Supporting Information

High 3D Proton Conductivity of a 2D Zn(II) Metal Organic Framework Synthesized via Water-Assisted Single-Crystal-to-Single-Crystal Phase Transformation

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Physical Measurements.

Infrared spectra were obtained (KBr disk, 400-4000 cm^{-1}) using a Perkin-Elmer model 1320 spectrometer. Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). Thermograms were recorded on a Mettler Toledo (heating rate of 10°C/min) TGA instrument. Powder X-ray diffraction (PXRD) was performed using a Rigaku Rint 2000 X-ray diffractometer with CuKα radiation. ac electrochemical impedance spectroscopy was performed using the impedance analyzer (Solartron 1260, UK) across the frequency range of 5 MHz to 1 Hz with an applied voltage of 50 mV, between 25−80 °C, in 3% H_2O-H_2 gaseous conditions.

X-ray Structural Studies.

Suitable single crystal of **1** was mounted on a Bruker SMART II diffractometer equipped with a graphite monochromator and MoKα (λ = 0.71073 Å, 140 K) radiation. Lorentz polarization and absorption corrections were applied using Bruker SAINT[1] and SADABS[2] software. Structures

were solved by direct methods and refined by full-matrix least-squares on F2 for all reflections using SHELXTL[3]. Subsequent difference Fourier synthesis and least squares refinement revealed the positions of the remaining non-hydrogen atoms. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction were applied. Non-hydrogen atoms were refined with hydrogen atoms placed geometrically and refined using the riding model. In structure **1** hydrogen atoms could not be located on the water molecules but in single crystal structure of **2** out of the total six water molecules only on two water molecules hydrogen atoms could be located. The water molecules though H-bonded in **1** but these are disordered and that is why H-bonding distances are coming as very short distances. Due to increasing maximum shift error value hydrogen molecules could not be located on the oxygen atoms of the water molecules as there are alerts for compound **1** and **2** as shown in check cif file. Contributions from all the hydrogen atoms of the solvent molecules have been incorporated in both the empirical formulas and formula weights as shown in the crystal and structure refinement data Table S1.

Crystallographic data have been deposited to the Cambridge Crystallographic Data Centre having CCDC deposition numbers: 1913647 and 1913648. The crystal and refinement data are collected in Table S1, while selected bond distances and angles are given in Tables S2-S5.

Table S1 Crystal data and structure refinement for **1** and **2**

Identification code	**1**	**2**
Empirical formula	$C_{54}H_{58}Cl_6N_{12}O_{11}Zn_3$	$C_{54}H_{48}Cl_6N_{12}O_6Zn_3$
Formula weight	1459.936	1369.854
Temperature/K	99.99	273.15
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$
a/Å	14.2687(6)	17.0787(14)
b/Å	15.2106(6)	10.9843(10)
c/Å	28.3438(13)	32.135(3)
α/°	90	90
β/°	97.383(2)	94.330(3)

γ/°	90	90
Volume/Å^3	6100.6(5)	6011.3(9)
Z	4	4
ρ_{calc}g2/cm^3	1.565	1.505
μ/mm^{-1}	1.500	1.512
F(000)	2896.0	2752.0
Crystal size/mm^3	1 × 0.8 × 0.6	1 × 0.8 × 0.6
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.316 to 50.998	4.412 to 50.994
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -34 ≤ l ≤ 34	-20 ≤ h ≤ 20, -13 ≤ k ≤ 13, -38 ≤ l ≤ 38
Reflections collected	37885	74364
Independent reflections	5694 [R_{int} = 0.0328, R_{sigma} = 0.0195]	11206 [R_{int} = 0.1041, R_{sigma} = 0.0616]
Data/restraints/parameters	5694/0/389	11206/0/736
Goodness-of-fit on F^2	1.544	1.406
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1669	R_1 = 0.0762, wR_2 = 0.1924
Final R indexes [all data]	R_1 = 0.0526, wR_2 = 0.1795	R_1 = 0.0943, wR_2 = 0.2077
Largest diff. peak/hole / e Å^{-3}	1.55/-1.13	1.85/-1.51

Table S2 Bond Lengths for **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	Cl2	2.1976(9)	C2	C7	1.390(5)
Zn1	Cl1	2.2538(9)	C27	C22	1.406(5)
Zn1	N1	2.026(3)	C27	C26	1.388(5)
Zn1	N5[1]	2.026(3)	C3	C4	1.381(5)
Zn2	Cl3[2]	2.2304(10)	C23	C22	1.395(5)
Zn2	Cl3	2.2305(10)	C23	C24	1.370(6)
Zn2	N3	2.028(3)	C7	C6	1.387(5)
Zn2	N3[2]	2.028(3)	C26	C25	1.401(6)
N2	C7	1.382(4)	C10	C9	1.384(5)
N2	C1	1.364(4)	C10	C11	1.381(5)
N2	C8	1.433(4)	C15	C20	1.393(5)
N1	C2	1.397(4)	C15	C16	1.389(5)
N1	C1	1.311(4)	C8	C9	1.381(5)
N6	C27	1.390(5)	C8	C13	1.379(5)
N6	C21	1.349(4)	C12	C11	1.395(5)

N6	C10	1.427(4)	C12	C13	1.393(5)
N5	C22	1.387(5)	C24	C25	1.404(6)
N5	C21	1.308(4)	C4	C5	1.399(6)
N3	C14	1.313(4)	C20	C19	1.393(5)
N3	C20	1.397(5)	C16	C17	1.374(5)
N4	C14	1.359(4)	C6	C5	1.385(6)
N4	C15	1.396(4)	C19	C18	1.392(6)
N4	C12	1.424(4)	C18	C17	1.388(6)
C2	C3	1.393(5)			

[1]1-X,1-Y,1-Z; [2]-X,+Y,3/2-Z

Table S3. Bond Angles for **1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Zn1	Cl1	118.56(4)	N5	C22	C27	108.6(3)
N1	Zn1	Cl2	112.82(8)	N5	C22	C23	130.7(3)
N1	Zn1	Cl1	102.54(8)	C23	C22	C27	120.7(3)
N1	Zn1	N5[1]	102.37(11)	N2	C7	C2	105.7(3)
N5[1]	Zn1	Cl2	114.74(9)	N2	C7	C6	131.9(3)
N5[1]	Zn1	Cl1	103.87(9)	C6	C7	C2	122.3(3)
Cl3[2]	Zn2	Cl3	118.21(7)	C27	C26	C25	116.2(3)
N3	Zn2	Cl3	110.38(9)	N5	C21	N6	113.3(3)
N3[2]	Zn2	Cl3[2]	110.38(9)	N1	C1	N2	111.7(3)
N3[2]	Zn2	Cl3	106.70(9)	N3	C14	N4	112.6(3)
N3	Zn2	Cl3[2]	106.70(8)	C9	C10	N6	117.8(3)
N3	Zn2	N3[2]	103.51(17)	C11	C10	N6	120.1(3)
C7	N2	C8	128.2(3)	C11	C10	C9	122.0(3)
C1	N2	C7	107.5(3)	C20	C15	N4	105.0(3)
C1	N2	C8	123.9(3)	C16	C15	N4	132.1(3)
C2	N1	Zn1	128.2(2)	C16	C15	C20	122.8(3)
C1	N1	Zn1	124.7(2)	C9	C8	N2	119.2(3)
C1	N1	C2	106.3(3)	C13	C8	N2	118.8(3)
C27	N6	C10	130.5(3)	C13	C8	C9	122.0(3)
C21	N6	C27	106.7(3)	C8	C9	C10	118.4(3)
C21	N6	C10	122.7(3)	C11	C12	N4	120.2(3)
C22	N5	Zn1[1]	134.3(2)	C13	C12	N4	118.1(3)
C21	N5	Zn1[1]	119.6(2)	C13	C12	C11	121.7(3)
C21	N5	C22	106.0(3)	C23	C24	C25	122.5(4)
C14	N3	Zn2	127.6(2)	C3	C4	C5	121.3(4)
C14	N3	C20	105.6(3)	C10	C11	C12	117.8(3)
C20	N3	Zn2	126.7(2)	C8	C13	C12	118.1(3)

C14	N4	C15	107.2(3)	C15	C20	N3	109.6(3)
C14	N4	C12	125.4(3)	C15	C20	C19	120.7(3)
C15	N4	C12	127.3(3)	C19	C20	N3	129.7(3)
C3	C2	N1	130.0(3)	C17	C16	C15	115.4(4)
C7	C2	N1	108.7(3)	C5	C6	C7	116.0(4)
C7	C2	C3	121.3(3)	C26	C25	C24	121.0(4)
N6	C27	C22	105.4(3)	C18	C19	C20	116.8(4)
C26	C27	N6	132.1(3)	C6	C5	C4	122.2(4)
C26	C27	C22	122.4(3)	C17	C18	C19	120.9(4)
C4	C3	C2	116.9(3)	C16	C17	C18	123.3(4)
C24	C23	C22	117.1(3)				

[1]1-X,1-Y,1-Z; [2]-X,+Y,3/2-Z

Table S4. Bond Lengths for **2**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn2	Cl4	2.2354(15)	C49	C50	1.393(8)
Zn2	Cl3	2.2218(17)	C3	C2	1.381(8)
Zn2	N7	2.015(5)	C3	C4	1.370(8)
Zn2	N3	2.034(4)	C9	C8	1.404(7)
Zn3	Cl6	2.2294(14)	C29	C34	1.388(8)
Zn3	Cl5	2.2523(16)	C29	C30	1.389(8)
Zn3	N11	2.002(4)	C13	C8	1.382(7)
Zn3	N9[1]	2.014(5)	C13	C12	1.396(7)
Zn1	Cl2	2.240(2)	C54	C53	1.395(7)
Zn1	Cl1	2.2136(19)	C11	C12	1.388(7)
Zn1	N1	2.029(5)	C27	C22	1.403(7)
Zn1	N5[2]	2.042(4)	C27	C26	1.375(8)
N2	C8	1.427(6)	C34	C33	1.389(8)
N2	C2	1.395(7)	C15	C20	1.389(8)
N2	C1	1.349(7)	C15	C16	1.406(8)
N11	C54	1.396(7)	C7	C2	1.385(8)
N11	C48	1.317(7)	C7	C6	1.398(8)
N6	C10	1.427(6)	C22	C23	1.387(8)
N6	C27	1.398(7)	C39	C40	1.384(8)
N6	C21	1.360(7)	C39	C38	1.386(7)
N1	C7	1.390(7)	C50	C51	1.397(8)
N1	C1	1.299(7)	C40	C35	1.384(7)
N8	C34	1.401(7)	C35	C36	1.378(7)
N8	C28	1.353(7)	C6	C5	1.367(9)
N8	C35	1.420(7)	C4	C5	1.396(9)
N5	C22	1.406(7)	C33	C32	1.370(8)

N5	C21	1.307(7)	C53	C52	1.386(8)
N4	C15	1.405(7)	C20	C19	1.382(8)
N4	C12	1.430(6)	C30	C31	1.380(8)
N4	C14	1.349(7)	C37	C36	1.400(8)
N12	C49	1.398(7)	C37	C38	1.379(8)
N12	C39	1.430(7)	C51	C52	1.388(8)
N12	C48	1.359(7)	C23	C24	1.376(8)
N7	C29	1.393(7)	C47	C46	1.408(8)
N7	C28	1.298(7)	C47	C42	1.388(8)
N3	C14	1.313(7)	C24	C25	1.395(9)
N3	C20	1.401(7)	C46	C45	1.386(9)
N9	C47	1.387(7)	C31	C32	1.382(9)
N9	C41	1.305(7)	C16	C17	1.363(8)
N10	C37	1.425(7)	C26	C25	1.392(8)
N10	C41	1.354(7)	C19	C18	1.393(9)
N10	C42	1.391(7)	C43	C42	1.370(9)
C10	C9	1.372(7)	C43	C44	1.369(9)
C10	C11	1.393(7)	C18	C17	1.374(9)
C49	C54	1.385(7)	C45	C44	1.403(9)

[1]-X,1/2+Y,1/2-Z; [2]2-X,-Y,1-Z

Table S5. Bond Angles for **2**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl3	Zn2	Cl4	122.45(6)	C26	C27	C22	122.2(5)
N7	Zn2	Cl4	103.55(13)	C29	C34	N8	105.4(5)
N7	Zn2	Cl3	113.25(14)	C29	C34	C33	122.4(5)
N7	Zn2	N3	99.39(18)	C33	C34	N8	132.1(5)
N3	Zn2	Cl4	111.56(14)	N4	C15	C16	132.8(5)
N3	Zn2	Cl3	104.41(14)	C20	C15	N4	105.4(5)
Cl6	Zn3	Cl5	116.58(6)	C20	C15	C16	121.9(5)
N11	Zn3	Cl6	105.49(14)	N1	C7	C6	130.9(5)
N11	Zn3	Cl5	106.51(14)	C2	C7	N1	108.9(5)
N11	Zn3	N9[1]	107.53(18)	C2	C7	C6	120.3(5)
N9[1]	Zn3	Cl6	109.79(14)	C9	C8	N2	118.7(4)
N9[1]	Zn3	Cl5	110.42(14)	C13	C8	N2	119.9(5)
Cl1	Zn1	Cl2	112.32(9)	C13	C8	C9	121.4(5)
N1	Zn1	Cl2	109.99(15)	C3	C2	N2	131.5(5)
N1	Zn1	Cl1	109.69(14)	C3	C2	C7	122.7(5)
N1	Zn1	N5[2]	100.13(18)	C7	C2	N2	105.6(5)
N5[2]	Zn1	Cl2	110.81(13)	N7	C28	N8	112.9(5)
N5[2]	Zn1	Cl1	113.23(14)	C13	C12	N4	118.6(5)

C2	N2	C8	125.8(4)	C11	C12	N4	120.0(5)
C1	N2	C8	125.9(4)	C11	C12	C13	121.4(5)
C1	N2	C2	106.4(4)	N1	C1	N2	113.1(5)
C54	N11	Zn3	128.3(4)	C27	C22	N5	108.9(5)
C48	N11	Zn3	125.6(4)	C23	C22	N5	130.6(5)
C48	N11	C54	105.5(4)	C23	C22	C27	120.4(5)
C27	N6	C10	127.3(5)	N5	C21	N6	112.8(5)
C21	N6	C10	125.0(5)	C40	C39	N12	118.3(5)
C21	N6	C27	107.3(4)	C40	C39	C38	122.4(5)
C7	N1	Zn1	128.1(4)	C38	C39	N12	119.3(5)
C1	N1	Zn1	125.9(4)	C49	C50	C51	114.9(5)
C1	N1	C7	106.0(5)	C39	C40	C35	118.5(5)
C34	N8	C35	127.8(4)	C40	C35	N8	119.2(5)
C28	N8	C34	106.6(4)	C36	C35	N8	119.7(5)
C28	N8	C35	125.5(4)	C36	C35	C40	121.1(5)
C22	N5	Zn1[2]	127.3(3)	C5	C6	C7	116.5(6)
C21	N5	Zn1[2]	126.7(4)	N11	C48	N12	112.6(5)
C21	N5	C22	105.9(4)	C3	C4	C5	121.2(6)
C15	N4	C12	126.5(4)	C32	C33	C34	115.8(6)
C14	N4	C15	107.1(4)	C6	C5	C4	122.5(6)
C14	N4	C12	126.4(4)	C52	C53	C54	117.5(5)
C49	N12	C39	127.6(5)	N3	C14	N4	112.5(5)
C48	N12	C49	106.8(4)	C15	C20	N3	108.8(5)
C48	N12	C39	124.8(5)	C19	C20	N3	130.1(5)
C29	N7	Zn2	126.0(4)	C19	C20	C15	121.1(5)
C28	N7	Zn2	126.8(4)	C31	C30	C29	116.2(6)
C28	N7	C29	106.3(5)	C36	C37	N10	118.2(5)
C14	N3	Zn2	128.5(4)	C38	C37	N10	120.0(5)
C14	N3	C20	106.2(4)	C38	C37	C36	121.7(5)
C20	N3	Zn2	123.9(4)	C52	C51	C50	122.8(5)
C47	N9	Zn3[3]	126.4(4)	C24	C23	C22	117.4(5)
C41	N9	Zn3[3]	127.6(4)	C35	C36	C37	118.7(5)
C41	N9	C47	105.4(5)	C53	C52	C51	121.0(5)
C41	N10	C37	126.7(5)	N9	C47	C46	129.6(6)
C41	N10	C42	107.7(5)	N9	C47	C42	110.3(5)
C42	N10	C37	125.4(5)	C42	C47	C46	120.1(6)
C9	C10	N6	119.9(5)	C23	C24	C25	122.0(6)
C9	C10	C11	121.4(5)	C45	C46	C47	116.3(6)
C11	C10	N6	118.5(5)	C30	C31	C32	122.2(6)
C54	C49	N12	105.5(5)	C33	C32	C31	122.3(6)
C54	C49	C50	123.4(5)	C37	C38	C39	117.6(5)
C50	C49	N12	131.1(5)	C17	C16	C15	115.7(5)

C4	C3	C2	116.4(6)	C27	C26	C25	116.9(5)
C10	C9	C8	118.7(5)	N9	C41	N10	112.4(5)
C34	C29	N7	108.9(5)	C26	C25	C24	120.9(6)
C34	C29	C30	121.0(5)	C20	C19	C18	116.8(5)
C30	C29	N7	130.2(5)	C44	C43	C42	117.3(6)
C8	C13	C12	118.3(5)	C47	C42	N10	104.1(5)
C49	C54	N11	109.6(4)	C43	C42	N10	132.6(5)
C49	C54	C53	120.4(5)	C43	C42	C47	123.2(5)
C53	C54	N11	130.0(5)	C17	C18	C19	121.3(6)
C12	C11	C10	118.7(5)	C16	C17	C18	123.2(6)
N6	C27	C22	105.1(5)	C46	C45	C44	122.1(6)
C26	C27	N6	132.6(5)	C43	C44	C45	121.0(6)

[1]-X,1/2+Y,1/2-Z; [2]2-X,-Y,1-Z; [3]-X,-1/2+Y,1/2-Z

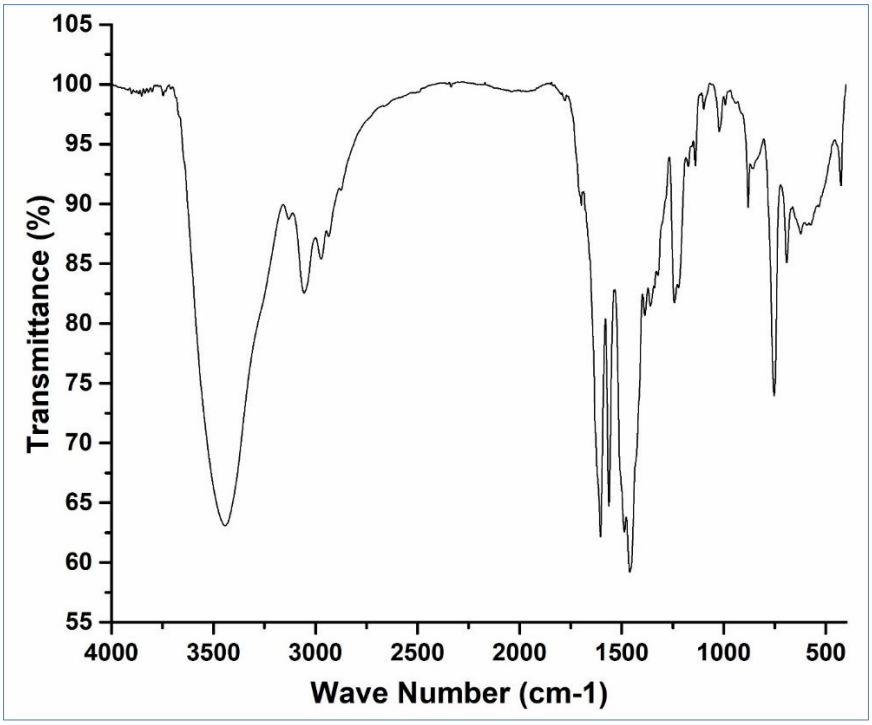


Figure S1. IR spectrum of complex **1.**

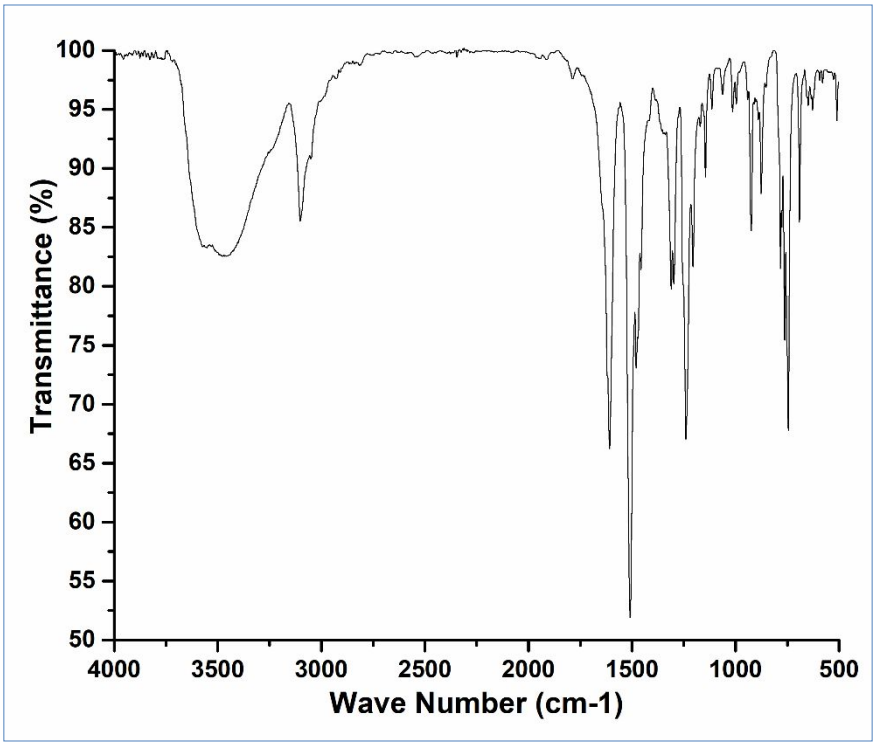
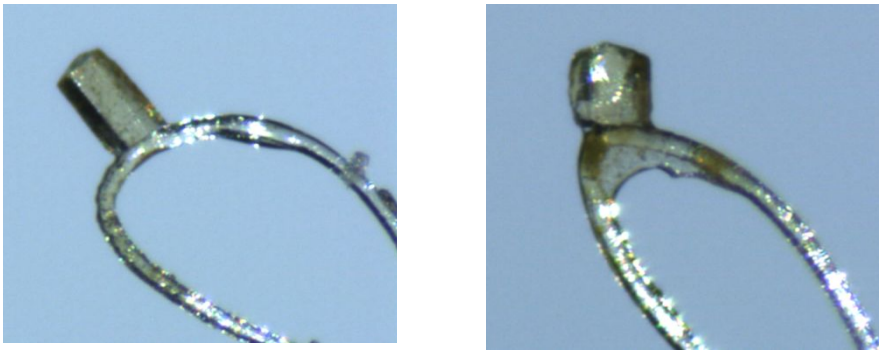


Figure S2. IR spectrum of complex **2.**



(a) **(b)**

Figure S3. Crystal images of compound (a) **1** and (b) **2**.

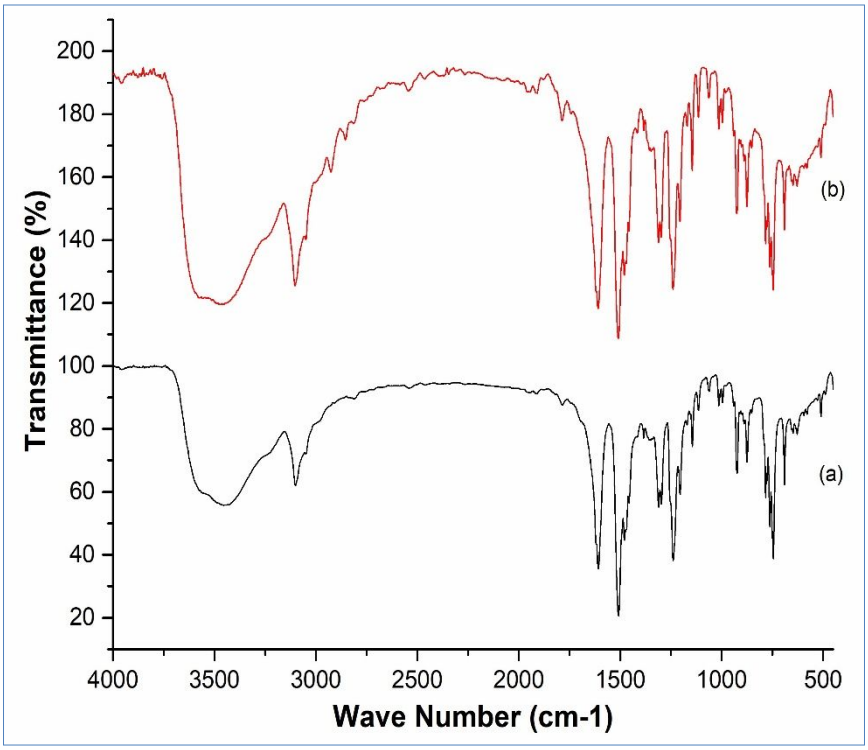


Figure S4. IR spectrum of compound **2** immersed in (a) ethanol and (b) ethanol/water solvent.

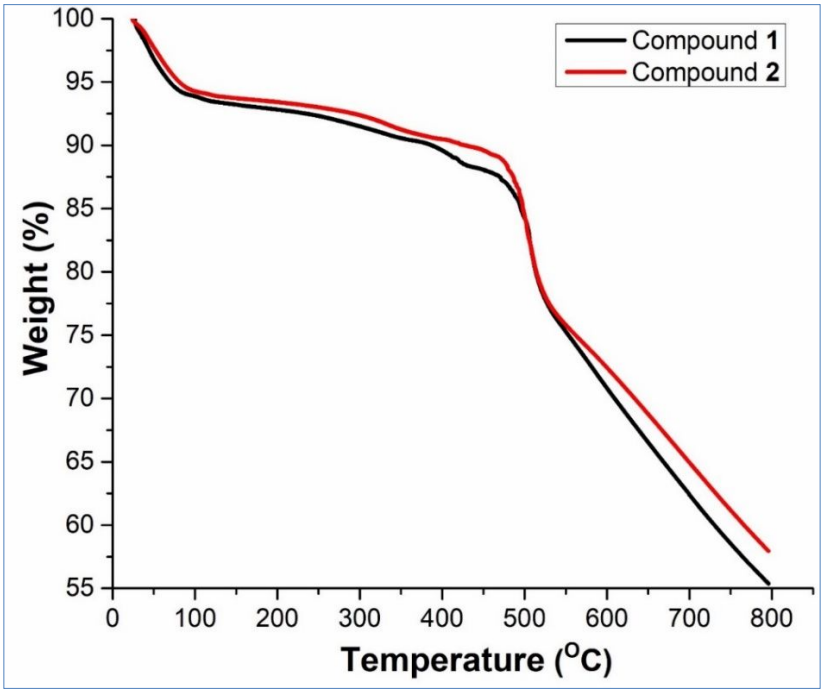


Figure S5. Thermogravimetric analysis curves for compounds **1** and **2**.

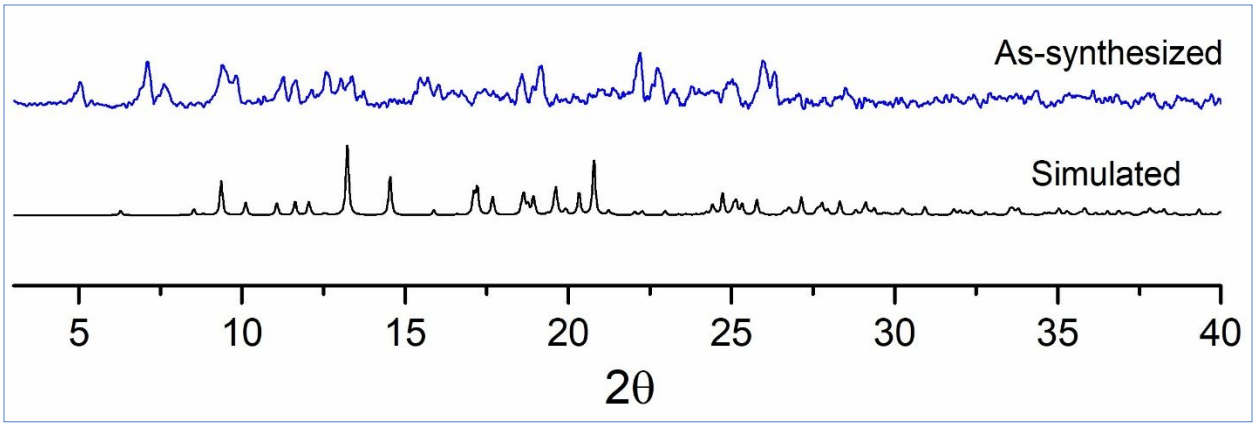


Figure S6. PXRD patterns of simulated and as-synthesized compound **1**.

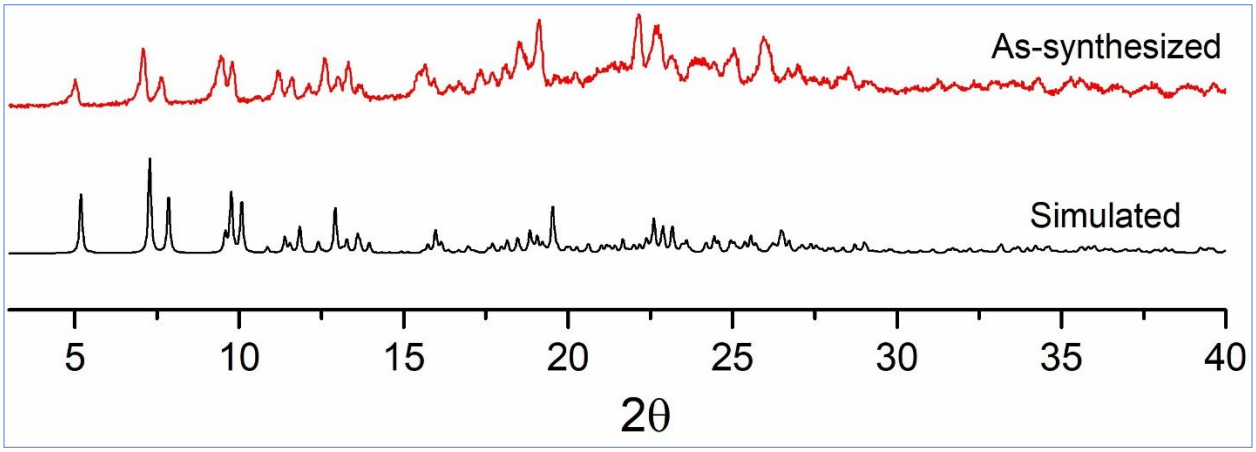


Figure S7. PXRD patterns of simulated and as-synthesized compound **2**.

References

(1) SAINT v.6.22, Bruker AXS Inc., Madison, WI, USA, **2001**.

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