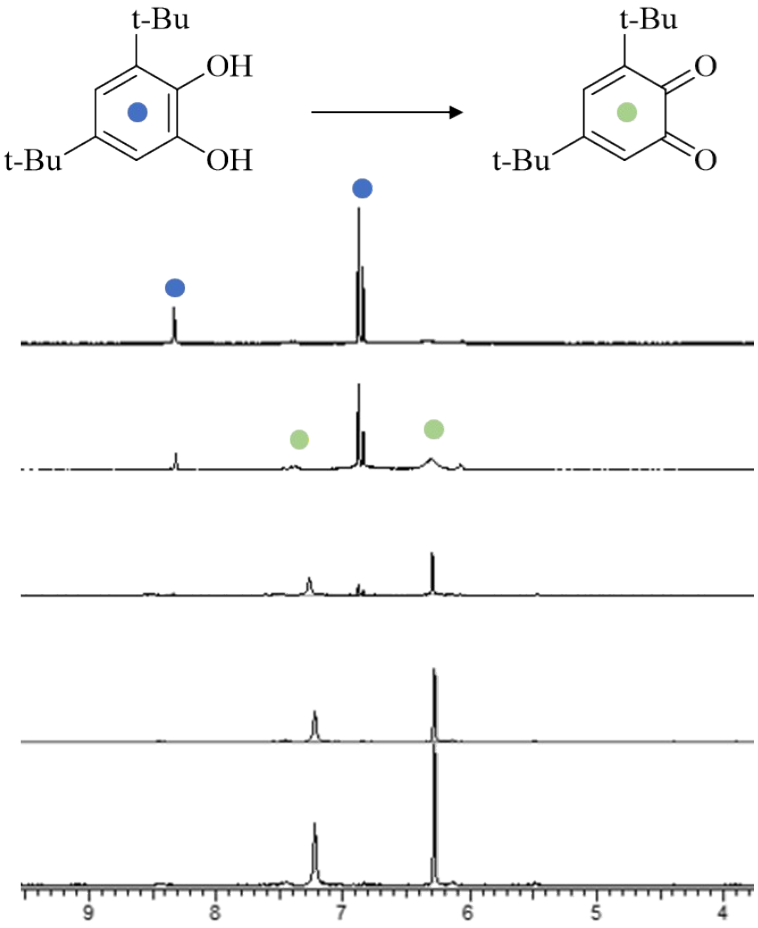

Fig. S8 ^{1}H NMR spectral change (in Me_2CO-d_6) on catalytic oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylorthoquinone using $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$ in acetone.

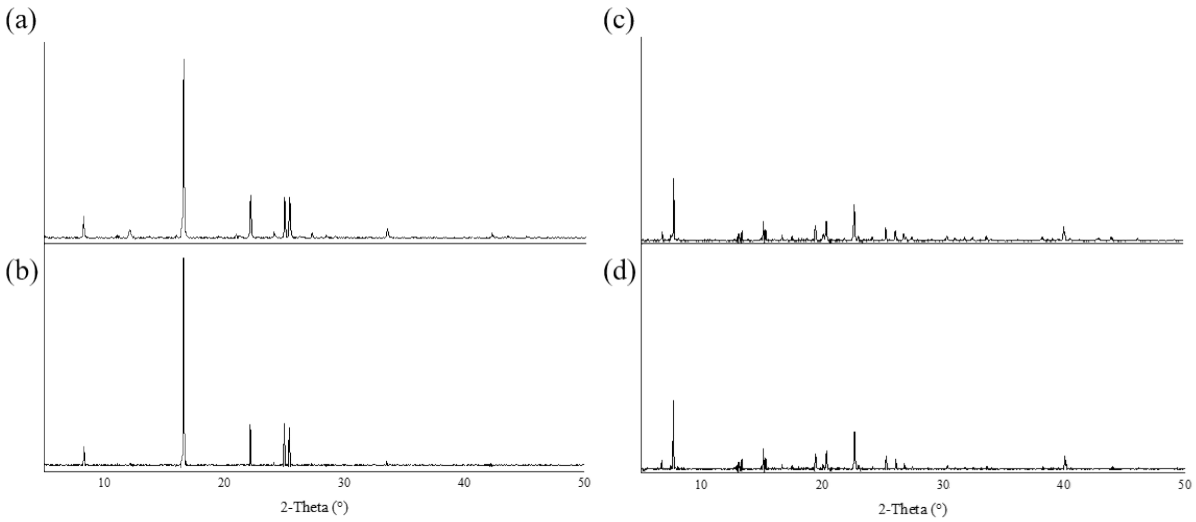

Fig. S9 Powder X-ray diffraction patterns of catalysis -before (a) and -after (b) of $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ and catalysis -before (c) and -after (d) of $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$.

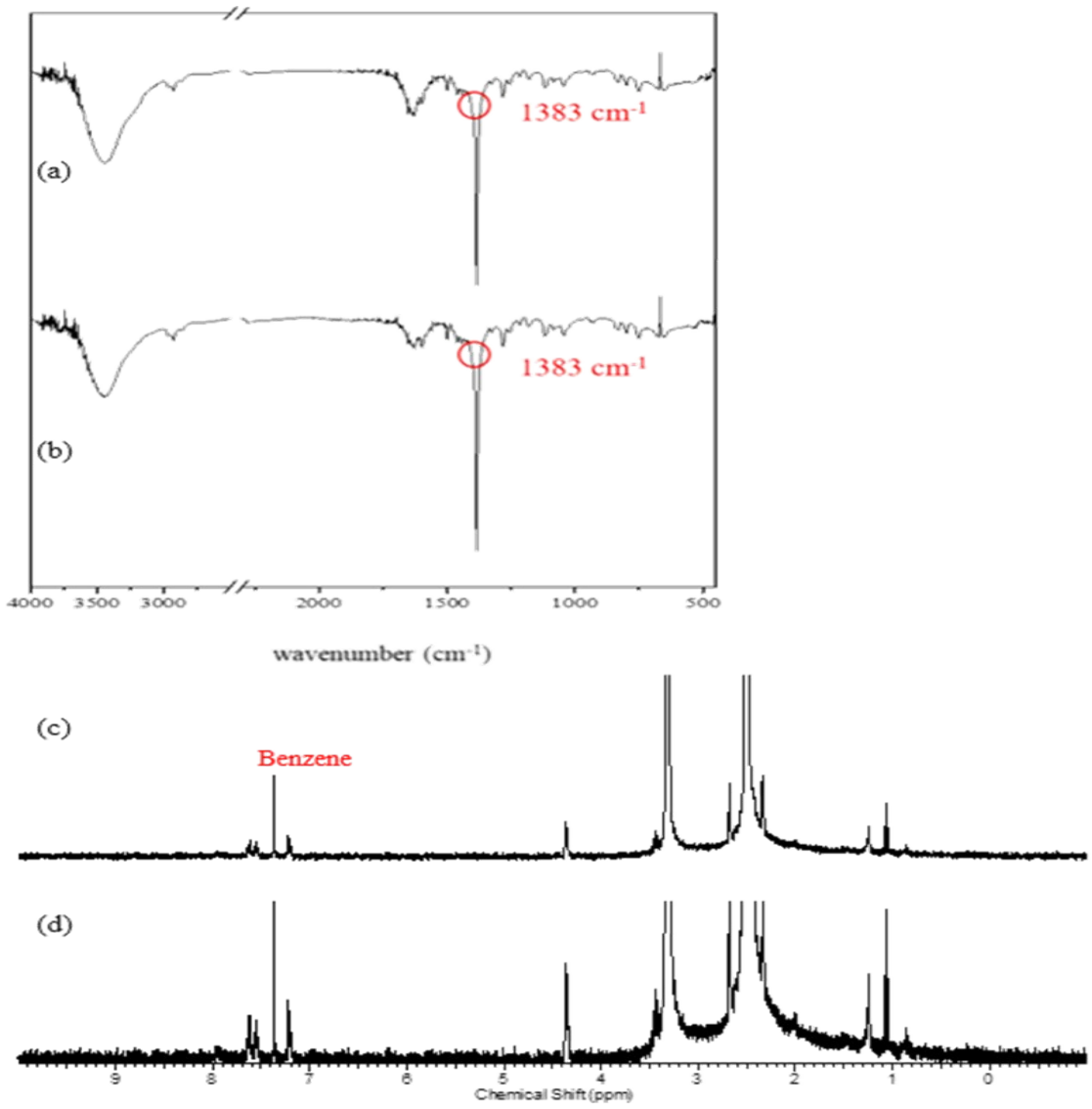

Fig. S10 IR spectra of original $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$ (a) and the recycled crystals after catechol oxidation (b). ^1H NMR spectra of original $[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$ (c) and the recycled crystals after catechol oxidation (d).

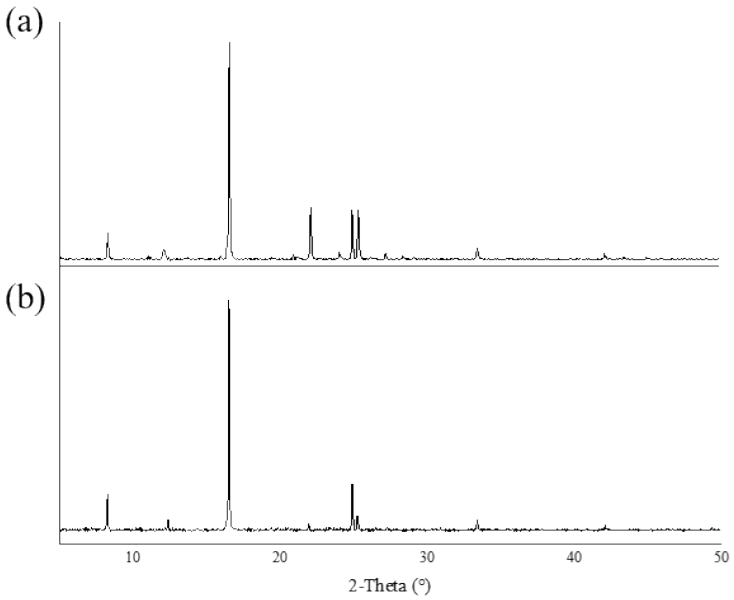

Fig. S11 Powder X-ray diffraction patterns of 3D networks $[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (a) and $[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$ (b).

Table S1. Crystallographic data

	$[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$	$[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$	$[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$	$[NO_3@Ni_3(NO_3)_3L_2(H_2O)_6]2NO_3\cdot C_2H_5OH\cdot C_6H_6$	$[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$
Formula	$C_{33}H_{34}ZnN_6O_{11}Zn$	$C_{70}H_{66}N_{16}O_{24}Zn_3$	$C_{33}H_{34}CoN_6O_{11}$	$C_{74}H_{84}N_{14}Ni_3O_{31}$	$C_{82}H_{84}Cu_3N_{14}O_{26}$
M_w	756.03	1711.49	749.59	1841.68	1872.25
Cryst. sys.	Monoclinic	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group	*Cc*	$P2_1/m$	*Cc*	*P*-3	$P2_1/m$
a (Å)	17.513(5))	11.732(2)	17.551(4)	14.608(2)	21.195(2)
b (Å)	14.247(3)	23.592(5)	14.217(3)	14.608(2)	18.926(2)
c (Å)	14.249(3)	14.243(3)	14.235(3)	24.244(5)	22.497(2)
α (°)	-	-	-	-	-
β (°)	112.70(3)	111.45(3)	112.49(3)	-	105.855(2)
γ (°)	-	-	-	120	-
V (Å^3)	3280(1)	3669(2)	3282(1)	4480(2)	8681(1)
Z	4	2	4	2	4
ρ (g cm^{-3})	1.531	1.549	1.517	1.365	1.433
μ (mm^{-1})	0.595	1.020	0.430	0.679	0.813
R_{int}	0.0223	0.0696	0.1035	0.1116	0.1769
GoF on F^2	1.077	1.072	0.851	1.389	1.075
R_1 [$I>2\sigma(I)$][a]	0.0332	0.0766	0.0631	0.1458	0.1061
wR_2 (all data)[b]	0.0853	0.2679	0.1256	0.4034	0.3305

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°)

$[Zn(NO_3)L(H_2O)](NO_3)\cdot H_2O$		$[NO_3@Zn_3(NO_3)_5L_2]\cdot 2CH_3CN$		$[Co(NO_3)L(H_2O)](NO_3)\cdot H_2O$		$[NO_3@Ni_3(NO_3)_3L_2(H_2O)_6]2NO_3\cdot C_2H_5OH\cdot C_6H_6$		$[NO_3@Cu_3(NO_3)_5L_2(C_2H_5OH)]\cdot C_2H_5OH\cdot 2C_6H_6$	
Zn(1)-O(1C)	2.031(3)	Zn(1)-O(9')	1.89(3)	N(1)-Co(2)$^{\#1}$	2.157(4)	Ni(1)-O(3)	2.036(8)	Cu(1)-O(1)	1.983(16)
Zn(1)-N(13)	2.091(3)	Zn(1)-N(3A)$^{\#1}$	2.044(3)	N(2)-Co(2)	2.103(3)	Ni(1)-O(5)	2.055(10)	Cu(1)-N(2B)	1.992(7)
Zn(1)-N(39)$^{\#1}$	2.168(3)	Zn(1)-N(3A)	2.044(3)	Co(2)-O(3)	2.056(3)	Ni(1)-O(4)	2.073(10)	Cu(1)-N(2A)	2.002(7)
Zn(1)-N(26)$^{\#2}$	2.179(3)	Zn(2)-N(4A)$^{\#1}$	2.001(4)	Co(2)-N(4)$^{\#2}$	2.175(3)	Ni(1)-N(3)	2.114(10)	Cu(1)-O(4)	2.061(10)
Zn(1)-O(2A)	2.206(3)	Zn(2)-N(4A)	2.001(4)	Co(2)-O(7)	2.191(3)	Ni(1)-N(1)	2.131(4)	Cu(1)-O(3C)	2.256(9)
Zn(1)-O(3A)	2.339(3)	Zn(2)-O(3)	2.063(4)	Co(2)-O(6)	2.197(3)	Ni(1)-O(7)	2.158(11)	Cu(1)-O(3)	2.40(3)
		Zn(2)-O(10')	2.18(4)						
O(1C)-Zn(1)-N(13)	104.17(14)	Zn(2)-O(10')$^{\#1}$	2.18(4)	C(2)-N(1)-Co(2)$^{\#1}$	122.6(3)	O(3)-Ni(1)-O(5)	93.7(4)	O(1)-Cu(1)-N(2B)	89.3(4)
O(1C)-Zn(1)-N(39)$^{\#1}$	94.01(10)	Zn(2)-N(4')	2.45(4)	C(3)-N(1)-Co(2)$^{\#1}$	121.0(3)	O(3)-Ni(1)-O(4)	178.0(4)	O(1)-Cu(1)-N(2A)	87.8(4)
N(13)-Zn(1)-N(39)$^{\#1}$	93.47(12)			O(3)-Co(2)-N(2)	98.78(16)	O(5)-Ni(1)-O(4)	87.7(5)	N(2B)-Cu(1)-N(2A)	175.4(3)
O(1C)-Zn(1)-N(26)$^{\#2}$	93.03(12)	N(3)-O(7)-Zn(1)	116.1(5)	O(3)-Co(2)-N(1)$^{\#3}$	93.88(12)	O(3)-Ni(1)-N(3)	91.0(3)	O(1)-Cu(1)-O(4)	176.2(4)
N(13)-Zn(1)-N(26)$^{\#2}$	88.43(11)	O(9')-Zn(1)-N(3A)	109.7(3)	N(2)-Co(2)-N(1)$^{\#3}$	93.06(14)	O(5)-Ni(1)-N(3)	88.5(4)	N(2B)-Cu(1)-O(4)	93.5(3)
N(39)$^{\#1}$-Zn(1)-N(26)$^{\#2}$	172.02(12)	O(16)-Zn(1)-N(3A)	124.9(2)	O(3)-Co(2)-N(4)$^{\#2}$	91.70(14)	O(4)-Ni(1)-N(3)	90.4(4)	N(2A)-Cu(1)-O(4)	89.6(3)
O(1C)-Zn(1)-O(2A)	101.85(13)	N(3A)$^{\#1}$-Zn(1)-N(3A)	122.76(17)	N(2)-Co(2)-N(4)$^{\#2}$	87.85(13)	O(3)-Ni(1)-N(1)	87.3(3)	O(1)-Cu(1)-O(3C)	93.0(4)
N(13)-Zn(1)-O(2A)	153.73(11)	N(3A)$^{\#1}$-Zn(1)-O(7)	105.9(2)	N(1)$^{\#3}$-Co(2)-N(4)$^{\#2}$	174.14(14)	O(5)-Ni(1)-N(1)	89.5(3)	N(2B)-Cu(1)-O(3C)	90.0(3)
N(39)$^{\#1}$-Zn(1)-O(2A)	88.25(12)	N(3A)-Zn(1)-O(7)	85.8(2)	O(3)-Co(2)-O(7)	160.72(14)	O(4)-Ni(1)-N(1)	91.3(3)	N(2A)-Cu(1)-O(3C)	93.7(3)
N(26)$^{\#2}$-Zn(1)-O(2A)	86.64(11)	O(11)-Zn(2)-N(4A)$^{\#1}$	129.6(3)	N(2)-Co(2)-O(7)	100.44(13)	N(3)-Ni(1)-N(1)	177.3(3)	O(4)-Cu(1)-O(3C)	84.5(4)
O(1C)-Zn(1)-O(3A)	158.33(12)	O(11)-Zn(2)-N(4A)	85.1(2)	N(1)$^{\#3}$-Co(2)-O(7)	86.55(12)	O(3)-Ni(1)-O(7)	86.0(5)	O(1)-Cu(1)-O(3)	55.6(4)
N(13)-Zn(1)-O(3A)	97.50(11)	N(4A)$^{\#1}$-Zn(2)-N(4A)	128.50(19)	N(4)$^{\#2}$-Co(2)-O(7)	87.59(12)	O(5)-Ni(1)-O(7)	179.7(5)	N(2B)-Cu(1)-O(3)	85.7(5)
N(39)$^{\#1}$-Zn(1)-O(3A)	84.37(11)	O(11)-Zn(2)-O(3)	107.5(3)	O(3)-Co(2)-O(6)	102.07(15)	O(4)-Ni(1)-O(7)	92.6(6)	N(2A)-Cu(1)-O(3)	89.8(5)
N(26)$^{\#2}$-Zn(1)-O(3A)	87.71(10)	N(4A)$^{\#1}$-Zn(2)-O(3)	101.38(10)	N(2)-Co(2)-O(6)	158.98(13)	N(3)-Ni(1)-O(7)	91.5(4)	O(4)-Cu(1)-O(3)	127.1(5)
O(2A)-Zn(1)-O(3A)	56.55(10)	N(4A)-Zn(2)-O(3)	101.38(10)	N(1)$^{\#3}$-Co(2)-O(6)	88.18(14)	N(1)-Ni(1)-O(7)	90.6(4)	O(3C)-Cu(1)-O(3)	148.2(4)
		N(4A)$^{\#1}$-Zn(2)-O(10')	124.8(11)	N(4)$^{\#2}$-Co(2)-O(6)	88.90(13)	N(5)-O(3)-Ni(1)	129.0(6)		
		N(4A)-Zn(2)-O(10')	71.2(8)	O(7)-Co(2)-O(6)	58.66(12)	N(6)-O(7)-Ni(1)	163.9(10)		
		O(3)-Zn(2)-O(10')	126.9(16)			C(2)-N(1)-Ni(1)	119.0(3)		
		N(4A)$^{\#1}$-Zn(2)-O(10')$^{\#1}$	71.2(8)			C(1)-N(1)-Ni(1)	120.4(3)		
		N(4A)-Zn(2)-O(10')$^{\#1}$	124.8(11)						
		O(3)-Zn(2)-O(10')$^{\#1}$	126.9(16)						
		N(4A)$^{\#1}$-Zn(2)-N(4')	101.4(5)						
		N(4A)-Zn(2)-N(4')	101.4(5)						
		O(3)-Zn(2)-N(4')	126.0(12)						
		O(10')-Zn(2)-N(4')	30.7(6)						
		O(10')$^{\#1}$-Zn(2)-N(4')	30.7(6)						
$^{\#1}$ x-1/2, y-1/2, z-1 $^{\#2}$ x, -y+1, z-1/2		$^{\#1}$ x, -y+1/2, z		$^{\#1}$ x-1/2, y+1/2, z-1 $^{\#2}$ x, -y+1, z+1/2 $^{\#3}$ x+1/2, y-1/2, z+1					