<Electronic Supplementary Information>

Reversible supra-channel effects: 3D kagome structure and catalysis via molecular array of 1D coordination polymers

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Experimental Section

Materials and measurements. All chemicals including copper(II) perchlorate, copper(II) tetrafluoroborate, and 2,3-dihydroxynaphthalene were purchased from Aldrich, and used without further purification. Elemental microanalyses (C, H, N) were performed on crystalline samples at the KBSI Pusan Center using a Vario-EL III. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. The infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with sample prepared as KBr pellets. ¹H (300MHz) and ¹³C (75 MHz) NMR spectra were recorded on a Varian Mercury Plus 300. The absorption spectra were recorded on a UV-vis spectrophotometer S-3150. Powder X-ray diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Kα.

Synthesis of 2,3-bis(nicotinoyloxy)naphthalene (L). Triethylamine (22 mmol, 2.67 g) was added to a stirred mixture of 2,3-dihydroxynaphthalene (5 mmol, 0.80 g) and nicotinoyl chloride hydrochloride (12 mmol, 2.14 g) in chloroform (120 mL) at 60 °C. The reaction mixture was refluxed for 24 h. The solution was filtered, and then the filtrate was washed

with 0.5 *N* NaOH aqueous solution several times. The chloroform layer was dried over anhydrous magnesium sulfate and filtered. Evaporation of the chloroform gave a white product. The product was finally recrystallized in a solvent pair of chloroform and diethyl ether to give pure 2,3-bis(nicotinoyloxy)naphthalene (L) as yellow crystalline solids in a 78% yield. Anal. Calcd for C₂₂H₁₄N₂O₄: C, 71.35; H, 3.81; N, 7.56%; found: C, 71.20; H, 3.74; N, 7.37%; IR (KBr pellet): 1755 (s), 1729 (s), 1591 (s), 1275 (s), 1020 (s), 904 (m), 737 (s) cm⁻¹. ¹H NMR (CDCl₃): δ = 9.29 (s, 2H), 8.78 (d, *J* = 5.0 Hz, 2H), 8.35 (d, *J* = 8.0 Hz, 2H), 7.89 (t, *J* = 3.3 Hz, 2H), 7.88 (s, 2H), 7.56 (dd, *J* = 6.3 Hz, 3.3 Hz, 2H), 7.37 (dd, *J* = 8.0 Hz, 5.0 Hz, 2H). ¹³C NMR (CDCl₃): δ = 163.00, 154.10, 151.01, 140.47, 137.26, 131.50, 127.45, 126.62, 124.55, 123.36, 121.05.

Preparation of [Cu(L)₂(CH₃COCH₃)₂]₃(ClO₄)₆·11CH₂Cl₂ (1). An acetone solution (3 mL) of Cu(ClO₄)₂·6H₂O (11 mg, 0.03 mmol) was slowly diffused into a dichloromethane solution (3 mL) of L (22 mg, 0.06 mmol). Violet crystals of [Cu(L)₂(CH₃COCH₃)₂]₃(ClO₄)₆·11CH₂Cl₂ formed at the interface and were obtained in 20 days in a 79% yield. m.p. 228 °C (dec.); Anal. Calcd for C₁₆₁H₁₄₁N₁₂O₅₄Cu₃Cl₂₈: C, 45.05; H, 3.33; N, 3.92%; found: C, 44.90; H,3.30; N,3.85%; IR (KBr pellet): 3068 (w), 1751 (s), 1612 (w), 1508 (m), 1467 (w), 1436 (w), 1363 (w), 1282 (s), 1251 (s), 1108 (s), 1089 (s, ClO₄⁻), 732 (m) cm⁻¹.

Preparation of $[Cu(L)_2(CH_3CN)_2]_3(ClO_4)_6 \cdot 10H_2O \cdot 8CH_2Cl_2$ (1'). An acetonitrile solution (3 mL) of Cu(ClO_4)_2 \cdot 6H_2O (11 mg, 0.03 mmol) was slowly diffused into a dichloromethane solution (3 mL) of L (22 mg, 0.06 mmol). Blue crystals of $[Cu(L)_2(CH_3CN)_2]_3(ClO_4)_6 \cdot 10H_2O \cdot 8CH_2Cl_2$ formed at the interface and were obtained in 5 days in a 74% yield in refrigerator (2 °C). m.p. 227 °C; Anal. Calcd for

C₁₅₂H₁₃₈N₁₈O₅₈Cu₃Cl₂₂: C, 44.36; H, 3.38; N, 6.13%; found: C, 43.90; H, 3.40; N, 6.05%; IR (KBr pellet): 3546 (br), 3062 (w), 1751 (s), 1612 (w), 1508 (m), 1469 (w), 1434 (w), 1363 (w), 1280 (s), 1249 (s), 1147 (s), 1108(s), 1087 (s, ClO₄⁻), 732 (m) cm⁻¹.

Preparation of [Cu(L)₂(CH₃CN)(CH₃COCH₃)]₃(BF₄)₆·17H₂O·6CH₂Cl₂ (2). A mixed solution acetone (2.2 mL) and acetonitrile (0.8 mL) of Cu(BF₄)₂·*n***H₂O (7.1 mg, 0.03 mmol) was slowly diffused into a dichloromethane solution (3 mL) of L (22 mg, 0.06 mmol). Blue crystals of [Cu(L)₂(CH₃CN)(CH₃COCH₃)]₃(BF₄)₆·17H₂O·6CH₂Cl₂ formed at the interface and were obtained in 3 days in a 70% yield. m.p. 219 °C(dec.); Anal. Calcd for C_{153}H_{157}N_{15}O_{44}Cu_{3}Cl_{12}B_{6}F_{24}: C, 45.41; H, 3.91; N, 5.19%; found: C,44.90; H, 3.88; N, 5.10%. IR (KBr pellet): 3450 (br), 3062 (w), 1751 (s), 1610 (w), 1508 (m), 1469 (w), 1434 (w), 1280 (s), 1249 (s), 1149 (w), 1083 (s), 1051 (s), 1029 (s, BF₄⁻), 732 (m) cm⁻¹.**

Crystallographic structure determinations. X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo K*a* radiation ($\lambda = 0.71073$ Å) and a CCD detector at ambient temperature. Thirty-six frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method (SADABS).¹ The structures were solved using the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).¹ The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (CCDC-928711, 928712, and 928713 for **1**, **1**', and

2, respectively). The data can be obtained free of charge via

http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk). The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table S1, and the relevant bond lengths and angles are listed in Table 2.

References

 G. M. Sheldrick, SHELXS-97: A Program for Structure Determination; University of Göttingen, Germany, 1997; G. M. Sheldrick, SHELXL-97: A Program for Structure Refinement; University of Göttingen, Germany, 1997.

	1	1'	2	
Formula	$C_{161}H_{142}N_{12}O_{54}Cl_{28}Cu_3$	$C_{152}H_{138}N_{18}O_{58}Cu_3Cl_{22}$	$C_{153}H_{157}B_6N_{15}O_{44}F_{24}Cu_3Cl_{12}\\$	
$M_{ m w}$	4292.09	4115.32	4046.82	
Crystal system	Trigonal	Monoclinic	Monoclinic	
Space group	<i>P</i> -3 <i>c</i> 1	C2/c	C2/c	
<i>a</i> (Å)	22.6009(4)	38.9150(7)	38.6764(4)	
<i>b</i> (Å)	22.6009(4)	22.2085(3)	22.1804(2)	
<i>c</i> (Å)	22.3136(6)	21.7493(3)	21.8948(4)	
α (°)	90	90	90	
eta (°)	90	98.683(2)	96.284(1)	
γ (°)	120	90	90	
$V(\text{\AA}^3)$	9870.8(4)	18581.3(5)	18669.8(4)	
Ζ	2	4	4	
ρ (g cm ⁻³)	1.444	1.471	1.440	
$\mu (\mathrm{mm}^{-1})$	0.779	0.743	0.611	
<i>R</i> _{int}	0.1777	0.0892	0.1253	
GoF on F^2	1.017	1.035	1.283	
$R_1 \left[I > 2\sigma(I)\right]^a$	0.0902	0.1148	0.1195	
wR_2 (all data) ^b	0.3103	0.3728	0.3911	

Table S1 Crystal and Refinement Parameters for 1, 1', and 2.

^a $R_1 = \Sigma ||F_o| - |F_c|| \Sigma |F_o|, {}^{b} w R_2 = (\Sigma [w (F_o^2 - F_c^2)^2] \Sigma [w (F_o^2)^2])^{1/2}$

1		1'		2	
Cu(1)–N(1)	2.02(2)	Cu(1)–N(1)	2.037(6)	Cu(1)–N(1)	2.026(6)
$Cu(1)-N(2)^{\#1}$	2.01(2)	Cu(1)-N(2) ^{#4}	2.046(6)	Cu(1)-N(2)#8	2.049(6)
Cu(1)–O(5)	2.39(3)	Cu(1)–N(3)	2.037(6)	Cu(1)–N(3)	2.029(6)
Cu(1)–O(6)	2.59(3)	$Cu(1) - N(4)^{\#5}$	2.040(6)	Cu(1)-N(4) ^{#9}	2.041(6)
Cu…Cu	11.1592(4)	Cu(1)–N(5)	2.406(9)	Cu(1)–N(5)	2.490(6)
		Cu(1)–N(6)	2.661(9)	Cu(1)–O(9)	2.498(6)
N(1)-Cu(1)-N(2) ^{#1}	87.7(9)	Cu(2)–N(7)	2.014(6)	Cu(2)–N(6)	2.055(7)
$N(1)-Cu(1)-N(1)^{#2}$	174.6(1)	Cu(2)-N(8) ^{#6}	2.059(7)	Cu(2)-N(7) ^{#10}	2.012(6)
$N(2)^{\#1}$ -Cu(1)-N(2) ^{#3}	175.8(2)	Cu(2)–N(9)	2.43(1)	Cu(2)–N(8)	2.368(8)
$N(1)^{#2}$ -Cu(1)-N(2) ^{#3}	87.7(9)	Cu(2)–N(10)	2.57(1)	Cu(2)–O(14)	2.579(8)
N(1)-Cu(1)-O(5)	92.7(7)	Cu(1)···Cu(1)	10.986(2)	Cu(1)···Cu(1)	11.189(2)
$N(2)^{\#1}$ -Cu(1)-O(5)	92.1(7)	Cu(2)…Cu(2)	10.9097(3)	Cu(2)…Cu(2)	10.9703(3)
N(1)-Cu(1)-O(6)	87.3(7)				
$N(2)^{\#1}$ -Cu(1)-O(6)	87.9(7)	$N(1)-Cu(1)-N(2)^{#4}$	92.4(2)	$N(1)-Cu(1)-N(2)^{\#8}$	92.5(2)
O(5)-Cu(1)-O(6)	180.0(0)	$N(3)-Cu(1)-N(4)^{\#5}$	90.2(2)	N(3)-Cu(1)-N(4) ^{#9}	91.3(2)
		$N(1)-Cu(1)-N(4)^{\#5}$	177.5(3)	N(1)-Cu(1)-N(3)	179.0(3)
		$N(2)^{#4}$ -Cu(1)-N(3)	176.5(3)	$N(2)^{#8}$ -Cu(1)-N(4) ^{#9}	178.2(3)
		N(1)-Cu(1)-N(5)	88.8(3)	N(1)-Cu(1)-N(5)	91.0(2)
		N(1)-Cu(1)-N(6)	87.7(3)	N(1)-Cu(1)-O(9)	91.9(2)
		$N(2)^{#4}$ -Cu(1)-N(5)	93.1(3)	$N(2)^{\#8}$ -Cu(1)-N(5)	88.7(2)
		$N(2)^{#4}$ -Cu(1)-N(6)	89.3(3)	N(2) ^{#8} -Cu(1)-O(9)	88.0(2)
		N(5)-Cu(1)-N(6)	175.8(2)	N(5)-Cu(1)-O(9)	175.6(2)
		N(7)-Cu(2)-N(8) ^{#6}	92.3(3)	$N(6)-Cu(2)-N(7)^{\#10}$	92.3(3)
		N(7)-Cu(2)-N(7)#7	177.3(4)	N(6)-Cu(2)-N(6) ^{#11}	172.8(3)
		N(7)-Cu(2)-N(9)	91.4(2)	N(6)-Cu(2)-N(8)	93.6(2)
		N(7)-Cu(2)-N(10)	88.6(2)	N(6)-Cu(2)-O(14)	86.4(2)
		N(8) ^{#6} -Cu(2)-N(9)	91.6(2)	$N(7)^{\#10}$ -Cu(2)-N(8)	91.5(2)
		N(8) ^{#6} -Cu(2)-N(10)	88.4(2)	N(7) ^{#10} -Cu(2)-O(14)	88.5(2)
		N(9)-Cu(2)-N(10)	180.0(0)	N(8)-Cu(2)-O(14)	180.0(0)



Fig. S1 1 H (top) and 13 C (bottom) NMR spectra for the present ligand.



Fig. S2 ORTEP drawings of **1** (a), **1'** (b), and **2** (c). The hydrogen atoms and solvate molecules are omitted for clarity.



Fig. S3 The C–H··· π interaction and dihedral angle between the naphthyl moieties of adjacent loop-chains.



Fig. S4 The infinite structures showing the solvate molecules inside the 1D loop-chain (blue), trigonal channel (yellow), and hexagonal channel (purple) of **1** (a), **1'** (b) and **2** (c). The anions were omitted for clarity.



Fig. S5 TGA curves of 1 (black), 1' (red) and 2 (blue) at a scan rate of 10 °C/min.



Fig. S6 ¹H NMR (300 MHz) spectra of **1** (a), **1'** (b) and **2** (c) in Me₂SO- d_6 . Top: solvate crystals; bottom: solvate molecules-evaporated sample. Asterisk, dagger, circles, square, and triangle indicate Me₂SO, water, dichloromethane, acetone, and acetonitrile, respectively.



Fig. S7 UV spectra (in chloroform) showing oxidation of 3,5-di-*tert*-butylcatechol (3,5-DBCat) using 0.2 mol% **1**' (top) and **2** (bottom) catalysts.



Fig. S8 UV spectra (in chloroform) showing oxidation of 3,5-di-*tert*-butylcatechol (3,5-DBCat) using 0.2 mol% **1**. Top: dried sample **1** in vacuum at 95 °C; bottom: acetone/dichloromethane re-absorbed **1**.



Fig. S9 ¹H NMR (300 MHz) spectra in Me₂SO- d_6 (left) and powder XRD patterns (right) for 1: as-synthesized sample 1 (a), solvate molecules-evaporate sample 1 (b) and acetone/dichloromethane re-absorbed 1 (c).



Fig. S10 IR spectra of **1** showing the coordinate CO moiety at 2102 cm^{-1} along with the adsorption/desorption processes for CO: (a) solvate molecules-evaporated sample and (b) CO-adsorbed sample.



Fig. S11 ¹H NMR spectra in CDCl₃ (top) and FAB-Mass data (bottom) for the solution after the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DBCat) with 0.2 mol% **1**. Asterisk and dagger indicate the resonance of CHCl₃ and water, respectively.