Supporting information

Flexible porous coordination polymers constructed by 1,2-bis(4-pyridyl)hydrazine via solvothermal in situ reduction of 4,4'-Azopyridine

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Supplementary Index

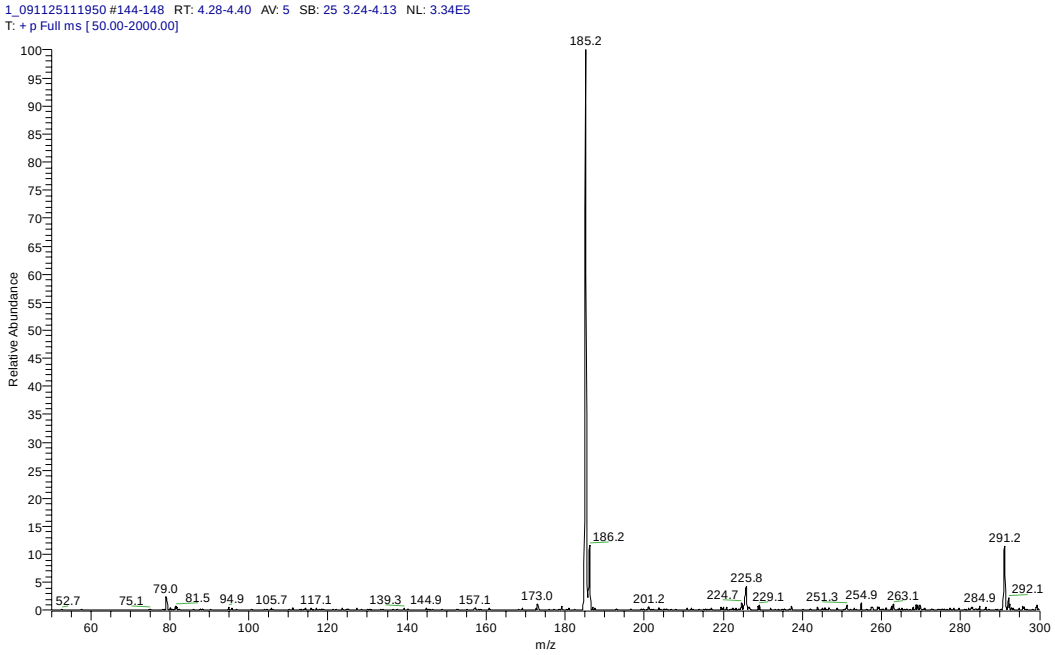

Figure S1. LC-MS (ESI) spectrum for starting material 4,4'-azopyridine (azpy). m/z = 185.2 ($M+H^+$).

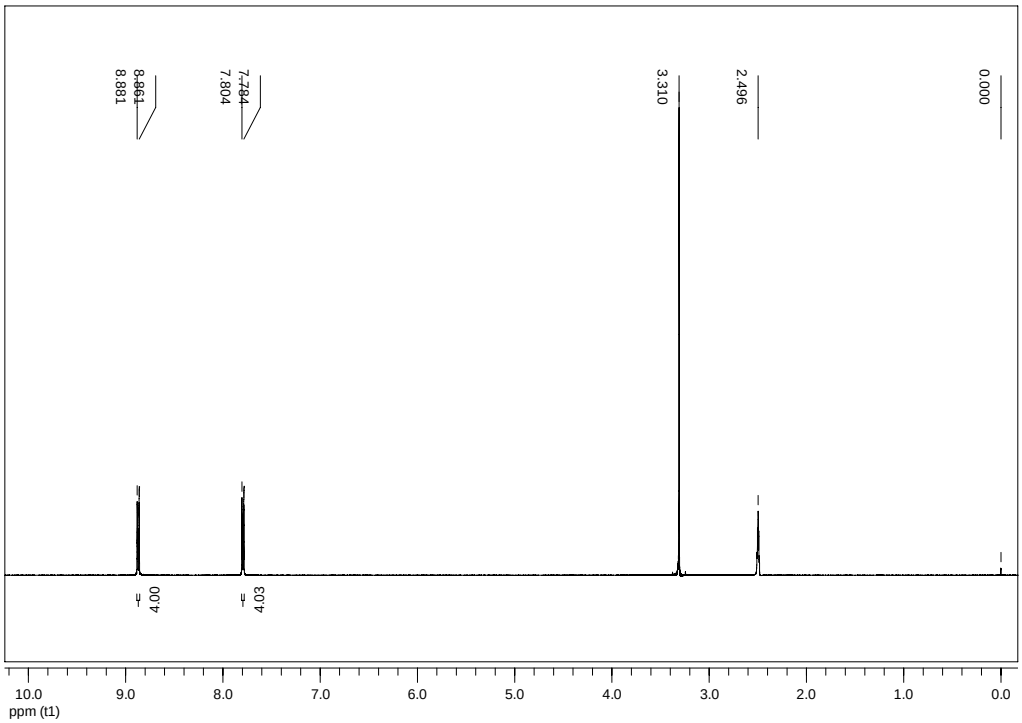

Figure S2. ^{1}H-NMR spectrum (300 MHz, [D_6] DMSO) [ppm] for 4,4'-azopyridine (azpy): δ = 8.87 (d, J = 6Hz, 4H, Ar-H), δ = 7.79 (d, J = 6Hz, 4H, Ar-H). (δ = 3.3 (H_2O) and δ = 2.5 (DMSO)).

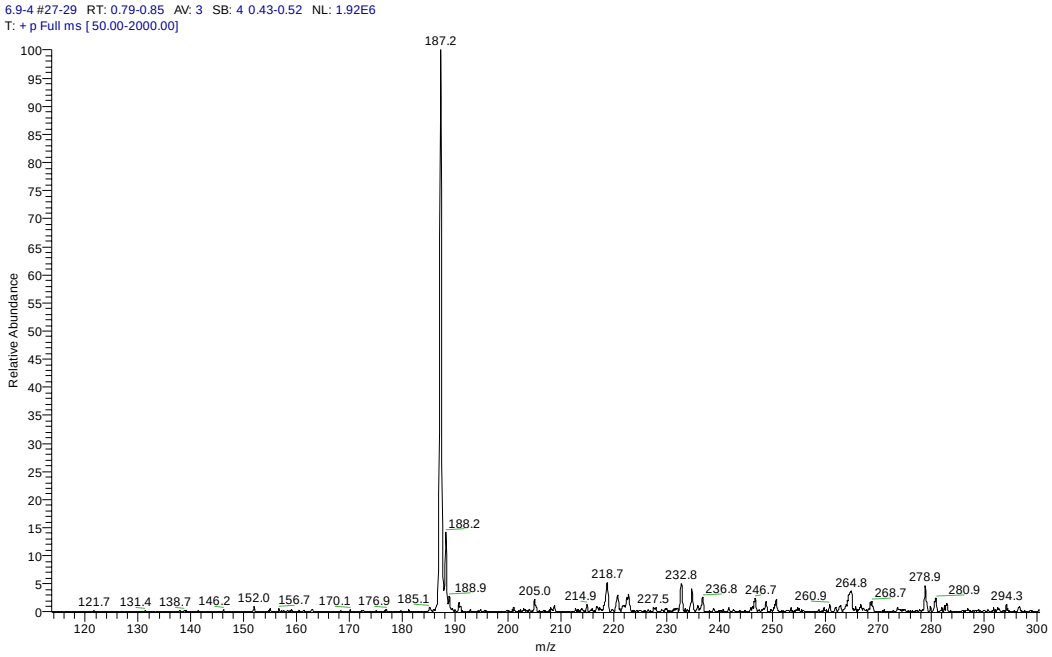

Figure S3. LC-MS (ESI) spectrum for acid digested **1a**, 1,2-bis(4-pyridyl)hydrazine (bphy). m/z = 187.2 ($M+H^+$).

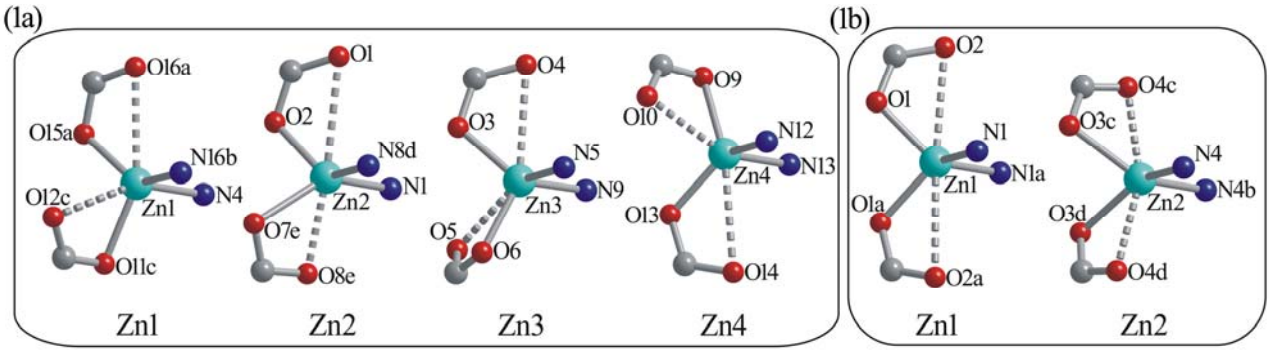

Figure S4. Coordination environments of each independent Zn^{2+} in **1a** (left: Zn1, Zn2, Zn3, Zn4) and **1b** (right: Zn1, Zn2).

Symmetry codes: a, x-0.5, y+0.5, z; b, -x+2.25, y+0.25, z+0.25; c, x, y+0.5, z+0.5; d, -x+1.25, y+0.25, z+0.25; e, x-0.5, y, z+0.5 (**1a**). a, x, -y+2.5, -z+1.5; b, x, -y+1.5, -z+1.5; c, x+0.5, y, -z+2; d, x+0.5, -y+1.5, z-0.5 (**1b**).

Table S1. Zn-O and Zn-N bond lengths in **1a** and **1b** as shown in Figure S4.

1a (*Fdd*2)								**1b** (*Pnna*)			
Zn1		Zn2		Zn3		Zn4		Zn1		Zn2	
Zn1-O15a	1.925(3)	Zn2-O2	1.978(2)	Zn3-O3	1.968(3)	Zn4-O10	2.378(3)	Zn1-O1	2.007(4)	Zn2-O3c	2.149(6)
Zn1-O16a	2.762(4)	Zn2-O1	2.915(3)	Zn3-O4	2.853(3)	Zn4-O9	2.089(4)	Zn1-O2	2.836(6)	Zn2-O4c	2.345(9)
Zn1-O12c	2.513(3)	Zn2-O7e	2.187(3)	Zn3-O5	2.672(3)	Zn4-O13	1.954(3)	Zn1-O1a	2.007(4)	Zn2-O3d	2.149(6)
Zn1-O11c	2.027(3)	Zn2-O8e	2.299(4)	Zn3-O6	2.009(4)	Zn4-O14	2.870(3)	Zn1-O2a	2.836(6)	Zn2-O4d	2.345(9)
Zn1-N16b	2.007(3)	Zn2-N8d	2.004(3)	Zn3-N5	2.073(3)	Zn4-N12	2.020(3)	Zn1-N1	2.022(5)	Zn2-N4	2.031(5)
Zn1-N4	2.046(3)	Zn2-N1	2.020(3)	Zn3-N9	2.032(4)	Zn4-N13	2.019(3)	Zn1-N1a	2.022(5)	Zn2-N4b	2.031(5)

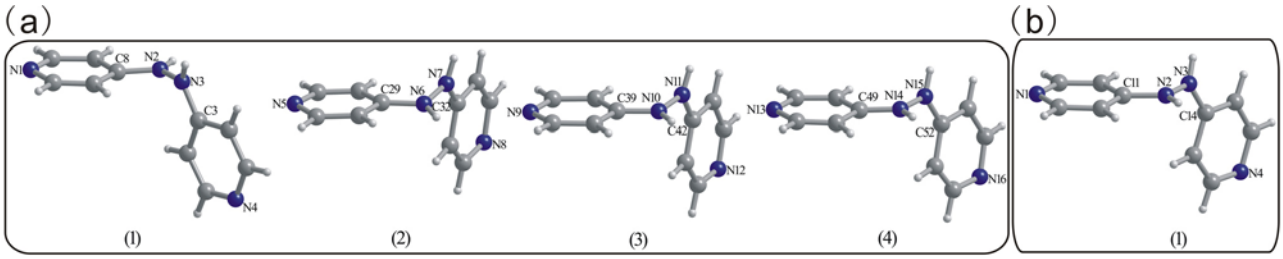

Figure S5. Conformations of bphy ligands in **1a** ((1), (2), (3), (4)) and **1b** ((1)).

Table S2. N-N bond lengths and C-N-N-C torsion angles in **1a** and **1b** as shown in Figure S5.

			1a (*Fdd*2)					**1b** (*Pnna*)	
(1)		(2)		(3)		(4)		(1)	
N2-N3	1.431(5)	N6-N7	1.365(5)	N10-N11	1.440(5)	N14-N15	1.424(6)	N2-N3	1.386(8)
C8-N2-N3-C3	100.8(5)	C29-N6-N7-C32	89.6(5)	C39-N10-N11-C42	89.3(5)	C49-N14-N15-C52	96.2(6)	C11-N2-N3-C14	98.7(7)

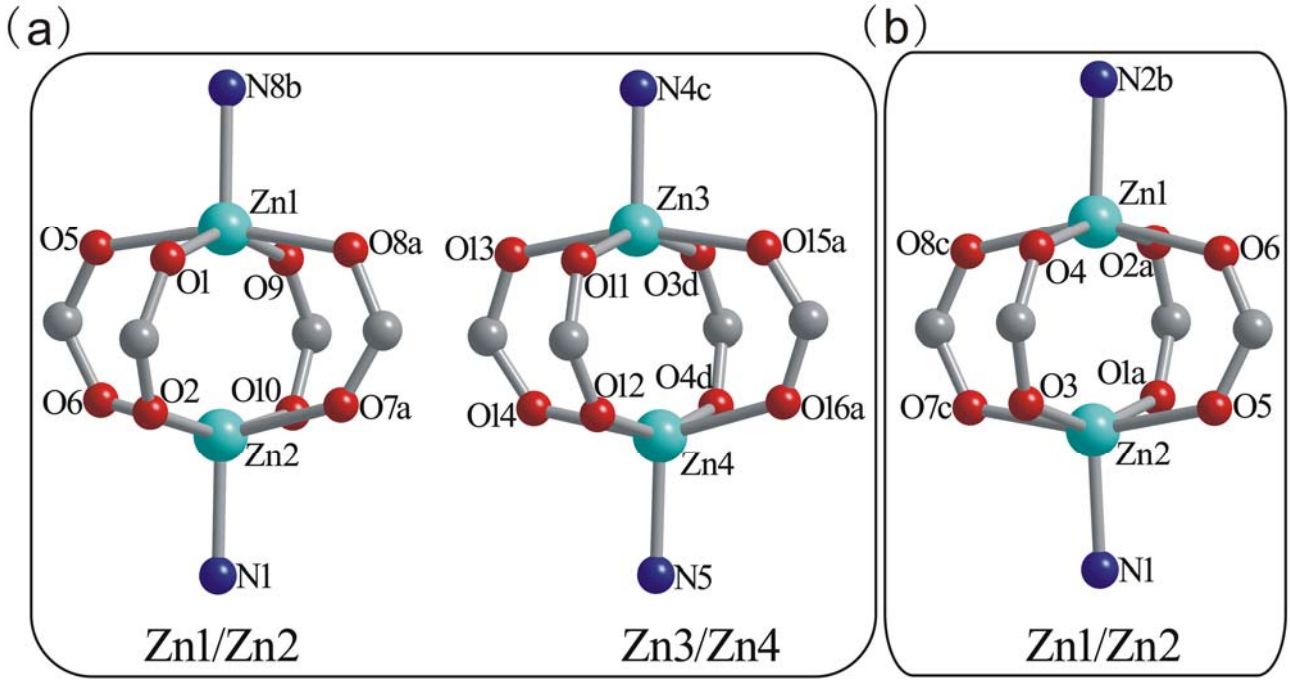

Figure S6. Coordination environments of Zn^{2+} for **2a** (left: Zn1/Zn2, Zn3/Zn4) and **2b** (right: Zn1/Zn2). Symmetry codes: a, x+1, y, z; b, x, y+1, z; c, x, y, z-1; d, x, y-1, z-1 (**2a**). a, x-1, y, z; b, x, y, z+1; c, x, y-1, z (**2b**).

Table S3. Zn-O and Zn-N bond lengths in **2a** and **2b** as shown in Figure S6.

2a (*P*-1)								**2b** (*P*-1)			
Zn1/Zn2				Zn3/Zn4				Zn1/Zn2			
Zn1-O1	2.051(4)	Zn2-O2	2.024(4)	Zn3-O11	2.013(4)	Zn4-O12	2.019(4)	Zn1-O4	2.014(2)	Zn2-O3	2.033(2)
Zn1-O5	2.008(4)	Zn2-O6	2.047(4)	Zn3-O13	2.010(4)	Zn4-O14	2.061(4)	Zn1-O8c	2.060(2)	Zn2-O7c	2.030(2)
Zn1-O8a	2.009(4)	Zn2-O7a	2.058(4)	Zn3-O3d	2.047(4)	Zn4-O4d	2.031(4)	Zn1-O6	2.056(2)	Zn2-O5	2.024(2)
Zn1-O9	2.047(4)	Zn2-O10	2.007(4)	Zn3-O15a	2.031(4)	Zn4-O16a	2.033(4)	Zn1-O2a	2.018(2)	Zn2-O1a	2.040(2)
Zn1-N8b	2.011(4)	Zn2-N1	2.008(4)	Zn3-N4c	2.015(4)	Zn4-N5	1.993(4)	Zn1-N2b	2.018(3)	Zn2-N1	2.013(3)

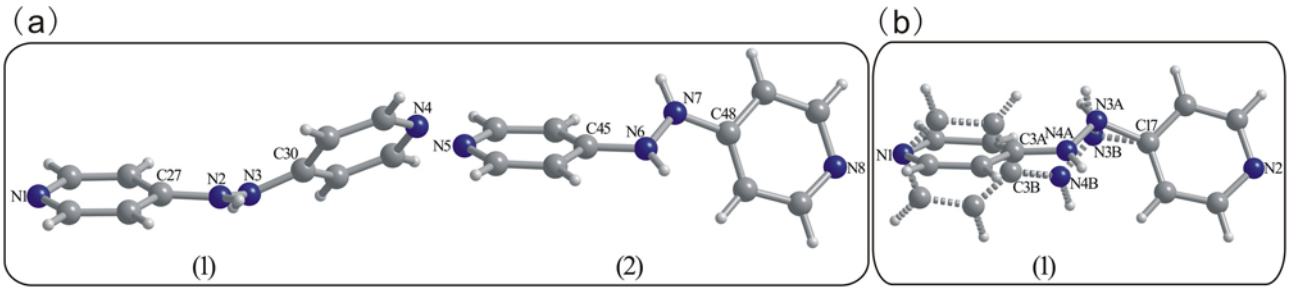

Figure S7. Conformations of bphy ligands in **2a** ((1), (2)) and **2b** ((1)).

Table S4. N-N bond lengths and C-N-N-C torsion angles in **2a** and **2b** as shown in Figure S7.

	2a (*P*-1)			**2b** (*P*-1)			
(1)		(2)		(1)			
N2-N3	1.371(6)	N6-N7	1.375(8)	N3A-N4A	1.419(16)	N3B-N4B	1.364(14)
C27-N2-N3-C30	149.4(6)	C45-N6-N7-C48	142.9(7)	C17-N3A-N4A-C3A	142.0(13)	C17-N3B-N4B-C3B	144.5(14)

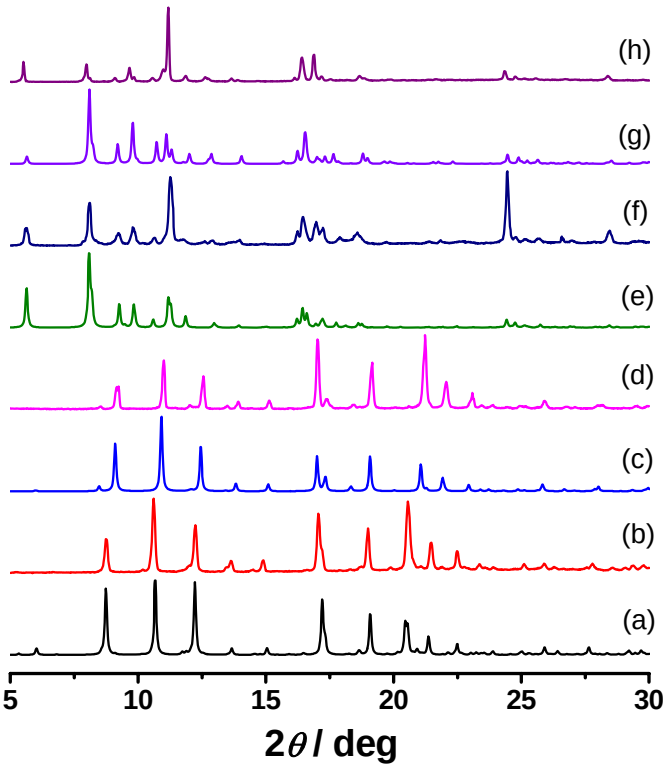

Figure S8. PXRD patterns for (a) simulated **1a**, (b) as-synthesized **1a**, (c) simulated **1b**, (d) as-synthesized **1b**, (e) simulated **2a**, (f) as-synthesized **2a**, (g) simulated **2b**, and (h) as-synthesized **2b**.

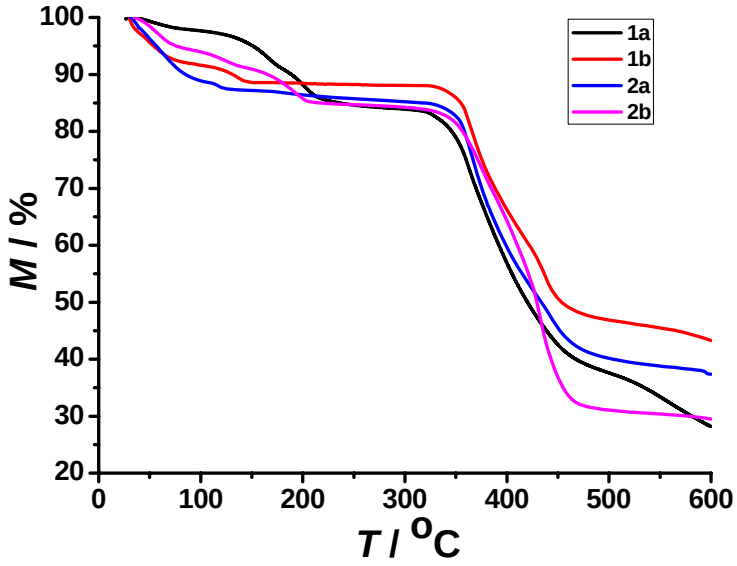

Figure S9. TG curves of **1a**, **1b**, **2a** and **2b**.

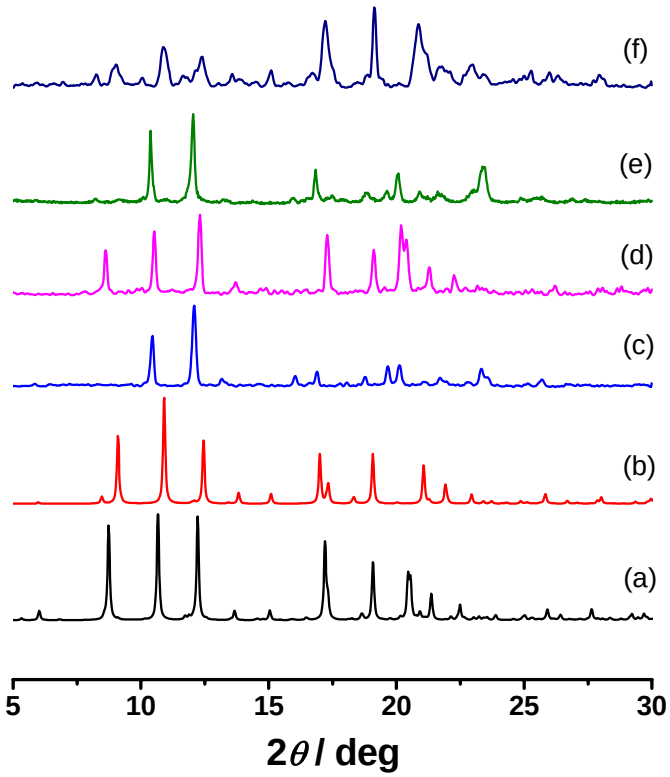

Figure S10. PXRD patterns for (a) simulated **1a**, (b) simulated **1b**, (c) **1** obtained by **1a** activated at 200°C, (d) **1** adsorbed DMF, (e) **1** obtained by **1b** activated at 150°C and (f) **1** adsorbed EtOH.

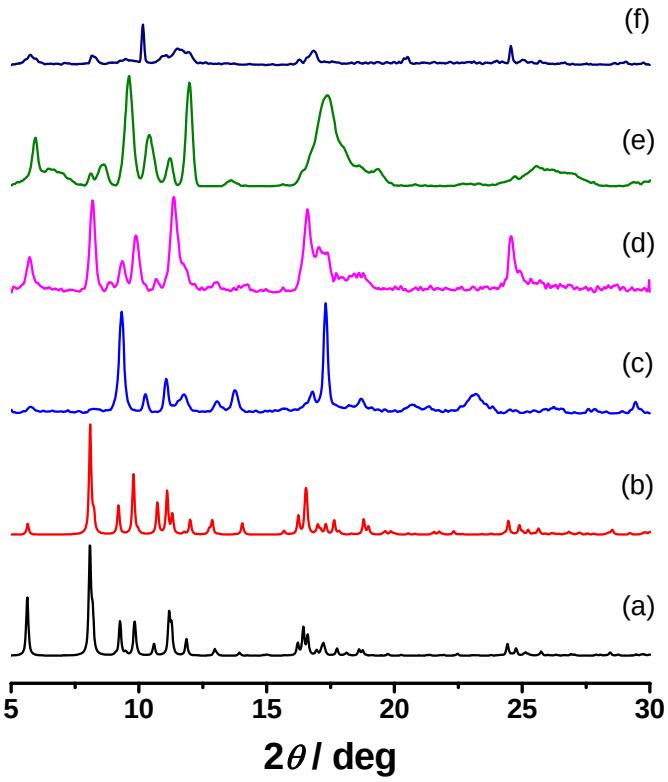

Figure S11. PXRD patterns for (a) simulated **2a**, (b) simulated **2b**, (c) **2** obtained by **2a** activated at 110^{o}C, (d) **2** adsorbed EtOH, (e) **2** obtained by **2b** activated at 200^{o}C and (f) **2** adsorbed DMA.

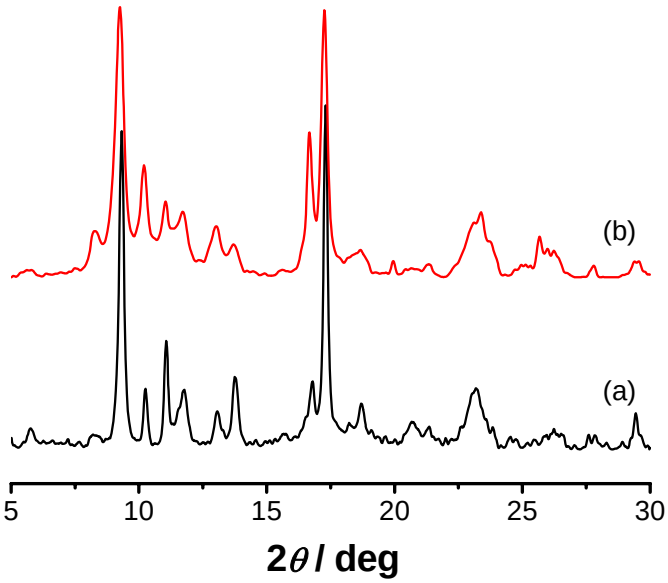

Figure S12. PXRD patterns for **2** (a) before adsorption and (b) after desorption.