Supporting Information

Solvent induced single-crystal to single-crystal structural transformation and concomitant transmetalation in a 3D cationic Zn(II)-framework

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EXPERIMENTAL SECTION

Materials and Method. Reagent grade $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, 5-aminoisophthalic acid were purchased from Sigma-Aldrich and used without further purification. All solvents were purified following the established procedures prior to use.

Physical measurements. Spectroscopic data were collected as follows: IR spectra (KBr disk, 400–4000 cm⁻¹) were recorded on a Perkin-Elmer Model 1320 spectrometer. Powder X-Ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with nickel filtered CuK_{α} radiation. The tube voltage and current were 40 kV and 40 mA, respectively. Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). Thermogravimetric analyses (TGA) (5 °C/min heating rate under nitrogen atmosphere) were performed with a Mettler Toledo Star System. ¹H-NMR spectra were recorded on a JEOL JNM-LA500 FT instrument (500 MHz) in DMSO-*d*₆ with TMS as the internal standard. Melting points were recorded on an electrical melting point apparatus by PERFIT India and are uncorrected. Elemental analyses were obtained from the Central Drug Research Institute, Lucknow, India. EDS spectra were recorded on a JSM-6010A;JEOL Tungsten-Electron Microscope (W- SEM) (BSE resolusion: 5mn at 20kV). XRF experiment was carried out on a Rigaku WD-XRF system (X-Ray generation 4kW, 60kV-150mA) instrument.

X-ray structural studies. Single crystal X-ray data were collected at 100 K on a Bruker SMART APEX-II CCD diffractometer using graphite-monochromated MoK_{α} radiation (λ = 0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Data integration and reduction were processed with SAINT^{1a} software. An

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empirical absorption correction was applied to the collected reflections with SADABS^{1b} using XPREP1^c. The structure was solved by the direct method using SHELXTL^{1d} and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97^{1e} program package. The unit cell includes disordered guest anion and solvent molecules, which could not be modeled as discrete atomic sites. Therefore, we employed PLATON/SQUEEZE² to calculate the diffraction contribution of solvent molecules and anions and to produce a set of solvent free diffraction intensities. Structures were then refined again using the data generated. The lattice parameters and structural data are collected in Table S1.

Synthesis of H₄L⁺Cl⁻:

Synthesis of the ligand 1,3-*bis*-(3,5-dicarboxyphenyl)imidazolium chloride ($H_4L^+Cl^-$) was achieved in two steps following the procedure, reported in our earlier report³

Synthesis of { $[Zn_2(L_2)(H_2O)_2]$.NO₃.xDMF.yH₂O}_n (1): A mixture of H₄L⁺Cl⁻ (30 mg, 0.069 mmol) and Zn(NO₃)₂·6H₂O (82.5 mg, 0.279 mmol) in 3 mL of DMF was sealed in a Teflonlined stainless steel autoclave and heated under autogenous pressure at 90 °C for 72 h. Cooling to room temperature at the rate of 10 °C per h, afforded compound **1** as colorless octagonal crystals in 60% yield. FT-IR (KBr pellets, cm⁻¹): 3419 vs, 3074 w, 1663 vs, 1617 s, 1585 s , 1384 vs, 1218 m, 1099m, 1073 s, 1014 w, 920 w , 806 m , 778 m, 724 m , 636 s , 489 w.

Synthesis of $\{[Zn_2(L)(H_2O)_2]\cdot NO_3\cdot yH_2O\cdot zMeCN\}_n$ (2-MeCN): Single crystals of 1 were dipped into a solution of CH₃CN for 48 h at room temperature, whereupon they change to 2-MeCN. FT-IR (KBr pellets, cm⁻¹): 3419 vs, 3132 w, 3106 w, 3074 w, 2260 s, 1631 vs, 1517 vs, 1384 vs, 1073 s, 778 m, 744 m, 723 s.

Synthesis of $\{[Cu_2(L)(H_2O)_2]:NO_3:yH_2O:zMeCN\}_n (2_{Cu}-MeCN):$ Colorless crystals of 1 when immersed in a MeCN solution of $Cu(NO_3)_2:3H_2O$ (0.04 M) at room temperature, gradually turned into green-blue crystals of 2_{Cu} -MeCN within 48 h. FT-IR (KBr pellets, cm⁻¹): 3439 vs, 2428s, , 2260 s, 1647 vs, 1586 vs, 1384 vs, 1073 s, 778 m, 744 m, 723 s.

Synthesis of { $[Cu_2(L)(H_2O)_2]$ ·NO₃·yH₂O·zDMF}_n (1_{Cu}-DMF): The blue crystals of 2_{Cu}-MeCN change to 1_{Cu}-DMF, when kept in DMF solvent at room temperature for 24 h. Alternatively, 1_{Cu}-DMF is obtained when the colorless crystals of 2-MeCN are dipped into the Cu(NO₃)₂·3H₂O solution of DMF at room temperature for 48 h. FT-IR (KBr pellets, cm⁻¹): 3421 vs, 3092 w, 2927 w, 1663 vs, 1585 s, 1383 vs, 1103 s, 1073 s, 778 s, 724 s, 664 s.



Figure S1 500 MHz ¹H-NMR spectrum of $H_4L^+CI^-$.



Figure S2 500 MHz ¹³C-NMR spectrum of H₄L⁺Cl⁻.







Figure S4 Bonding pattern of carboxylate ligand and view of the $Zn_2(CO_2)_4$ paddle-wheel secondary building units in framework 1. Green dotted lines indicate the distance between Zn-atoms.



Figure S5 Bonding pattern of carboxylate ligand and view of the $Zn_2(CO_2)_4$ paddle-wheel secondary building units in framework 2-MeCN (described as 2 in the main text). Green dotted lines indicate the distance between Zn-atoms.



Figure S6 Bonding pattern of carboxylate ligand and view of the $Cu_2(CO_2)_4$ paddle-wheel secondary building units in framework 2_{Cu} -MeCN. Green dotted lines indicate the distance between Cu-atoms.



Figure S7 Bonding pattern of carboxylate ligand and view of the $Cu_2(CO_2)_4$ paddle-wheel secondary building units in framework 1_{Cu} -DMF. The dotted lines indicate the distance between Cu-atoms.



Figure S8 (a) IR spectrum of 1, corroborating the presence of NO_3^- anion (1384 Cm⁻¹) and its (b) TGA curve.



Figure S9 (a) IR spectrum of **2**-MeCN corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) and acetonitrile solvent (2260 Cm⁻¹), (b) its TGA curve.



Figure S10 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹), (b) TGA curve for **2**-DCM.



Figure S11 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b) TGA curve for of **1**-MeOH.



Figure S12 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **1**-DMSO.



Figure S13 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **1**-EtOAC.



Figure S14 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **1**-Acetone.



Figure S15 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of 1-dioxane.



Figure S16 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b) TGA curve for of **1**-THF.



Figure S17 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **2**-CCl₄



Figure S18 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **2**-Benzene.



Figure S19 (a) IR spectrum corroborating the presence of NO₃⁻ anion (1384 Cm⁻¹) (b)TGA curve for of **2**-toluene.



Figure S20 (a) IR spectrum corroborating the presence of NO_3^- anion (1384 Cm⁻¹) (b)TGA curve for of 1_{Cu} -DMF.



Figure S21 (a) IR spectrum corroborating the presence of NO_3^- anion (1384 Cm⁻¹) (b) TGA curve for of 2_{Cu} -MeCN.



Figure S22 Hexagonal channels in framework 1 along *c*-axis (green dotted line indicates the cross sectional dimension of the channels).



Figure S23 Channels in framework **1** (a) along *a*-axis and (b) along *b*-axis (green dotted lines indicate various cross sectional dimensions of the channels).



Figure S24 Powder X-Ray Diffraction Pattern of simulated and as-synthesized (obtained by solvothermal reaction) framework **1**.



Figure S25 Powder X-Ray Diffraction Pattern of simulated and as-synthesized (obtained by solvent induced SC-SC transformation) framework 2-MeCN.



Figure S26 Powder X-Ray Diffraction Pattern of simulated and as-synthesized (obtained by solvent induced SC-SC transmetalation) framework 2_{Cu} -MeCN.



Figure S27 Powder X-Ray Diffraction Pattern of simulated and as-synthesized (obtained by solvent induced SC-SC transmetalation) framework 1_{Cu} -DMF.



Figure S28 Photograph of the single crystal of frameworks 1, 2-MeCN, 2Cu-MeCN and 1Cu-DMF(top) and time dependent single crystal images of transmetalation reaction from 1 to 2Cu-MeCN (bottom).



Figure S29 EPR spectrum of 2_{Cu}-MeCN.



Figure S30 Scanning electron image of 2_{Cu} -MeCN



 $\label{eq:Figure S31} \begin{array}{l} \mbox{The EDS spectrum of 2_{Cu}-MeCN$} \\ \mbox{Table S1. Crystal and Structure Refinement Data for 1, 2-MeCN, 2-DCM, 1_{Cu}-DMF and 2_{Cu}-} \\ \end{array}$ MeCN.

	1	2-MeCN	2- DCM	1 _{Cu} -DMF	2 _{Cu} -MeCN.
Empirical	$C_{19}H_9N_2O_{10}Zn_2$	$C_{19}H_9N_2O_{10}Zn_2$	$C_{19}H_9N_2O_{10}Zn_2$	$C_{19}H_9N_2O_{10}Cu_2$	$C_{19}H_9N_2O_{10}Cu_2$
formula					
Formula	556.02	556.02	556.02	552.36	552.36
weight					
Temperature	100(1) K				
Radiation	ΜοΚα	MoK _α	ΜοΚα	MoK _α	MoK _α
Wavelength	0.71069 Å				
Crystal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
system					
Space group	P4 ₂ /nnm	I4 ₁ /amd	I4 ₁ /amd	P4 ₂ /nnm	I4 ₁ /amd
<i>a</i> , Å	17.7349(6)	25.5552(11)	25.4440(14)	17.7179(7)	25.4117(14)
<i>b</i> , Å	17.7349(6)	25.5552(11)	25.4440(14)	27.7179(7)	25.4117(14)
<i>c</i> , Å	28.1732(10)	51.403(2)	53.616(3)	27.5566(13)	52.162(6)
V, Å ³	8861.2 (7)	33570(2)	34711(4)	8650.7(6)	33684(5)
Ζ	8	32	32	8	32
$\rho_{calc} Mg/m^3$	0.834	0.880	0.851	0.848	0.871
μ, mm ⁻¹	1.111	1.173	1.135	1.012	1.040
F(000)	2216	8864	8864	2200	8800
Independent refl.	5816	7752	9913	3999	10995

Re ¹ fl. used	4216	5222	6070	2876	6605
(I>2σ(I))				2870	
R _{int} value	0.0908	0.1638	0.1523	0.0599	0.1534
Refinement	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix
method	least-squares	least-squares	least-squares	least-squares	least-squares
	on F ²				
GOOF	1.093	1.064	1.030	1.120	1.034
R indices	R1=0.0703	R1= 0.0976	R1= 0.0707	R1= 0.0778	R1= 0.0692
[I>2σ(I)]	wR2=0.1860	wR2=0.27884	wR2=0.1670	wR2=0.2123	wR2=0.1873
R indices	R1=0.1149	R1=0.1422	R1=0.1433	R1=0.1075	R1=0.1595
(all data)	wR2=0.2089	wR2= 0.3065	wR2= 0.1925	wR2= 0.2255	wR2=0.1873

 Table S2. Table of Crystal Parameters in Different Solvent.

Crystal	a (Å)	<i>b</i> (Å)	c (Å)	α (degree)	β (degree)	γ (degree)	V (Å ³)
1	17.73	17.73	28.17	90	90	90	8861
1-MeOH	17.77	17.77	27.89	90	90	90	8818
1-EtOAC	17.75	17.75	28.21	90	90	90	8896
1- Acetone	17.72	17.72	28.09	90	90	90	8836
1- Dioxane	17.83	17.83	27.66	90	90	90	8789
1- THF	17.87	17.98	27.27	90	90	90	8707
1-DMSO	17.74	17.74	28.23	90	90	90	8885
2-MeCN	25.44	25.44	53.61	90	90	90	34710
2-CHCl ₃	25.48	25.48	52.27	90	90	90	33947
2- DCM	25.41	25.41	52.16	90	90	90	33648

2- CCl ₄	25.43	25.43	53.22	90	90	90	34416
2-Tolune	25.46	25.46	52.43	90	90	90	33985

 Table S3. Selective Bond Distances (Å).

1	2-MeCN	2 _{Cu} -MeCN	1 _{Cu} -DMF	
Zn1-Zn1 =	Zn1-Zn1 =	Cu1-Cu1 =	Cu1-Cu1 =	
3.0186(11)	3.0266(18)	2.6961(10)	2.6648(14)	
Zn2-Zn2 =	Zn2-Zn3 =	$C_{22} = 2(605(2))$	Cu2-Cu2 =	
2.9990(11)	3.0114(16)	Cu2-Cu3 - 2.0005(3)	2.6515(17)	
Zn1-O6 = 2.010(3)	Zn1-O1 = 2.000(5)	Cu1-O2 = 1.995(3)	Cu1-O3 = 1.962(4)	
Zn1-O1 = 2.021(3)	Zn1-O2 = 2.097(6)	Cu1-O1 = 1.937(3)	Cu1-O4 = 1.955(4)	
$Zn1-O2(H_2O)=$ 2.028(5)	Zn1-O3 = 1.989(6)	$Cu1-O9(H_2O) = 2.134(4)$	$Cu1-O6(H_2O) = 2.128(5)$	
Zn2-O3 = 2.019(3)	Zn1-O7 = 2.034(5)	Cu1-O7 = 1.937(3)	Cu2-O1 = 1.958(3)	
Zn2-O4 = 2.037(3)	$Zn1-O25(H_2O)=$ 2.024(7)	Cu1-O8 = 1.975(3)	Cu2-O2 = 1.956(4)	
$Zn2-O5(H_2O) = 2.057(7)$	Zn2-O5 =1.990(7)	Cu2-O3 = 1.966(3)	$Cu2-O5(H_2O) =$ 2.153(6)	
	Zn2-O9 = 2.020(6)	Cu2-O6 = 1.958(3)		
	$Zn2-O26(H_2O) =$	$Cu2-O21(H_2O) =$		
	1.959(8)	2.172(6)		
	Zn3-O4 = 2.044(6)	Cu3-O4 = 1.934(3)		
	Zn3-O8 = 2.008(6)	Cu3-O5 = 1.948(3)		
	$Zn3-O38(H_2O) =$	$Cu3-O11(H_2O) =$		
	2.014(10)	2.147(5)		

Table S4. Effect of solvent mixtures (oxygen atom containing solvents and solvents without any oxygen atom) on Zn(II)-framework transformation.

Framework exists	DMF/MeCN (%)	DMF/DCM (%)	MeOH/MeCN (%)	MeOH/DCM (%)	THF/CCl4 (%)
1	100/0	100/0	100/0	100/0	100/0
1	50/50	50/50	50/50	50/50	50/50
1	40/60	40/60	40/60	40/60	40/60
1	30/70	30/70	30/70	30/70	30/70
1	20/80	20/80	20/80	20/80	20/80
1	10/90	10/90	10/90	10/90	10/90
1	5/95	5/95	5/95	5/95	5/95
1	2/98	2/98	2/98	2/98	2/98
2	0/100	0/100	0/100	0/100	0/100

1: Zn(II)-framework, in the presence of a solvent, having at least one oxygen atom as a part of its molecule.

2: transformed Zn(II)-framework, in the presence of a solvent that does not have any oxygen atom as a part of its molecule.

- (a) SAINT+, version 6.02; Bruker AXS: Madison, WI, 1999; (b) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1997; (c) XPREP, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995. (d) Sheldrick, G. M. SHELXTL Reference Manual, version 5.1; Bruker AXS: Madison, WI, 1997; (e) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.
- 2. A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.
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