Supporting Information

Stitching 2D polymeric layers into flexible 3D metal-organic frameworks via the sequential self-assembly approach

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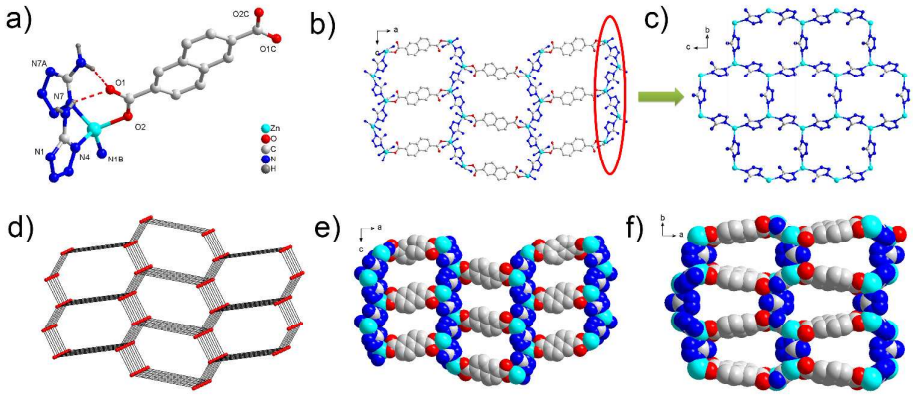

Figure S1. (a) Zn (II) coordination environments of **A3**. Symmetry codes: (A) −x, -y, 1-z; (B) x, 0.5-y, z; (C) 0.5−x, -y, 0.5+z. Part of hydrogen atoms are omitted for clarity. (b) View of the 3D framework from the bc plane layer. (c) 2D layer of **A3**. (d) 3D uninodal 4-connected network with a 'lon' topology with point symbol {66} of **A3**. (e) Space-filling model of **A3** along *b* crystallographic axis. (f) Space-filling model of **A3** along crystallographic *c* axis.

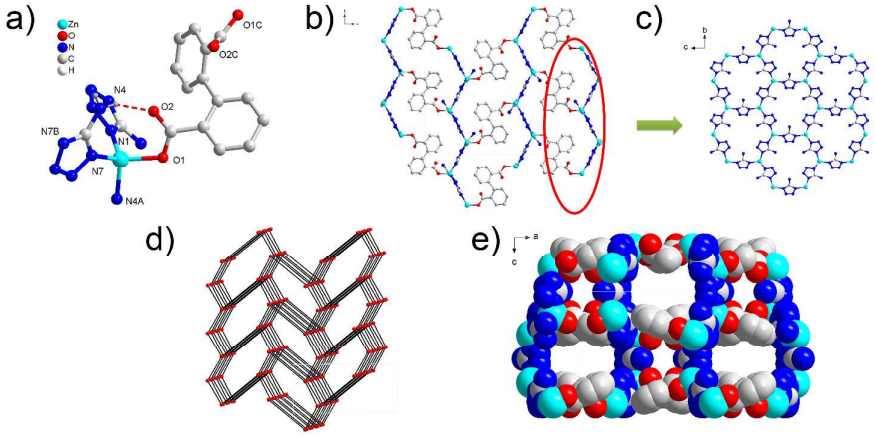

Figure S2. (a) Zn (II) coordination environments of **A4**. Symmetry codes: (A) −x, -0.5-y, z; (B) 0.5-x, -y, -0.5+z; (C) −x, -y, -z. Part of hydrogen atoms are omitted for clarity. (b) View of the 3D framework from the *bc* plane layer. (c) 2D layer of **A4**. (d) 3D uninodal 4-connected network with a 'lon' topology with point symbol {66} of **A4**. (e) Space-filling model of **A4** along crystallographic *b* axis.

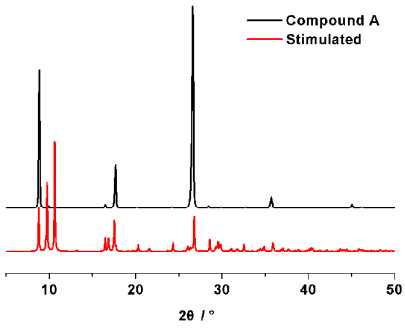

Figure S3. PXRD patterns of simulated from the single-crystal data of compound **A** (red); as-synthesized (black).

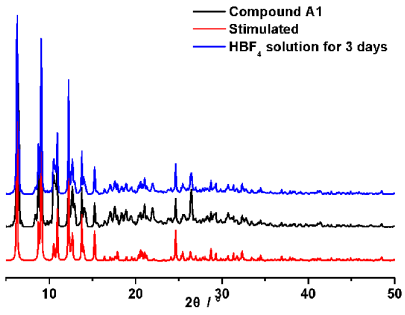

Figure S4. PXRD patterns of simulated from the single-crystal data of compound **A1** (red); as-synthesized (black); the sample soaked in HBF_4 solution for 3 days (blue). Note: 10 drops 50% HBF_4 is added into 15 ml DMF to obtain the HBF_4 solution.

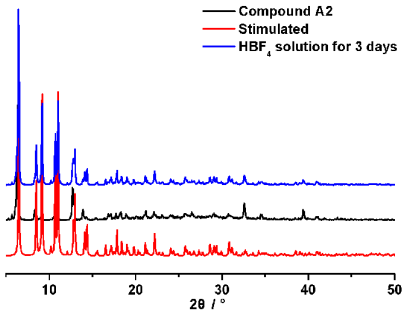

Figure S5. PXRD patterns of simulated from the single-crystal data of compound **A2** (red); as-synthesized (black) ; the sample soaked in HBF_4 solution for 3 days (blue). Note: 10 drops 50% HBF_4 is added into 15 ml DMF to obtain the HBF_4 solution.

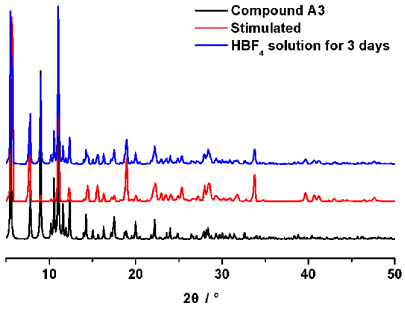

Figure S6. PXRD patterns of simulated from the single-crystal data of compound **A3**(red); as-synthesized (black) ; the sample soaked in HBF_4 solution for 3 days (blue). Note: 10 drops 50% HBF_4 is added into 15 ml DMF to obtain the HBF_4 solution.

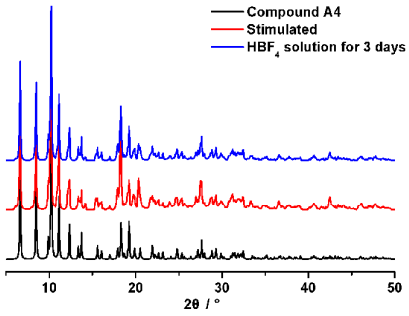

Figure S7. PXRD patterns of simulated from the single-crystal data of compound **A4** (red); as-synthesized (black) ; the sample soaked in HBF_4 solution for 3 days (blue). Note: 10 drops 50% HBF_4 is added into 15 ml DMF to obtain the HBF_4 solution.

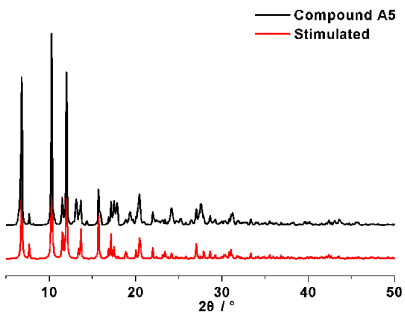

Figure S8. PXRD patterns of simulated from the single-crystal data of compound **A5** (red); as-synthesized (black).

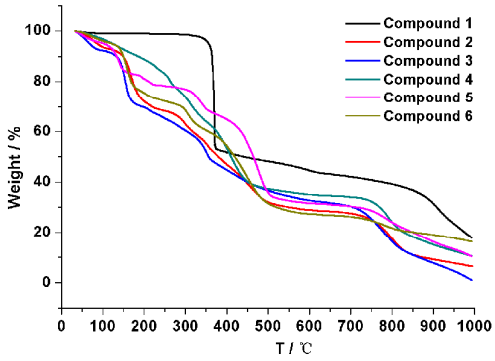

Figure S9. TGA curves for compounds **1-6**.

Table S1. Crystallographic Data for compounds **A** and **A1-A5**.

Compound	**A**	**A1**	**A2**	**A3**	**A4**	**A5**
Empirical formula	$C_2H_4N_{10}Zn$	$C_{6.5}H_9N_8O_2Zn$	$C_{6.5}H_{9.5}N_{8.5}O_2Zn$	$C_{10}H_{15.5}N_{8.5}O_{3.5}Zn$	$C_{9.5}H_{11}N_8O_2Zn$	$C_{15}H_{10}N_5O_4Zn$
Formula weight	233.54	296.59	304.10	319.60	334.63	389.67
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Cmcm*	*Pnma*	*Pnma*	*Pnma*	*Pnnm*	*Pbca*
a (Å)	17.949(7)	28.13(3)	27.250(15)	31.928(17)	20.818(9)	22.954(11)
b (Å)	10.453(4)	14.427(16)	16.002(9)	16.003(8)	9.887(4)	10.328(5)
c (Å)	19.881(9)	10.380(12)	10.292(5)	10.329(5)	17.281(7)	25.873(11)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00
V (Å^3)	3730(3)	4212(8)	4488(4)	5278(5)	3557(3)	6134(5)
Z	16	8	8	8	8	8
Dc (g/cm^3)	1.663	0.935	0.900	0.804	1.250	0.844
μ (mm^{-1})	2.609	1.170	1.100	0.937	1.394	0.817
F(000)	1855	1200	1232	1288	1360	1576
θ range (°)	2.48 - 27.51	2.02 - 25.00	2.35 - 27.44	2.35 - 27.38	2.28 - 27.48	2.30 - 25.00
R(int)	0.0662	0.0884	0.0621	0.0768	0.0772	0.0742
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0721, 0.1841	0.0863 , 0.2113	0.0549, 0.1681	0.0744, 0.2254	0.0833, 0.1974	0.0884 , 0.2103
GOF on F^2	0.984	0.967	1.022	0.934	1.001	0.922

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

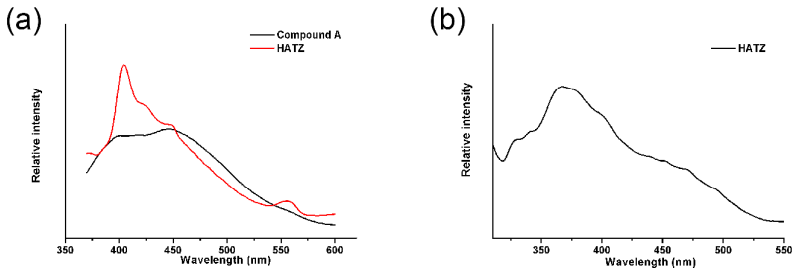

Figure S10. (a) Solid-state emission spectra for the HATZ ligand and Compound A, excited at 330 nm; (b) Solid-state emission spectra for the HATZ ligand, excited at 288 nm.

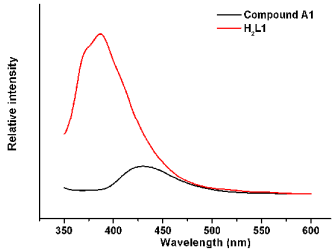

Figure S11. Solid-state emission spectra for the H_2L1 ligand and Compound A1, excited at 330 nm.

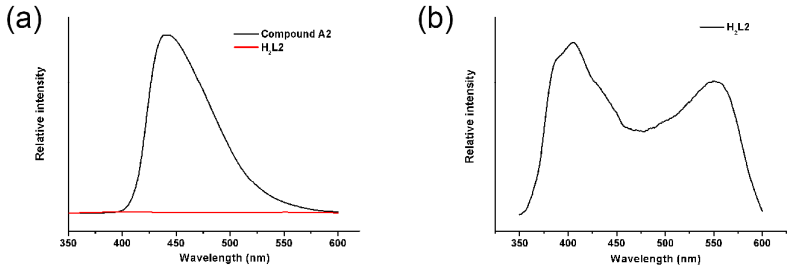

Figure S12. Solid-state emission spectra for the H_2L2 ligand (b) and Compound A2, excited at 330 nm.

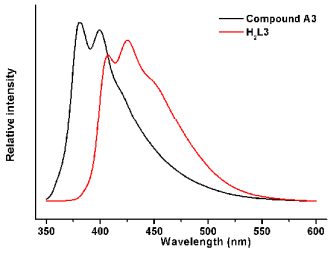

Figure S13. Solid-state emission spectra for the H_2L3 ligand and Compound A3, excited at 330 nm.

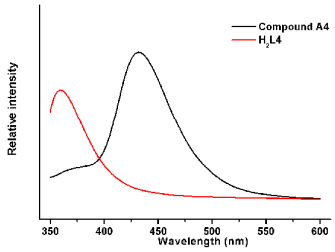

Figure S14. Solid-state emission spectra for the H_2L4 ligand and Compound A4, excited at 330 nm.

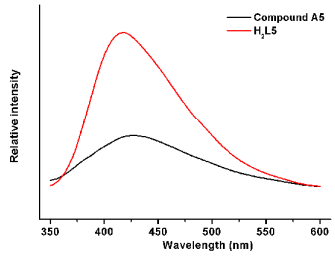

Figure S15. Solid-state emission spectra for the H_2L5 ligand and Compound A5, excited at 330 nm.