Supporting Information

Formation of Four Different [$MoOS_3Cu_3$]-Based Coordination Polymers from the Same Components via Four Synthetic Routes

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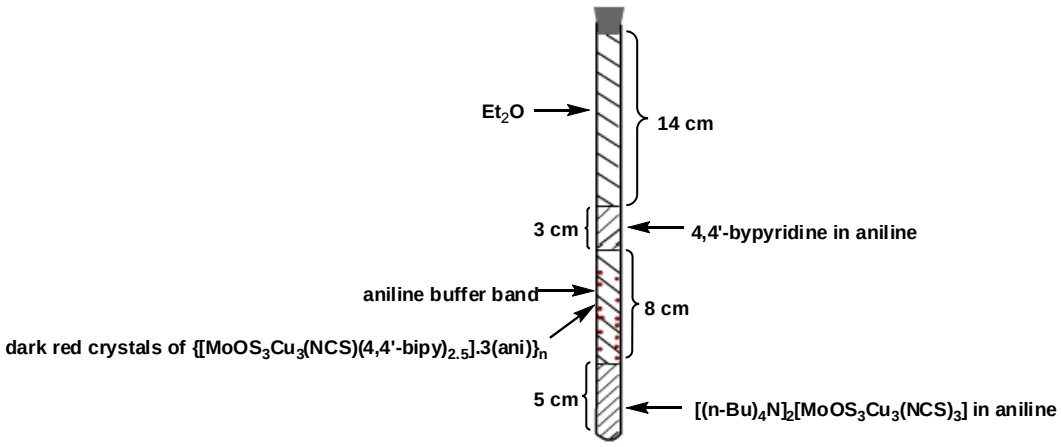

Figure S1. A sketch of the apparatus used to generate crystals of $\{[MoOS_3Cu_3(NCS)(4,4'\text{-bipy})_{2.5}]\cdot 3(ani)\}_n$ (**4**)

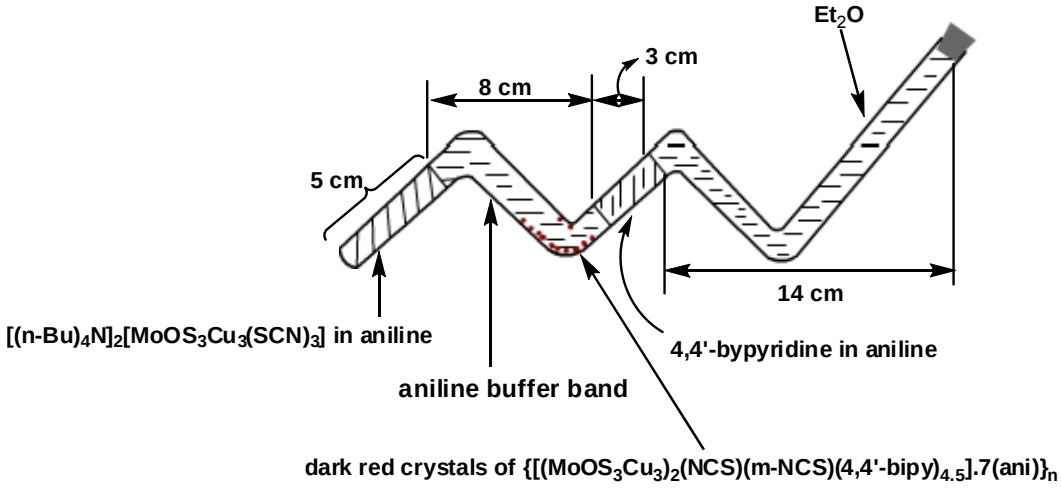

Figure S2. A sketch of the apparatus used to generate crystals of $\{[(MoOS_3Cu_3)_2(NCS)(\mu\text{-NCS})(4,4'\text{-bipy})_{4.5}]\cdot 7(ani)\}_n$ (**5**)

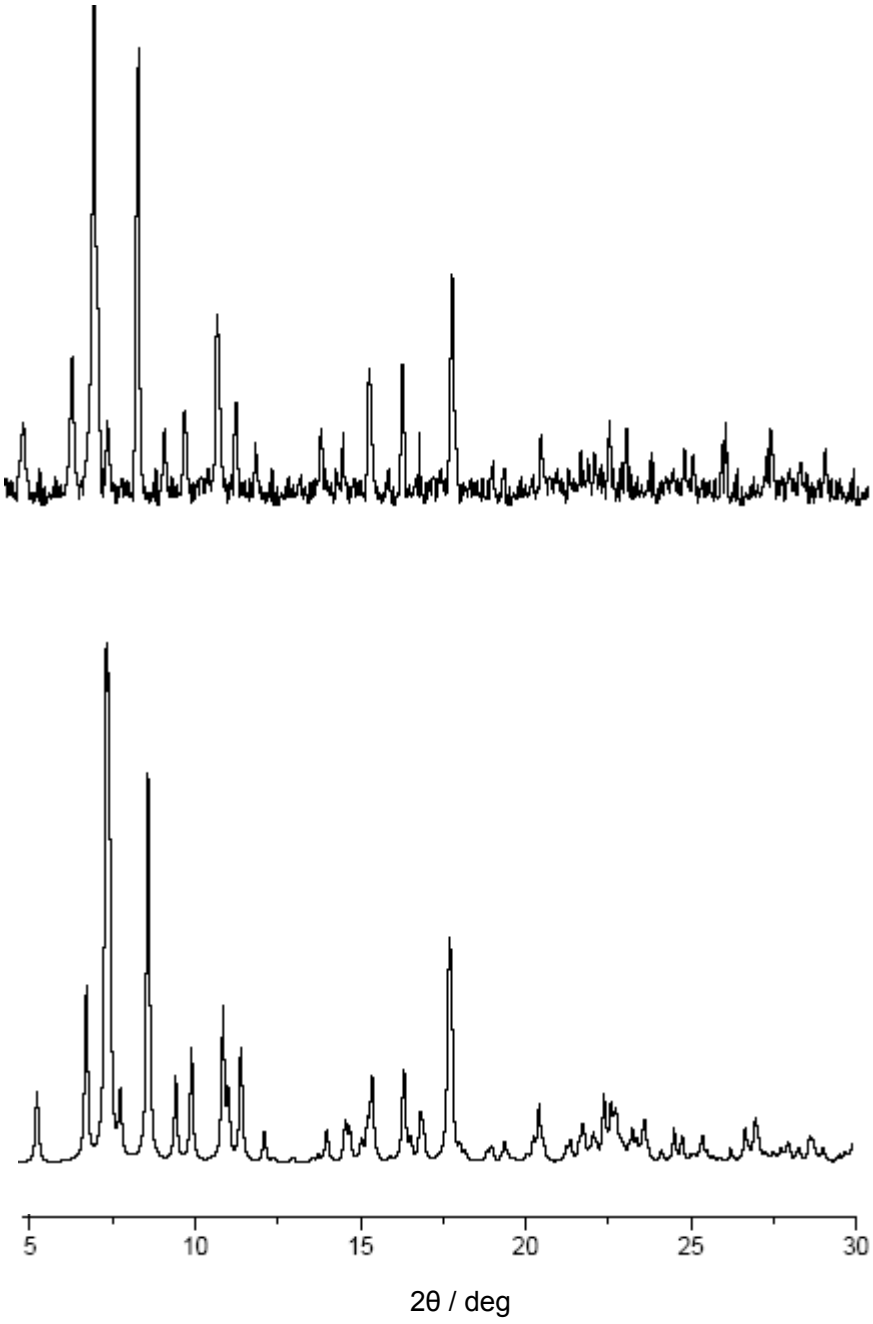

Figure S3a. Experimental (up) and simulated (down) PXRD patterns for 2

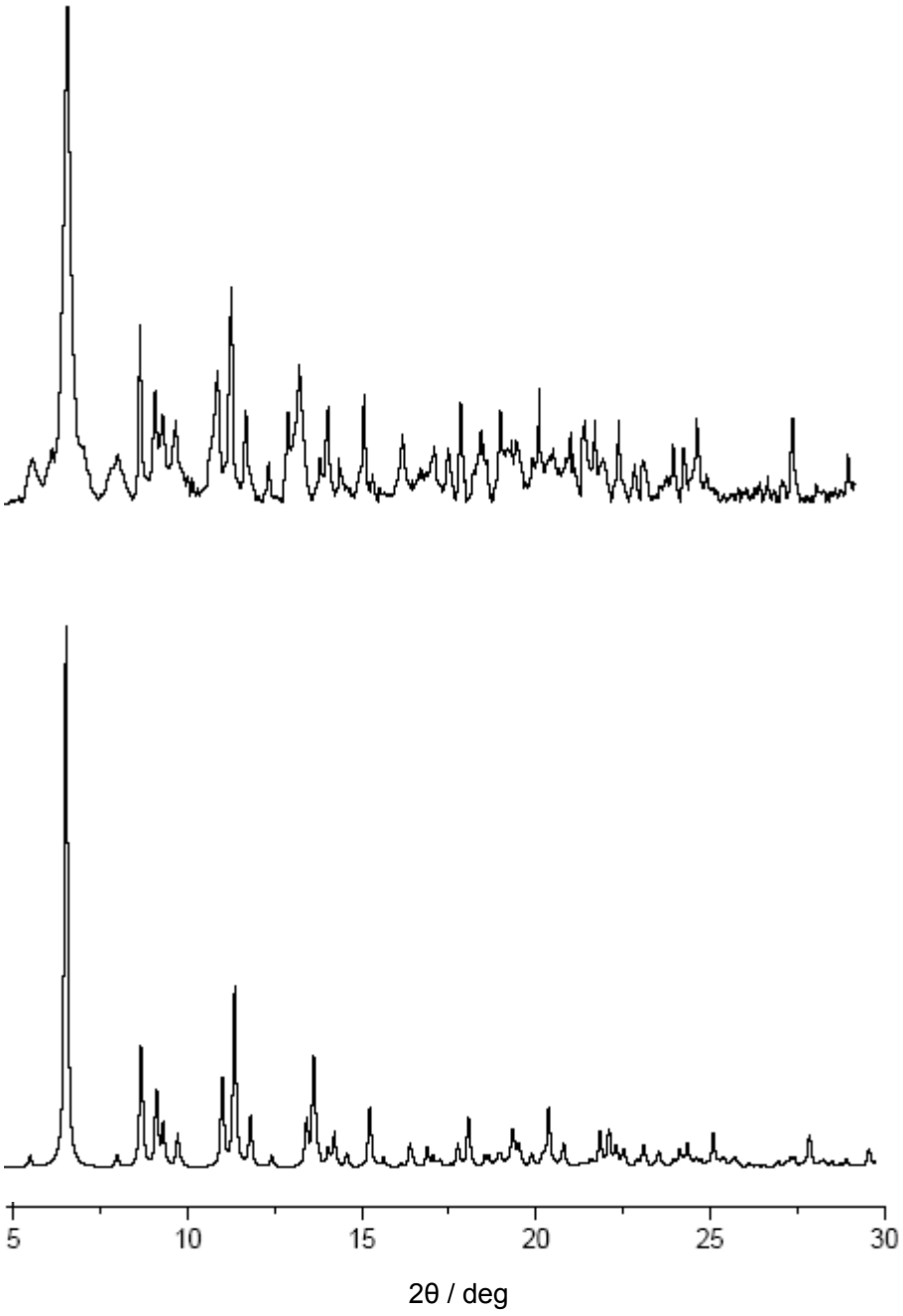

Figure S3b. Experimental (up) and simulated (down) PXRD patterns for 3

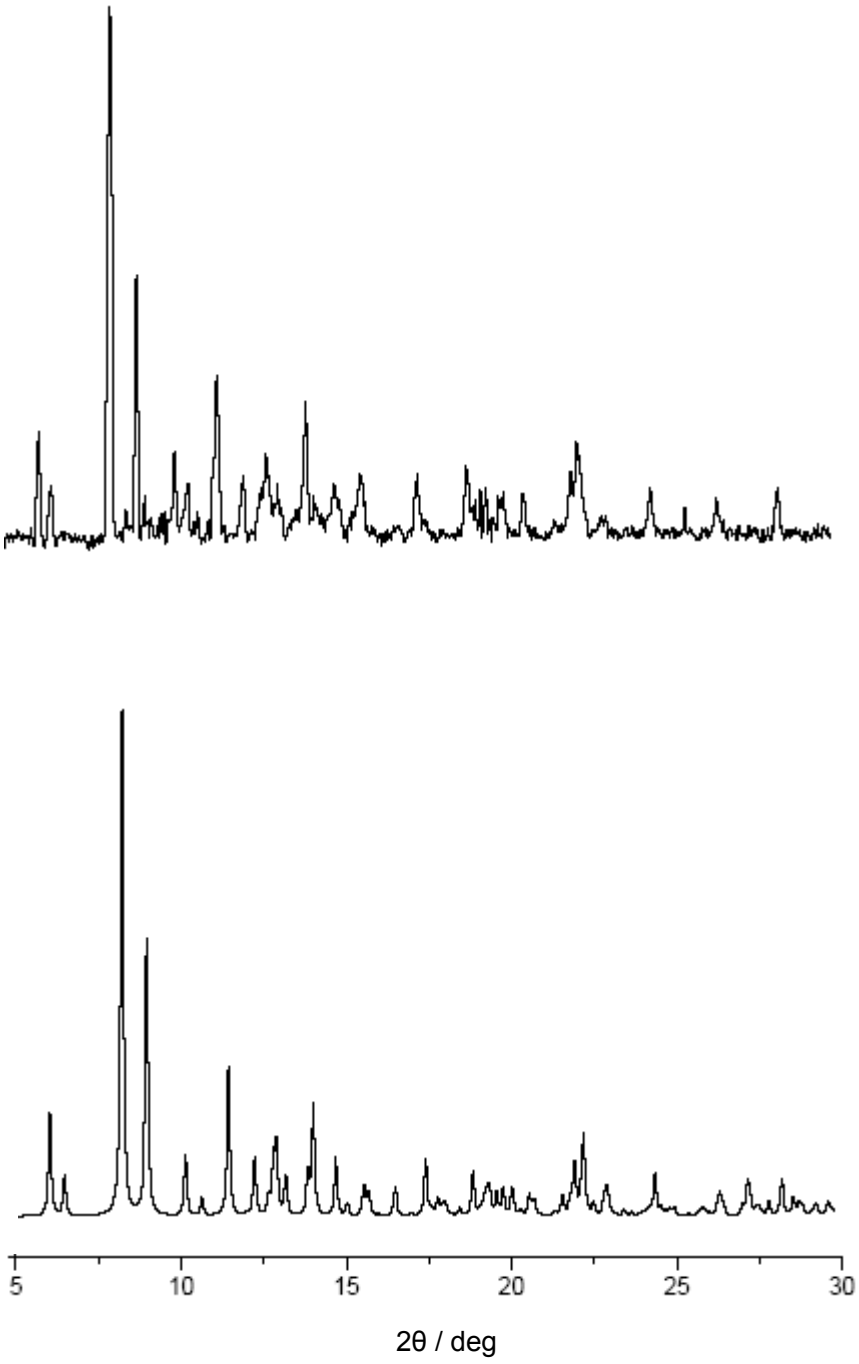

Figure S3c. Experimental (up) and simulated (down) PXRD patterns for 4

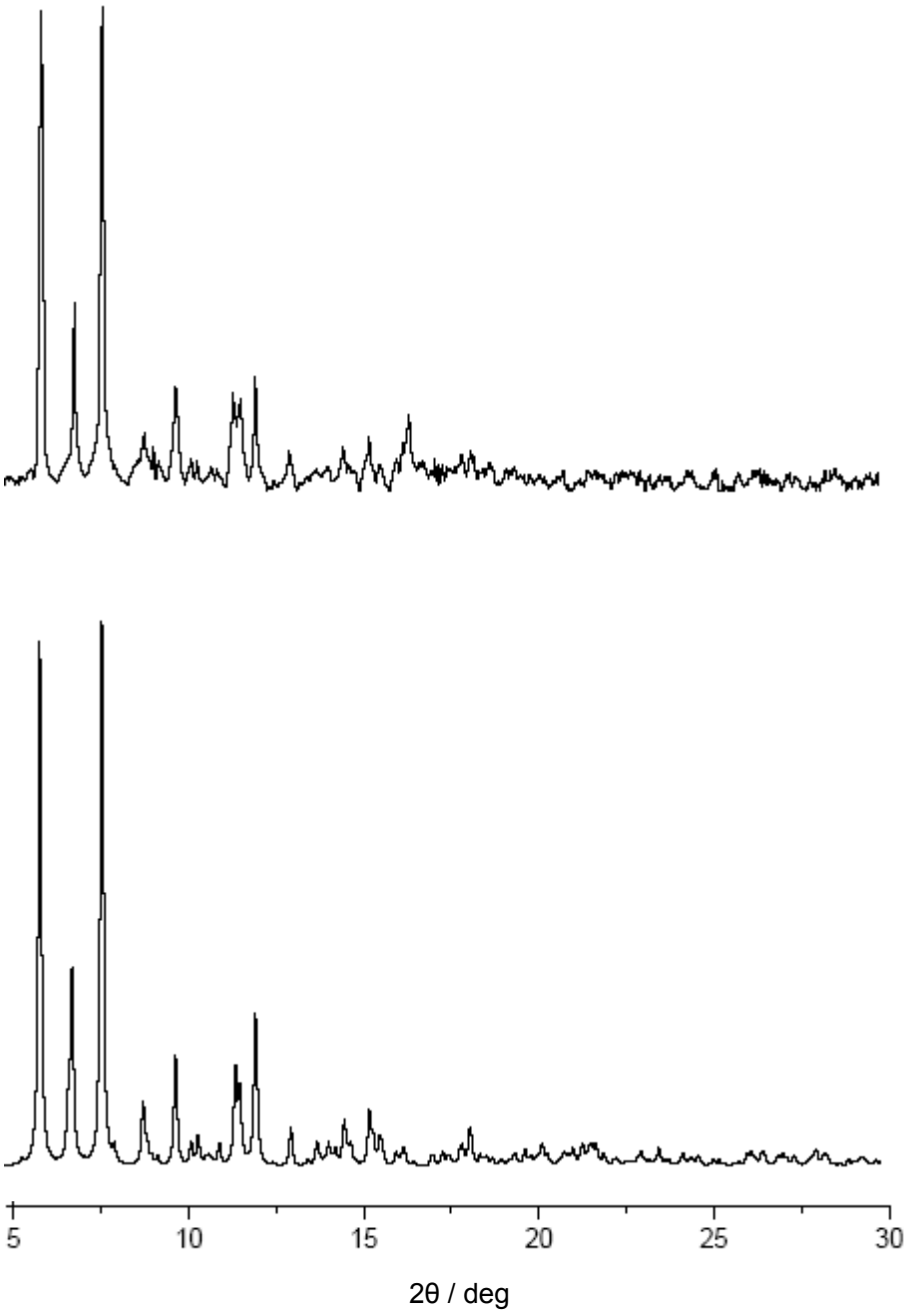

Figure S3d. Experimental (up) and simulated (down) PXRD patterns for 5

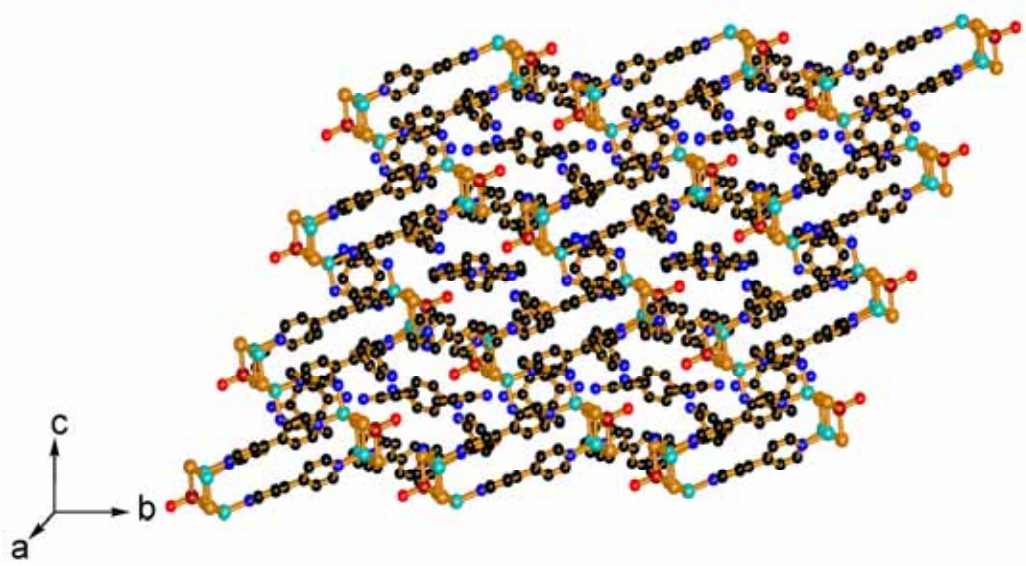

Figure S3. The cell packing diagram of **2** looking down in the *a* axis, showing that the solvent aniline molecules were crystallized in between the layers. All the hydrogen atoms were omitted.

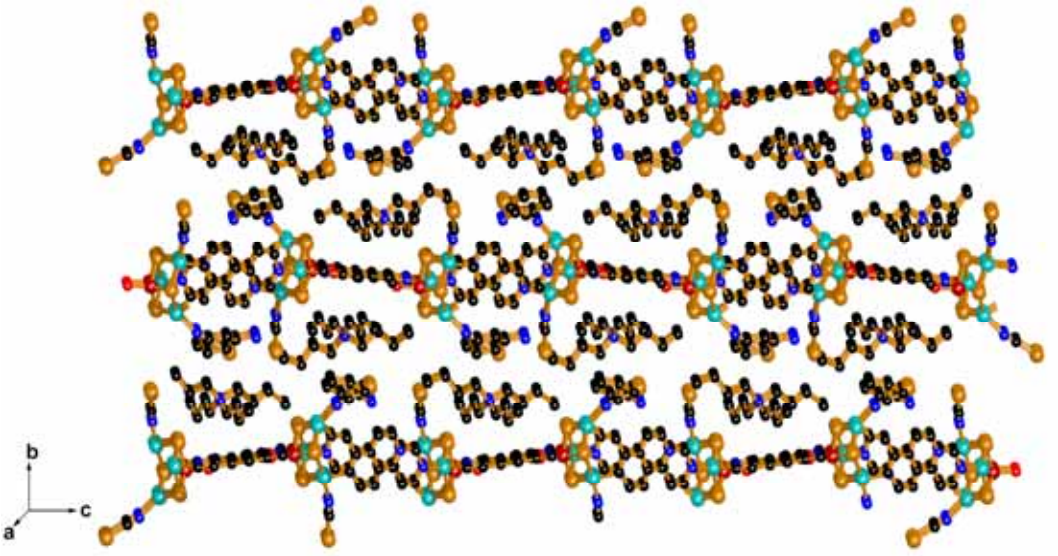

Figure S4. The cell packing diagram of **3** looking down in the *a* axis, showing that the solvent aniline molecules and $[(n\text{-Bu})_4N]^+$ cations were crystallized in between the layers. All the hydrogen atoms were omitted.

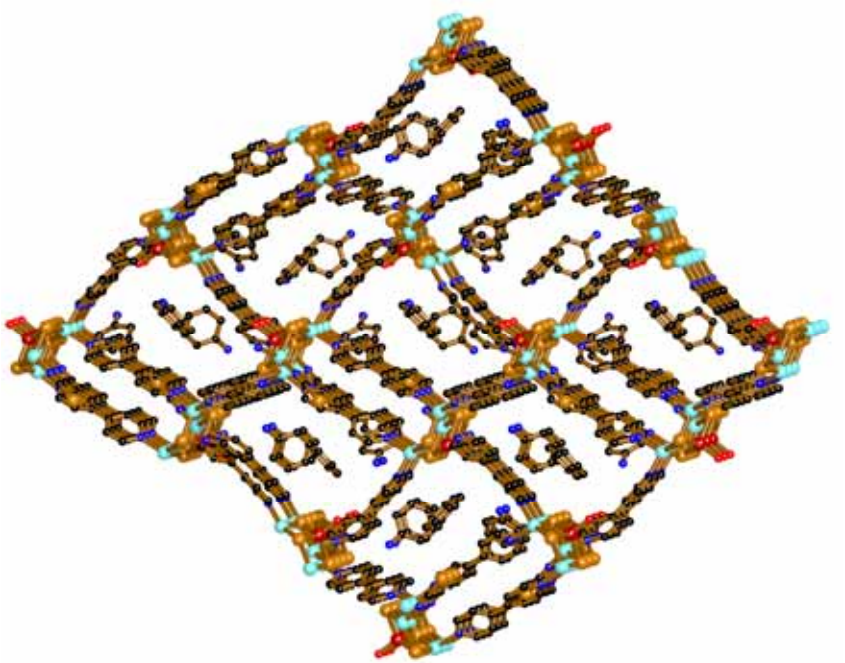

Figure S5. The cell packing diagram of **4** looking down in the *a* axis, showing 1D channels are stuffed by aniline solvent molecules. All the hydrogen atoms were omitted.

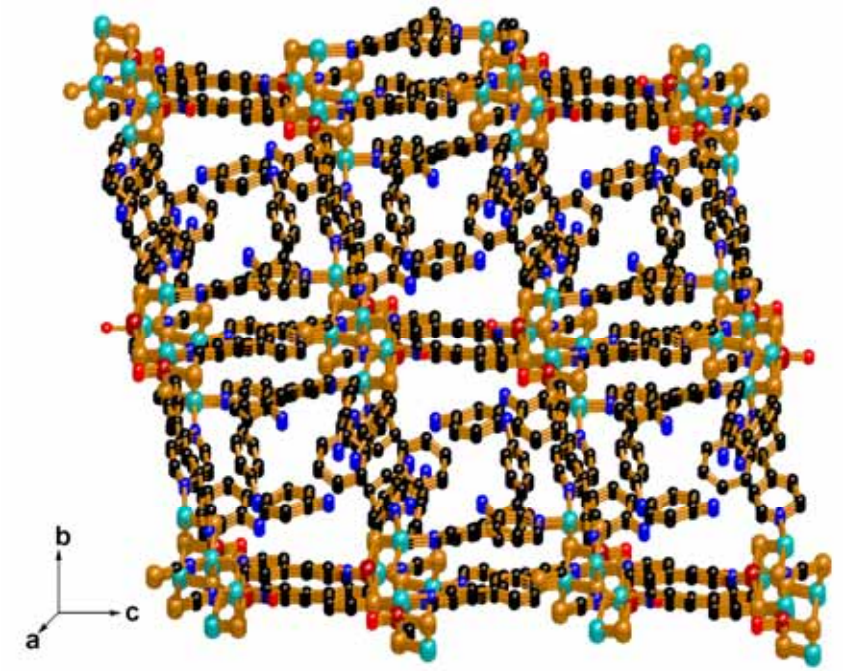

Figure S6. The cell packing diagram of **5** looking down in the *a* axis, 1D channels are stuffed by aniline solvent molecules. All the hydrogen atoms were omitted.

Table S1. Selected bond lengths (Å) and angles (deg) for compound **2**

Mo1-O1	1.700(5)	Mo1- S3	2.265(2)	Mo1-S2	2.2666(19)
Mo1-S1	2.269(2)	Mo1-Cu2	2.6560(12)	Mo1-Cu1	2.6771(11)
Mo1-Cu3	2.7019(11)	Mo2-O2	1.710(5)	Mo2-S7	2.257(2)
Mo2-S6	2.2726(19)	Mo2-S5	2.2728(19)	Mo2-Cu4	2.6665(11)
Mo2-Cu6	2.6751(12)	Mo2-Cu5	2.7073(11)	Cu1-N2	2.059(6)
Cu1-N1	2.125(8)	Cu1-S1	2.259(4)	Cu1-S2	2.281(2)
Cu2-N4	2.058(6)	Cu2-N3	2.126(7)	Cu2-S1	2.264(2)
Cu2-S3	2.272(2)	Cu3-N6	1.979(8)	Cu3-N5	2.119(7)
Cu3-S3	2.281(4)	Cu3-S2	2.290(2)	Cu4-N8	2.067(6)
Cu4-N7	2.101(7)	Cu4-S6	2.274(4)	Cu4-S5	2.274(2)
Cu5-N10	1.972(8)	Cu5-N9	2.124(7)	Cu5-S5	2.285(2)
Cu5-S7	2.293(4)	Cu6-N12	2.038(6)	Cu6-N11	2.156(7)
Cu6-S6	2.250(2)	Cu6-S7	2.290(2)		
O1-Mo1-S3	110.9(3)	O1-Mo1-S2	110.3(2)	S3-Mo1-S2	107.71(7)
O1-Mo1-S1	111.9(3)	S3-Mo1-S1	108.23(8)	S2-Mo1-S1	107.77(7)
Cu2-Mo1-Cu1	83.89(4)	Cu2-Mo1-Cu3	87.26(4)	Cu1-Mo1-Cu3	88.79(3)
O2-Mo2-S7	110.5(2)	O2-Mo2-S6	111.6(2)	S7-Mo2-S6	107.86(7)
O2-Mo2-S5	110.8(2)	S7-Mo2-S5	107.75(14)	S6-Mo2-S5	108.12(7)
Cu4-Mo2-Cu6	84.42(3)	Cu4-Mo2-Cu5	87.06(3)	Cu6-Mo2-Cu5	89.80(4)
N2-Cu1-N1	100.3(3)	N2-Cu1-S1	113.2(2)	N1-Cu1-S1	112.7(2)
N2-Cu1-S2	111.7(2)	N1-Cu1-S2	111.3(2)	S1-Cu1-S2	107.61(8)
N4-Cu2-N3	100.7(3)	N4-Cu2-S1	114.1(2)	N3-Cu2-S1	110.3(2)
N4-Cu2-S3	113.1(2)	N3-Cu2-S3	110.3(3)	S1-Cu2-S3	108.18(17)
N6-Cu3-N5	100.4(3)	N6-Cu3-S3	115.8(3)	N5-Cu3-S3	107.7(2)
N6-Cu3-S2	119.2(3)	N5-Cu3-S2	106.3(2)	S3-Cu3-S2	106.37(16)
N8-Cu4-N7	101.9(3)	N8-Cu4-S6	112.0(2)	N7-Cu4-S6	109.8(2)
N8-Cu4-S5	111.6(2)	N7-Cu4-S5	113.5(2)	S6-Cu4-S5	108.04(7)
N10-Cu5-N9	100.6(3)	N10-Cu5-S5	116.8(3)	N9-Cu5-S5	110.6(2)
N10-Cu5-S7	117.1(3)	N9-Cu5-S7	104.9(2)	S5-Cu5-S7	106.10(7)
N12-Cu6-N11	100.3(3)	N12-Cu6-S6	116.4(2)	N11-Cu6-S6	114.4(2)
N12-Cu6-S7	109.8(2)	11-Cu6-S7	108.1(3)	S6-Cu6-S7	107.53(8)
Cu1-S1-Cu2	104.03(15)	Cu1-S1-Mo1	72.48(6)	Cu2-S1-Mo1	71.74(6)
Mo1-S2-Cu1	72.12(6)	Mo1-S2-Cu3	72.74(6)	Cu1-S2-Cu3	110.82(16)
Mo1-S3-Cu2	71.68(6)	Mo1-S3-Cu3	72.94(7)	Cu2-S3-Cu3	108.60(18)
Mo2-S5-Cu4	71.81(6)	Mo2-S5-Cu5	72.87(6)	Cu4-S5-Cu5	108.54(16)
Cu6-S6-Mo2	72.54(6)	Cu6-S6-Cu4	105.01(15)	Mo2-S6-Cu4	71.83(6)
Mo2-S7-Cu6	72.07(6)	Mo2-S7-Cu5	73.01(6)	Cu6-S7-Cu5	111.99(8)

Table S2. Selected bond lengths (Å) and angles (deg) for compound **3**

Mo1-Cu1	2.647(3)	Mo1-Cu3	2.657(3)	Mo1-Cu2	2.689(3)
Mo2-Cu6	2.635(3)	Mo2-Cu4	2.662(3)	Mo2-Cu5	2.699(3)
Mo1-O1	1.684(10)	Mo1-S3	2.259(6)	Mo1-S2	2.260(6)
Mo1-S1	2.280(5)	Mo2-O2	1.702(12)	Mo2-S4	2.244(6)
Mo2-S6	2.253(5)	Mo2-S5	2.269(6)	Cu1-N1	2.028(13)
Cu1-S2	2.236(6)	Cu1-S1	2.246(6)	Cu2-N5	2.113(15)
Cu2-N2	2.139(14)	Cu2-S1	2.253(6)	Cu2-S3	2.309(6)
Cu3-N7	1.998(15)	Cu3-N9	2.144(15)	Cu3-S3	2.258(6)
Cu3-S2	2.286(6)	Cu4-N6A	1.982(13)	Cu4-N10	2.088(16)
Cu4-S4	2.231(6)	Cu4-S5	2.295(6)	Cu5-N3	2.085(13)
Cu5-N8A	2.120(14)	Cu5-S6	2.273(6)	Cu5-S4	2.317(6)
Cu6-N4	1.990(12)	Cu6-S5	2.224(6)	Cu6-S6	2.229(6)
Cu1-Mo1-Cu3	90.36(9)	Cu1-Mo1-Cu2	85.61(9)	Cu3-Mo1-Cu2	89.13(9)
Cu6-Mo2-Cu4	89.38(9)	Cu6-Mo2-Cu5	85.23(9)	Cu4-Mo2-Cu5	87.69(9)
O1-Mo1-S3	108.7(6)	O1-Mo1-S2	113.3(5)	S3-Mo1-S2	108.43(19)
O1-Mo1-S1	111.2(5)	S3-Mo1-S1	107.93(19)	S2- Mo1-S1	107.1(2)
O2-Mo2-S4	108.9(7)	O2-Mo2-S6	112.1(5)	S4-Mo2-S6	108.7(2)
O2-Mo2-S5	112.2(6)	S4-Mo2-S5	107.9(2)	S6-Mo2-S5	106.9(2)
N1-Cu1-S2	129.1(5)	N1-Cu1-S1	121.7(5)	S2-Cu1-S1	109.2(2)
N5-Cu2-N2	107.3(6)	N5-Cu2-S1	112.4(5)	N2-Cu2-S1	110.2(4)
N5-Cu2-S3	100.8(5)	N2-Cu2-S3	118.8(4)	S1-Cu2-S3	107.1(2)
N7-Cu3-N9	101.1(6)	N7-Cu3-S3	116.6(6)	N9-Cu3-S3	106.6(5)
N7-Cu3-S2	120.7(6)	N9-Cu3-S2	102.1(5)	S3-Cu3-S2	107.55(19)
N6A-Cu4-N10	98.5(6)	N6A-Cu4-S4	121.2(5)	N10-Cu4-S4	107.5(4)
N6A-Cu4-S5	116.5(5)	N10-Cu4-S5	103.2(5)	S4-Cu4-S5	107.5(2)
N3-Cu5-N8A	108.2(6)	N3-Cu5-S6	115.2(5)	N8A-Cu5-S6	112.0(5)
N3-Cu5-S4	115.5(5)	N8A-Cu5-S4	99.4(4)	S6-Cu5-S4	105.5(2)
N3-Cu5-Mo2	136.6(4)	N8A-Cu5-Mo2	114.9(4)	S6-Cu5-Mo2	53.05(14)
S4-Cu5-Mo2	52.49(14)	N4-Cu6-S5	127.5(5)	N4-Cu6-S6	123.2(5)
S5-Cu6-S6	109.3(2)	N4-Cu6-Mo2	176.9(5)	S5-Cu6-Mo2	54.87(17)
S6-Cu6-Mo2	54.41(15)	Cu1-S1-Cu2	107.4(2)	Cu1-S1-Mo1	71.57(17)
Cu2-S1-Mo1	72.77(17)	Cu1-S2-Mo1	72.13(18)	Cu1-S2-Cu3	112.6(2)
Mo1-S2-Cu3	71.52(19)	Cu3-S3-Mo1	72.05(18)	Cu3-S3-Cu2	110.5(2)
Mo1-S3-Cu2	72.12(17)	Cu4-S4-Mo2	73.00(19)	Cu4-S4-Cu5	109.4(2)
Mo2-S4-Cu5	72.53(17)	Cu6 S5 Mo2	71.81(18)	Cu6-S5-Cu4	111.1(2)
Mo2-S5-Cu4	71.38(19)	Cu6-S6-Mo2	72.02(17)	Cu6-S6-Cu5	106.7(2)
Mo2-S6-Cu5	73.22(18)				

Table S3. Selected bond lengths (Å) and angles (deg) for compound **4**

Mo1-O1	1.715(5)	Mo1-S2	2.2645(19)	Mo1-S1	2.2651(18)
Mo1-S3	2.2736(18)	Mo1-Cu3	2.6772(11)	Mo1-Cu2	2.6972(11)
Mo1-Cu1	2.7103(11)	Cu1-N6	1.953(7)	Cu1-N3A	2.134(6)
Cu1-S3	2.2945(19)	Cu1-S1	2.314(2)	Cu2-N4	2.038(6)
Cu2-N1	2.053(6)	Cu2-S2	2.276(2)	Cu2-S3	2.2831(19)
Cu3-N2	2.070(6)	Cu3-N5A	2.075(6)	Cu3-S2	2.2719(19)
Cu3-S1	2.277(2)				
O1-Mo1-S2	111.0(2)	O1-Mo1-S1	111.4(2)	S2-Mo1-S1	108.03(7)
O1-Mo1-S3	110.1(2)	S2-Mo1-S3	107.62(7)	S1-Mo1-S3	108.43(7)
Cu3-Mo1-Cu2	87.90(3)	Cu3-Mo1-Cu1	90.01(3)	Cu2-Mo1-Cu1	88.78(3)
N6-Cu1-N3A	105.9(3)	N6-Cu1-S3	118.8(2)	N3A-Cu1-S3	104.30(17)
N6-Cu1-S1	118.8(2)	N3A-Cu1-S1	100.47(18)	S3-Cu1-S1	106.05(7)
N4-Cu2-N1	113.6(3)	N4-Cu2-S2	110.62(19)	N1-Cu2-S2	106.36(18)
N4-Cu2-S3	109.75(19)	N1-Cu2-S3	109.32(18)	S2-Cu2-S3	106.90(7)
N2-Cu3-N5A	99.1(2)	N2-Cu3-S2	105.97(17)	N5A-Cu3-S2	117.1(2)
N2-Cu3-S1	120.13(19)	N5A-Cu3-S1	107.73(19)	S2-Cu3-S1	107.36(7)
Mo1-S1-Cu3	72.23(6)	Mo1-S1-Cu1	72.57(6)	Cu3-S1-Cu1	112.17(8)
Mo1-S2-Cu3	72.34(6)	Mo1-S2-Cu2	72.89(6)	Cu3-S2-Cu2	110.21(8)
Mo1-S3-Cu2	72.59(6)	Mo1-S3-Cu1	72.78(6)	Cu2-S3-Cu1	111.46(8)

Table S4. Selected bond lengths (Å) and angles (deg) for compound **5**

Mo1-O1	1.749(16)	Mo1-S2	2.263(5)	Mo1-S1	2.268(5)
Mo1-S3	2.276(6)	Mo1-Cu2	2.664(3)	Mo1-Cu1	2.670(3)
Mo1-Cu3	2.697(3)	Mo2-O2	1.767(18)	Mo2-S5	2.243(7)
Mo2-S6	2.261(5)	Mo2-S4	2.274(5)	Mo2-Cu5	2.666(3)
Mo2-Cu6	2.686(3)	Mo2-Cu4	2.695(3)	Cu1-N1	2.06(3)
Cu1-N5A	2.11(2)	Cu1-S1	2.230(6)	Cu1-S2	2.266(7)
Cu2-N7B	2.012(15)	Cu2-N9A	2.066(19)	Cu2-S3	2.259(5)
Cu2-S1	2.270(6)	Cu3-N10	1.965(18)	Cu3-N3C	2.121(15)
Cu3-S3	2.286(5)	Cu3-S2	2.302(6)	Cu4-N11	1.96(3)
Cu4-N2	2.086(17)	Cu4-S5	2.266(6)	Cu4-S4	2.280(6)
Cu5-N6	2.047(18)	Cu5-N4	2.069(19)	Cu5-S4	2.240(6)
Cu5-S6	2.277(6)	Cu6-N8	2.017(14)	Cu6-S6	2.275(6)
Cu6-S5	2.277(5)	Cu6-S7	2.353(6)	N3-Cu3C	2.121(15)
N5-Cu1A	2.11(2)	N7-Cu2B	2.012(15)	N9-Cu2A	2.066(18)
O1-Mo1-S2	111.0(6)	O1-Mo1-S1	111.3(6)	S2-Mo1-S1	106.9(2)
O1-Mo1-S3	111.5(7)	S2-Mo1-S3	108.1(2)	S1-Mo1-S3	107.7(2)
Cu2-Mo1-Cu1	83.72(10)	Cu2-Mo1-Cu3	86.91(9)	Cu1-Mo1-Cu3	89.83(9)
O2-Mo2-S5	111.4(7)	O2-Mo2-S6	110.8(6)	S5-Mo2-S6	107.9(2)
O2-Mo2-S4	111.6(5)	S5-Mo2-S4	107.5(2)	S6-Mo2-S4	107.5(2)
Cu5-Mo2-Cu6	85.95(10)	Cu5-Mo2-Cu4	88.31(9)	Cu6-Mo2-Cu4	84.95(10)
N1-Cu1-S1	108.7(8)	N1-Cu1-S2	106.0(10)	S1-Cu1-S2	108.1(2)
S3-Cu2-S1	108.2(2)	N10-Cu3-S3	123.1(6)	N10-Cu3-S2	113.1(6)
S3-Cu3-S2	106.5(2)	N11-Cu4-N2	104.6(8)	N11-Cu4-S5	116.7(6)
N2-Cu4-S5	105.4(6)	N11-Cu4-S4	119.9(7)	N2-Cu4-S4	101.6(5)
S5-Cu4-S4	106.5(2)	N6-Cu5-N4	101.3(7)	N6-Cu5-S4	115.8(6)
N4-Cu5-S4	113.9(5)	N6-Cu5-S6	108.8(5)	N4-Cu5-S6	108.5(6)
S4-Cu5-S6	108.1(2)	N8-Cu6-S6	114.0(5)	N8-Cu6-S5	116.1(5)
S6-Cu6-S5	106.3(2)	N8-Cu6-S7	98.2(5)	S6-Cu6-S7	112.9(2)
S5-Cu6-S7	109.3(2)	Cu1-S1-Mo1	72.81(18)	Cu1-S1-Cu2	104.5(2)
Mo1-S1-Cu2	71.88(16)	Mo1-S2-Cu1	72.24(17)	Mo1-S2-Cu3	72.43(18)
Cu1-S2-Cu3	112.1(3)	Cu2-S3-Mo1	71.95(16)	Cu2-S3-Cu3	108.4(2)
Mo1-S3-Cu3	72.49(17)	Cu5-S4-Mo2	72.38(17)	Cu5-S4-Cu4	111.4(3)
Mo2-S4-Cu4	72.56(17)	Mo2-S5-Cu4	73.41(19)	Mo2-S5-Cu6	72.93(19)
Cu4-S5-Cu6	106.2(2)	Mo2-S6-Cu6	72.63(17)	Mo2-S6-Cu5	71.94(17)
Cu6-S6-Cu5	106.6(2)				