Supporting information

Flexible and Porous Layered Structures Based Mixed-Linker Metal-Organic Frameworks for Gas Sorption Studies

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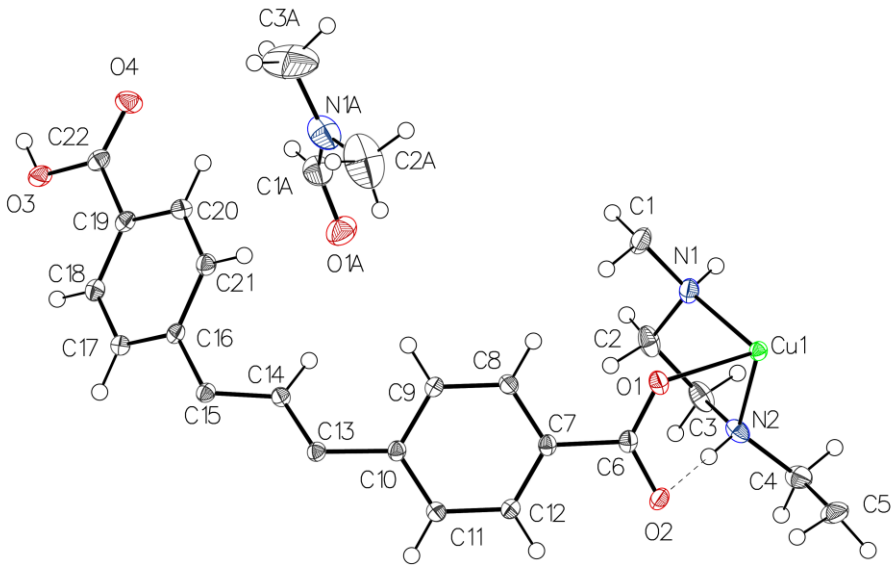


Figure S1. Thermal atomic displacement ellipsoid plot of the asymmetric unit of as-synthesized IRH-**4**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

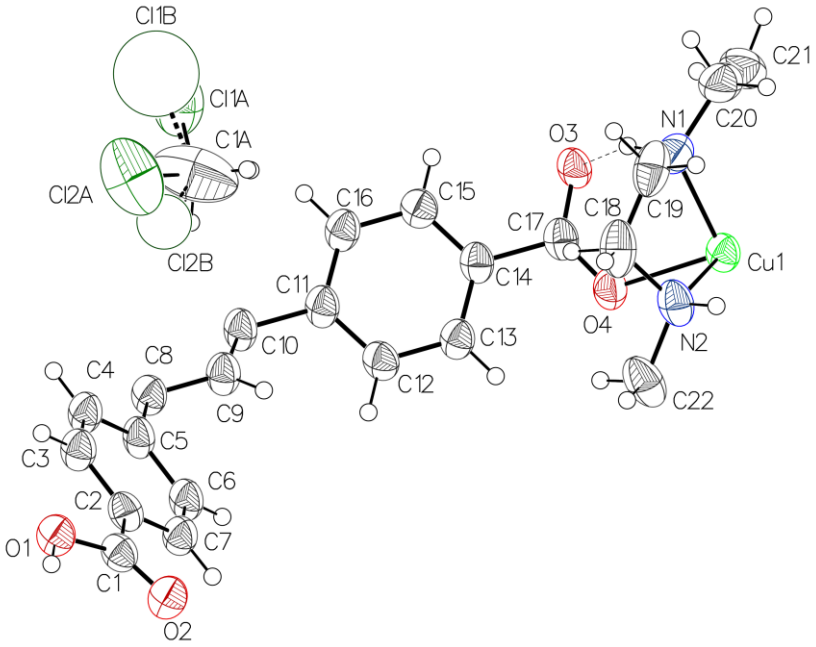


Figure S2. Thermal atomic displacement ellipsoid plot of the asymmetric unit of solvent exchanged IRH-**4**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

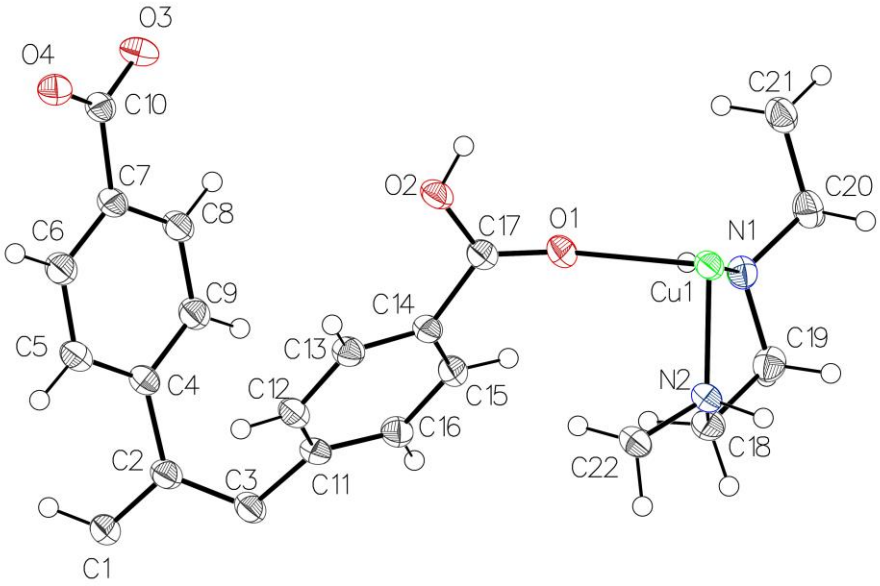
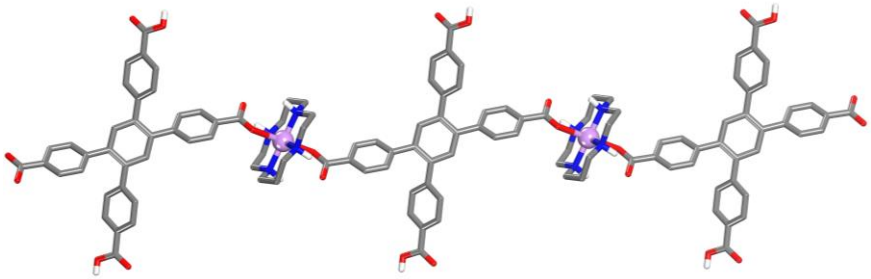


Figure S3. Thermal atomic displacement ellipsoid plot of the asymmetric unit of activated IRH-**4**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.



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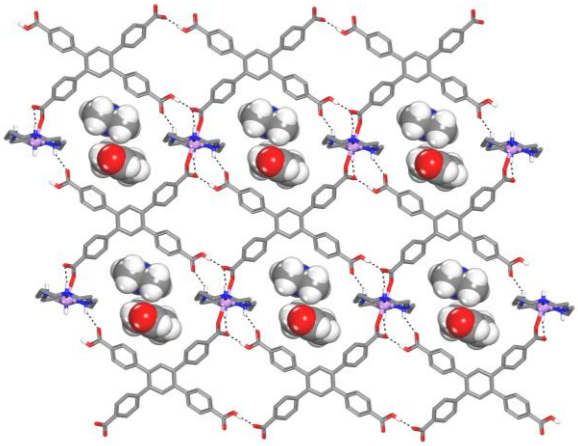

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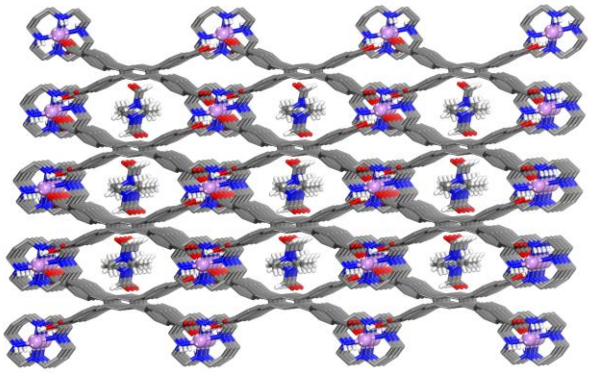

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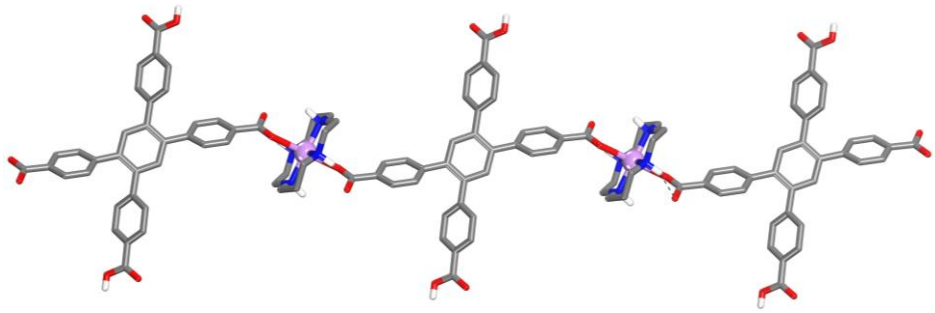
Figure S4. Crystal structure of as-synthesized IRH-**4**. Unless stated otherwise carbon atoms are shown in green, oxygen atoms in red, nitrogen atoms in blue and copper atoms in green. (a) 1D polymeric chain. (b) 2D frameworks with N,N'-dimethylformamide (DMF). (c) View showing the 1D microchannels filled with DMF molecules. Hydrogen

atoms attached to carbon atom have been omitted for clarity excepted for DMF molecules. Hydrogen bonds are shown as dotted lines.



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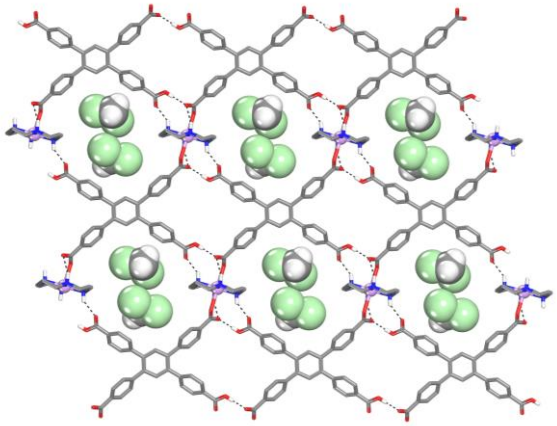

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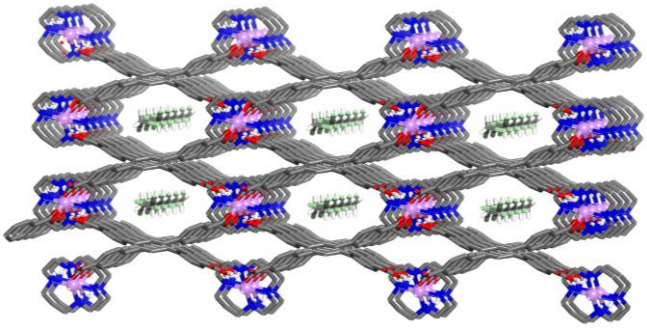

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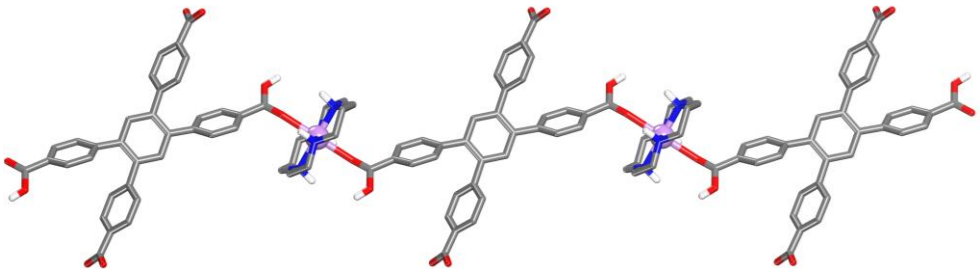
Figure S5. Crystal structure of solvent exchanged IRH-**4**. Unless stated otherwise carbon atoms are shown in green, oxygen atoms in red, nitrogen atoms in blue and copper atoms in violet. (a) 1D polymeric chain. (b) 2D frameworks after solvent exchanged with dichloromethane (DCM). (c) View showing the 1D microchannels filled with DCM

molecules. Hydrogen atoms attached to carbon atom have been omitted for clarity excepted for DCM molecules. Hydrogen bonds are shown as dotted lines.



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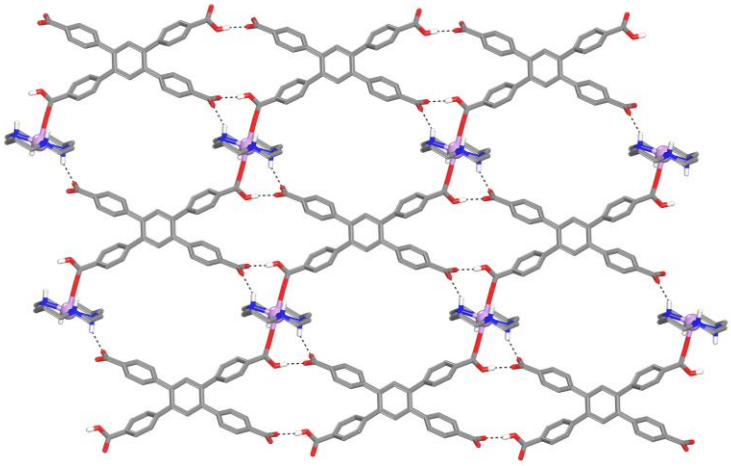

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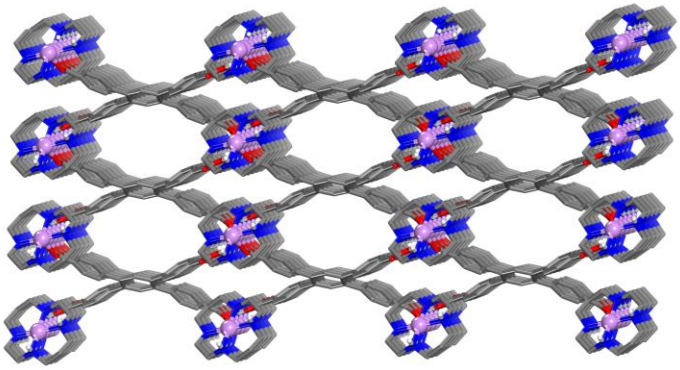

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Figure S6. Crystal structure of activated IRH-**4**. Unless stated otherwise carbon atoms are shown in green, oxygen atoms in red, nitrogen atoms in blue and zinc atoms in green. (a) 1D polymeric chain. (b) 2D frameworks after solvent exchanged with dichloromethane (DCM). (c) View showing the 1D microchannels filled with DCM molecules. Hydrogen

atoms attached to carbon atom have been omitted for clarity excepted for DCM molecules. Hydrogen bonds are shown as dotted lines.

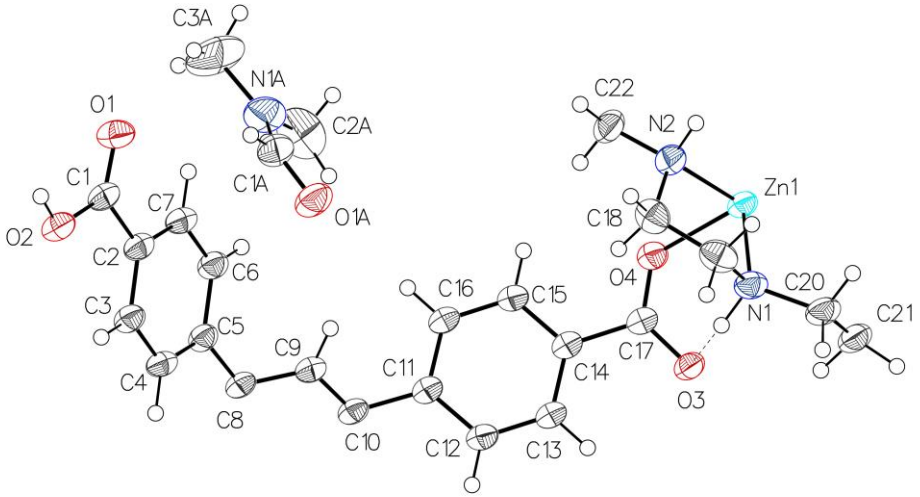


Figure S7. Thermal atomic displacement ellipsoid plot of the asymmetric unit of as-synthesized IRH-**5**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

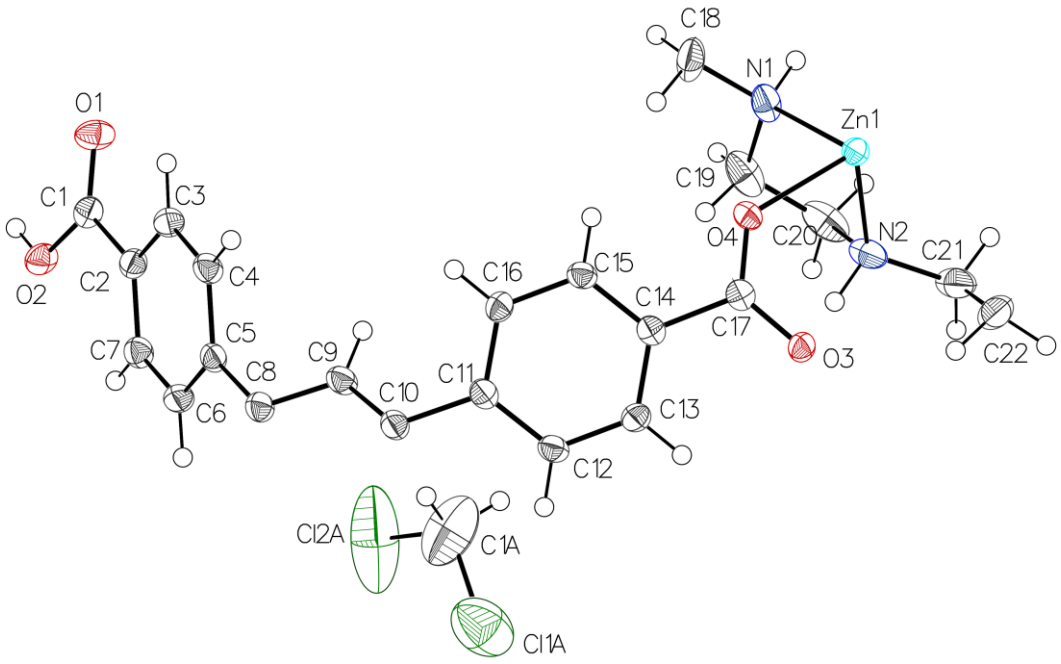


Figure S8. Thermal atomic displacement ellipsoid plot of the asymmetric unit of solvent exchanged IRH-**5**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.

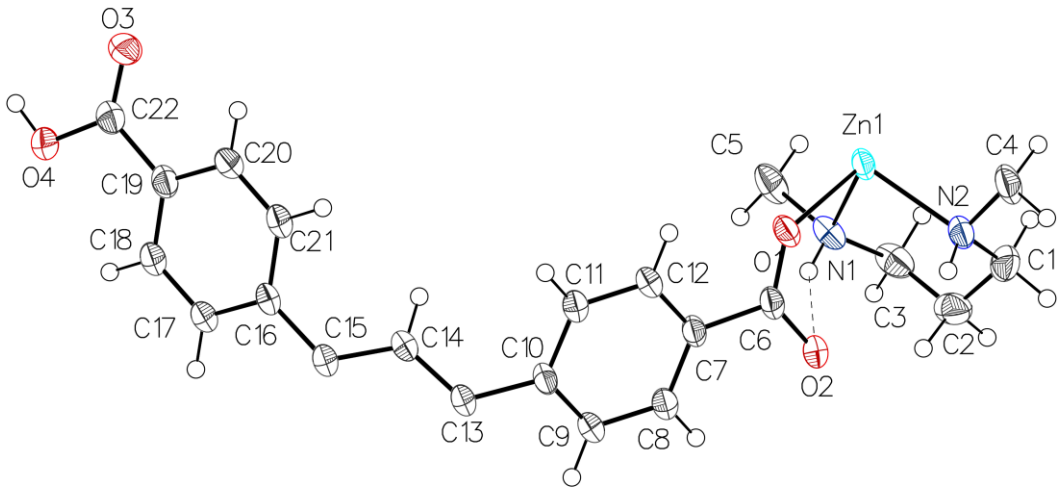
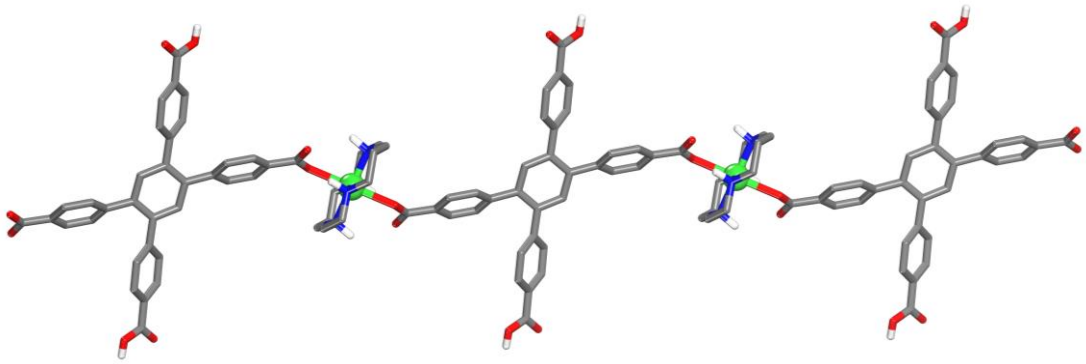


Figure S9. Thermal atomic displacement ellipsoid plot of the asymmetric unit of activated IRH-**5**. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level, and hydrogen atoms are represented by a sphere of arbitrary size.



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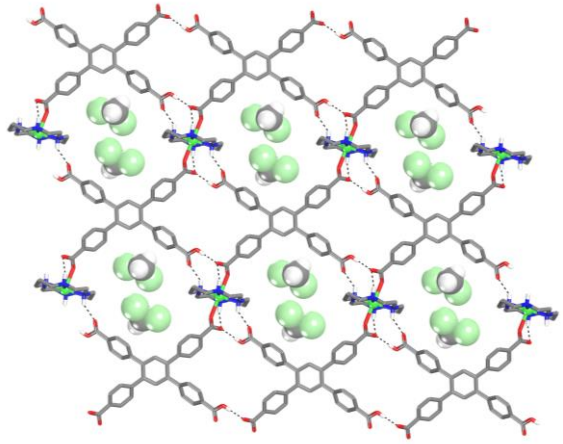

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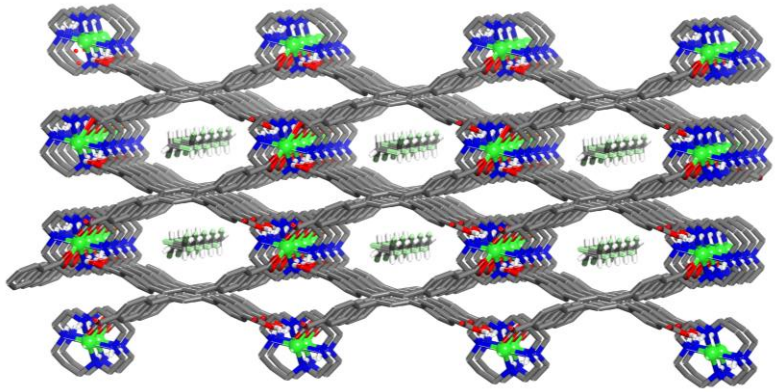

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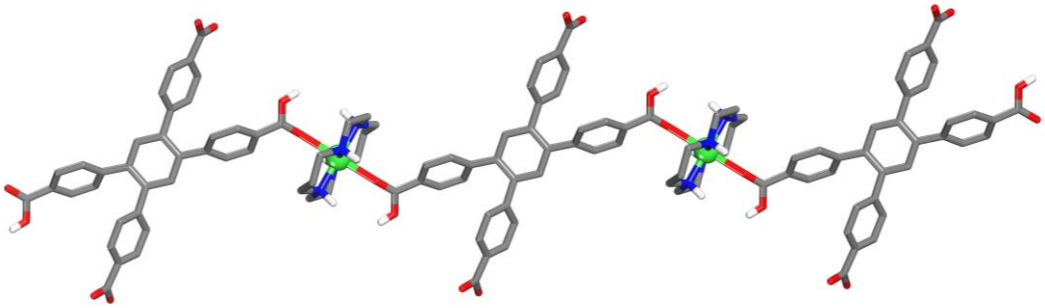
Figure S10. Crystal structure of solvent exchanged IRH-**5**. Unless stated otherwise carbon atoms are shown in green, oxygen atoms in red, nitrogen atoms in blue and zinc atoms in green. (a) 1D polymeric chain. (b) 2D frameworks after solvent exchanged with dichloromethane (DCM). (c) View showing the 1D microchannels filled with DCM molecules. Hydrogen atoms attached to carbon atom have been omitted for clarity excepted for DCM molecules. Hydrogen bond are shown as dotted lines.



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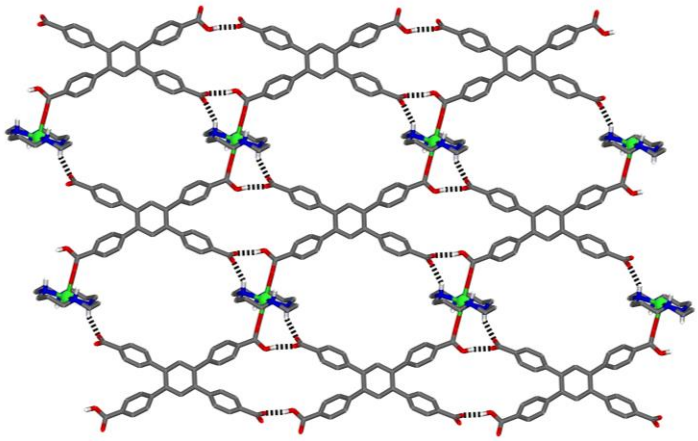

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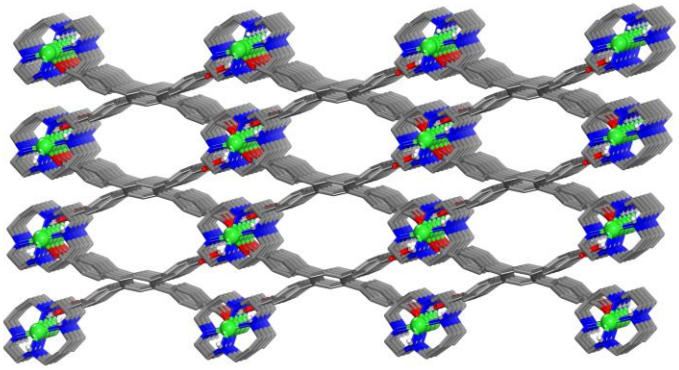

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Figure S11. Crystal structure of activated IRH-**5**. Unless stated otherwise carbon atoms are shown in green, oxygen atoms in red, nitrogen atoms in blue and copper atoms in green. (a) 1D polymeric chain. (b) 2D frameworks. (c) View showing the 1D microchannels. Hydrogen atoms attached to carbon atom have been omitted for clarity excepted for DMF molecules. Hydrogen bond are shown as dotted lines.

Table S1. Crystallographic Data of as-synthesized, solvent exchanged and activated IRH-**4**.

	As-synthesized IRH-**4**	Solvent exchanged IRH-**4**	Activated IRH-**4**
Cell Formula	$C_{50}H_{58}CuN_6O_{10}$	$C_{46}H_{48}Cl_4CuN_4O_8$	$C_{44}H_{44}CuN_4O_8$
Formula	$Cu(C_{10}N_4H_{20})(C_{34}H_{22}O_8)$ • $2(C_3H_7NO)$	$Cu(C_{10}N_4H_{20})$ $(C_{34}H_{22}O_8)$ • $2(CH_2Cl_2)$	$Cu(C_{10}N_4H_{20})$ $(C_{34}H_{22}O_8)$
Mr	966.57	990.25	820.39
CCDC Code	2045791	2045790	2045789
Crystal System	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	8.0072(3)	8.0935(8)	7.5883(4)
b /Å	10.2227(3)	10.0336(9)	9.4777(5)
c /Å	15.6669(5)	15.6580(12)	16.8623(10)
α /°	95.110(1)	96.030(5)	81.516(2)
β /°	98.690(1)	98.336(5)	80.992(2)
γ /°	109.430(1)	109.647(5)	72.616(2)
V /Å^3	1182.07(7)	1168.61(18)	1136.51(11)
Z	1	1	1
T (K)	100	100	100
Meas.	30946	8138	23181
Ind.	4334	4163	4214
R_{int}	0.0205	0.0330	0.0259
R_σ	0.0114	0.0486	0.0173
Param.	318	296	263
R_1 / I > 2σ(I)	0.0333	0.0611	0.0333
wR_2 / I> 2 σ(I)	0.0834	0.1685	0.0923
R_1 (all data)	0.0344	0.0731	0.0343
wR_2 (all data)	0.0875	0.1792	0.0938
GOF on F^2	1.064	1.056	1.047

Table S2. Crystallographic Data of as-synthesized, solvent exchanged and activated IRHs-**5**.

	As-synthesized IRH-**5**	Solvent exchanged IRH-**5**	Activated IRH-**5**
Cell Formula	$C_{50}H_{58}N_6O_{10}Zn$	$C_{46}H_{48}Cl_4N_4O_8Zn$	$C_{44}H_{44}N_4O_8Zn$
Formula	$Zn(C_{10}N_4H_{20})$ $(C_{34}H_{22}O_8)$ • $2(C_3H_7NO)$	$Zn(C_{10}N_4H_{20})$ $(C_{34}H_{22}O_8)$ • $2(CH_2Cl_2)$	$Zn(C_{10}N_4H_{20})$ $(C_{34}H_{22}O_8)$
Mr	968.42	992.10	822.23
CCDC Code	2045788	2045786	2045787
Crystal System	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	8.1297(17)	8.2596(5)	8.2782(5)
b /Å	10.1868(19)	9.9708(6)	10.0936(6)
c /Å	15.619(3)	15.6266(9)	15.6910(9)
α /°	94.957(13)	96.284(4)	95.712(2)
β /°	99.778(13)	99.271(4)	99.174(2)
γ /°	110.086(13)	110.636(4)	111.463(2)
V /Å^3	1182.4(4)	1169.21(12)	1186.65(12)
Z	1	1	1
T (K)	100	100	100
Meas.	12885	10190	23541
Ind.	4166	4192	4379
R_{int}	0.0669	0.0328	0.0415
R_σ	0.0463	0.0402	0.0281
Param.	307	287	271
R_1 / I > 2 σ(I)	0.0512	0.0534	0.0370
wR_2 / I> 2 σ(I)	0.1387	0.1368	0.1017
R_1 (all data)	0.0569	0.0581	0.0382
wR_2 (all data)	0.1445	0.1405	0.1027
GOF on F^2	1.053	1.065	1.050

Table S3. Bond lengths (Å) observed in as-synthesized IRH-**4**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Cu1-O1	2.4175(11)	N1-C1	1.479(2)	C8-C9	1.386(2)	C16-C21	1.401(2)
Cu1-O1[1]	2.4175(11)	N1-C2	1.476(2)	C9-C10	1.401(2)	C17-C18	1.389(2)
Cu1-N1	2.0153(13)	N2-C3	1.477(2)	C10-C11	1.399(2)	C18-C19	1.389(2)
Cu1-N1[1]	2.0153(14)	N2-C4	1.478(2)	C10-C13	1.492(2)	C19-C20	1.393(2)
Cu1-N2	2.0275(13)	C1-C5[1]	1.520(3)	C11 -C12	1.386(2)	C19-C22	1.494(2)
Cu1-N2[1]	2.0275(13)	C2-C3	1.509(3)	C13-C14	1.393(2)	C20-C21	1.388(2)
O1-C6	1.245(2)	C4-C5	1.519(3)	C13-C15[2]	1.411(2)	O1A-C1A	1.215(2)
O2-C6	1.2780(19)	C6-C7	1.511(2)	C14-C15	1.398(2)	N1A-C1A	1.332(3)
O3-C22	1.315(2)	C7-C8	1.394(2)	C15-C16	1.491(2)	N1A-C2 A	1.445(4)
O4-C22	1.216(2)	C7-C12	1.395(2)	C16-C17	1.397(2)	N1A-C3A	1.463(3)

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

Table S4. Bond angles (°) observed in as-synthesized IRH-**4**.

Type of bond	Angle/°	Type of bond	Angle/°
O1[1]-Cu1-O1	180.0	C12-C7-C6	120.19(13)
N1[1]-Cu1-O1	91.99(5)	C9-C8-C7	120.64(14)
N1-Cu1-O1	88.01(5)	C8-C9-C10	120.36(14)
N1-Cu1-O1[1]	91.99(5)	C9-C10-C13	119.86(13)
N11-Cu1-O1[1]	88.01(5)	C11-C10-C9	118.77(14)
N1-Cu1-N1[1]	180.0	C11-C10-C13	121.28(14)
N11-Cu1-N2	93.74(6)	C12-C11-C10	120.71(14)
N11-Cu1-N2[1]	86.26(6)	C11-C12-C7	120.31(14)
N1-Cu1-N2[1]	93.74(6)	C14-C13-C10	117.07(14)
N1-Cu1-N2	86.26(6)	C14-C13-C15[2]	118.41(14)
N2-Cu1-O1	93.83(5)	C152-C13-C10	124.47(14)
N2-Cu1-O1[1]	86.17(5)	C13-C14-C15	123.65(15)
N21-Cu1-O1	86.17(5)	C132-C15-C16	124.44(14)
N21-Cu1-O1[1]	93.83(5)	C14-C15-C13[2]	117.94(14)
N2-Cu1-N2[1]	180.0	C14-C15-C16	117.56(14)
C6-O1-Cu1	117.97(10)	C17-C16-C15	121.95(14)
C1-N1-Cu1	118.38(11)	C17-C16-C21	118.42(14)
C2-N1-Cu1	106.48(10)	C21-C16-C15	119.51(14)
C2-N1-C1	112.29(14)	C18-C17-C16	121.03(14)
C3-N2-Cu1	106.18(10)	C17-C18-C19	120.01(15)
C3-N2-C4	112.65(14)	C18-C19-C22	121.62(14)
C4-N2-Cu1	117.31(11)	C20-C19-C18	119.48(14)
N1-C1-C5[1]	111.96(14)	C20-C19-C22	118.89(14)
N1-C2-C3	108.33(14)	C21-C20-C19	120.26(15)
N2-C3-C2	108.22(13)	C20-C21-C16	120.79(15)
N2-C4-C5	111.80(14)	O3-C22 C19	113.18(14)
C4-C5-C1[1]	114.30(15)	O4-C22-O3	124.77(15)
O1-C6-O2	124.95(14)	O4-C22-C19	122.05(15)
O1-C6-C7	118.33(14)	C1A-N1A-C2A	120.5(2)
O2-C6-C7	116.62(14)	C1A-N1A-C3A	120.7(2)
C8-C7-C6	120.58(14)	C2A-N1A-C3A	118.8(2)
C8-C7-C12	119.20(14)	O1A-C1A-N1A	126.5(2)

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

Table S5. Hydrogen bond geometry (Å, °) of as-synthesized IRH-**4**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1-H1A-O1	0.99	2.64	3.206(2)	116.7
C4-H4A-O1[1]	0.99	2.54	3.142(2)	119.1
N1-H1-O4[2]	0.84(2)	2.15(2)	2.8838(18)	144.5(19)
N2-H2-O2	0.85(2)	2.09(2)	2.9019(18)	158.5(19)
O3-H3-O2[3]	0.85(3)	1.69(3)	2.5365(15)	175(3)

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

Table S6. Bond lengths (Å) observed in solvent exchanged IRH-**4**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Cu1 -O4	2.414(2)	N1-C19	1.480(5)	C5-C6	1.397(5)	C13-C14	1.388(5)
Cu1 -O4[1]	2.414(2)	N1-C20	1.474(5)	C5-C8	1.487(4)	C14-C15	1.385(5)
Cu1-N2	2.016(3)	C20-C21	1.521(6)	C6-C7	1.380(5)	C14-C17	1.519(4)
Cu1-N2[1]	2.016(3)	N2-C18	1.470(5)	C8-C9	1.393(4)	C15-C16	1.388(5)
Cu1-N1	2.024(3)	N2-C22	1.484(5)	C8-C10[2]	1.411(5)	C18-C19	1.509(6)
Cu1-N1[1]	2.024(3)	C1-C2	1.486(4)	C9-C10	1.391(5)	C1A-Cl2A	1.777(8)
O1-C1	1.322(4)	C2-C7	1.395(5)	C10-C11	1.492(4)	C21-C22[1]	1.505(7)
O3-C17	1.276(4)	C2-C3	1.389(5)	C11-C12	1.394(5)	C1A-Cl1A	1.650(8)
O4-C17	1.238(4)	C3-C4	1.385(5)	C11-C16	1.391(5)	C1A-Cl1B	1.90(2)
O2-C1	1.208(4)	C4-C5	1.402(5)	C12-C13	1.384(5)	C1A-Cl2B	1.678(11)

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

Table S7. Bond angles (°) observed in solvent exchanged IRH-**4**.

Type of bond	Angle/°	Type of bond	Angle/°
O4[1]-Cu1-O4	180.0	C6-C5-C4	118.2(3)
N1-Cu1-O4	93.10(10)	C6-C5-C8	120.8(3)
N1[1]-Cu1-O4[1]	93.10(10)	C7-C6-C5	120.9(3)
N1[1]-Cu1-O4	86.90(10)	C6-C7-C2	120.7(3)
N1-Cu1-O4[1]	86.90(10)	C9-C8-C5	117.8(3)
N1[1]-Cu1-N1	180.0	C9-C8-C10[2]	118.1(3)
N2-Cu1-O4[1]	91.67(10)	C102-C8-C5	123.9(3)
N2-Cu1-O4	88.33(10)	C10-C9-C8	123.7(3)
N2[1]-Cu1-O4[1]	88.33(10)	C82-C10-C11	124.4(3)
N2[1]-Cu1-O4	91.67(10)	C9-C10-C8[2]	118.2(3)
N2-Cu1-N1[1]	93.57(13)	C9-C10-C11	117.3(3)
N2[1]-Cu1-N1[1]	86.43(13)	C12-C11-C10	120.4(3)
N2[1]-Cu1-N1	93.57(13)	C16-C11-C10	121.2(3)
N2-Cu1-N1	86.43(13)	C16-C11-C12	118.3(3)
N2-Cu1-N2[1]	180.0(2)	C13-C12-C11	120.9(3)
C17-O4-Cu1	118.5(2)	C12-C13-C14	120.4(3)
C19-N1-Cu1	105.7(2)	C13-C14-C17	119.9(3)
C20-N1-Cu1	117.4(2)	C15-C14-C13	119.2(3)
C20-N1-C19	112.1(3)	C15-C14-C17	120.9(3)
C18-N2-Cu1	106.2(2)	C14-C15-C16	120.4(3)
C18-N2-C22	112.2(3)	C15-C16-C11	120.8(3)
C22-N2-Cu1	117.9(3)	O3-C17-C14	116.2(3)
O1-C1-C2	112.7(3)	O4-C17--O3	125.6(3)
O2-C1-O1	124.4(3)	O4-C17-C14	118.1(3)
O2-C1-C2	122.8(3)	N2-C18-C19	108.1(3)
C3-C2-C1	121.8(3)	N1-C19--C18	108.2(3)
C3-C2-C7	118.9(3)	N1-C20-C21	110.9(3)
C7-C2-C1	119.3(3)	C221-C21-C20	114.8(3)
C4-C3-C2	120.6(3)	N2-C22-C21[1]	112.2(3)
C3-C4-C5	120.7(3)	Cl1A-C1A-Cl2A	114.8(6)
C4-C5-C8	120.8(3)	Cl2B-C1A-Cl1B	119.4(9)

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

Table S8. Hydrogen bond geometry (Å, º) of solvent exchanged IRH-**4**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1-H1-O3	0.82	1.743	2.544	164.919
N1-H1A-O3[1]	0.98	2.094	2.943	143.873
N2-H2-O2	0.98	2.056	2.911	144.575

[1]1-X,1-Y,-Z

Table S9. Bond lengths (Å) observed in Activated IRH-**4**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Cu1-O1[1]	2.4005(10)	O2-C17	1.3012(18)	C1-C3[2]	1.395(2)	C7-C8	1.393(2)
Cu1-O1	2.4005(10)	O3-C10	1.2727(18)	C2-C3	1.408(2)	C7-C10	1.5163(19)
Cu1-N1	2.0204(12)	O4-C10	1.2463(18)	C2-C4	1.4930(19)	C8-C9	1.382(2)
Cu1-N1[1]	2.0204(12)	N1-C19	1.4799(18)	C3-C11	1.490(2)	C11-C12	1.395(2)
Cu1-N2	2.0168(12)	N1-C20	1.4821(18)	C4-C5	1.395(2)	C11-C16	1.398(2)
Cu1-N2[2]	2.0169(12)	N2-C18	1.4837(19)	C4-C9	1.398(2)	C12-C13	1.380(2)
Cu1-N2[1]	1.2279(17)	N2-C22	1.4816(18)	C5-C6	1.387(2)	C13-C14	1.395(2)
O1-C17	1.3012(18)	C1-C2	1.393(2)	C6-C7	1.396(2)	C14-C15	1.396(2)
C14-C17	1.4956(19)	C15-C16	1.390(2)	C18-C19	1.511(2)	C20-C21	1.519(2)
C21-C22[1]	1.521(2)						

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

Table S10. Bond angles (º) observed in activated IRH-**4**.

Type of bond	Angle/˚	Type of bond	Angle/˚
O11-Cu1-O1	180.0	C5-C4-C9	118.32(13)
N1-Cu1-O11	95.75(4)	C9-C4-C2	120.25(13)
N1-Cu1-O1	84.25(4)	C6-C5-C4	120.77(13)
N11-Cu1-O11	84.25(4)	C5-C6-C7	120.65(13)
N11-Cu1-O1	95.75(4)	C6-C7-C10	121.05(13)
N11-Cu1-N1	180.0	C8-C7-C6	118.53(13)
N21-Cu1-O1	86.45(4)	C8-C7-C10	120.38(13)
N21-Cu1-O11	93.55(4)	C9-C8-C7	120.83(13)
N2-Cu1-O1	93.55(4)	C8-C9-C4	120.80(13)
N2-Cu1-O11	86.45(4)	O3-C10-C7	115.13(12)
N21-Cu1-N1	94.16(5)	O4-C10-O3	126.11(13)
N2-Cu1-N11	94.16(5)	O4-C10--C7	118.77(13)
N2-Cu1-N1	85.84(5)	C12-C11-C3	119.88(13)
N21-Cu1-N11	85.84(5)	C12-C11-C16	118.74(13)
N2-Cu1-N21	180.00(7)	C16-C11-C3	121.29(13)
C17-O1-Cu1	149.43(10)	C13-C12-C11	121.01(13)
C19-N1-Cu1	107.21(9)	C12-C13-C14	119.87(13)
C19-N1-C20	111.21(11)	C13-C14-C15	119.81(13)
C20-N1-Cu1	117.67(9)	C13-C14-C17	121.11(13)
C18-N2-Cu1	107.46(9)	C15-C14-C17	118.86(12)
C22-N2-Cu1	117.13(9)	C16-C15-C14	119.77(13)
C22-N2-C18	111.94(11)	C15-C16-C11	120.56(13)
C2-C1-C32	122.00(14)	O1-C17-O2	124.92(14)
C1-C2-C3	118.89(13)	O1-C17-C14	121.55(13)
C1-C2-C4	120.30(13)	O2-C17-C14	113.48(12)
C3-C2-C4	120.75(13)	N2-C18-C19	108.42(11)
C12-C3-C2	119.11(13)	N1-C19-C18	108.23(11)
C12-C3-C11	120.71(13)	N1-C20-C21	111.68(12)
C2-C3-C11	120.14(13)	C20-C21-C22[1]	115.28(12)
C5-C4-C2	121.40(13)	N2-C22-C21[1]	111.12(12)

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

Table S11. Hydrogen bond geometry (Å, º) of activated IRH-**4**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1-H1-O4[1]	1.00	2.15	3.0626(16)	151.2
N2-H2A-O42	1.00	2.12	3.0183(15)	148.4
C19-H19A-O3[2]	0.99	2.58	3.3969(18)	139.6
O2-H2-O3[3]	0.85(3)	1.63(3)	2.4769(14)	168(3)

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

Table S12. Bond lengths (Å) observed in as-synthesized IRH-**5**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Zn1-O4[1]	2.2046(15)	N1-C20	1.481(3)	C8-C9	1.403(3)	C18-C19	1.522(4)
Zn1-O4	2.2046(15)	N2-C18	1.472(3)	C8-C10[2]	1.411(3)	C20-C21	1.522(4)
Zn1-N1	2.1080(18)	N2-C22	1.478(3)	C9-C10	1.392(3)	C21-C22[1]	1.530(4)
Zn1-N1[1]	2.1080(18)	C1-C2	1.491(3)	C10-C11	1.485(3)	O1A-C1A	1.210(3)
Zn1-N2[1]	2.0876(18)	C2-C3	1.393(3)	C11-C12	1.402(3)	N1A-C1A	1.333(4)
Zn1-N2	2.0876(18)	C2-C7	1.394(3)	C11-C16	1.402(3)	N1A-C2A	1.440(5)
O1-C1	1.213(3)	C3-C4	1.393(3)	C12-C13	1.382(3)	N1A-C3A	1.471(5)
O2-C1	1.321(3)	C4-C5	1.396(3)	C13-C14	1.398(3)		
O3-C17	1.257(3)	C5-C6	1.401(3)	C14-C15	1.394(3)		
O4-C17	1.259(3)	C5-C8	1.486(3)	C14-C17	1.509(3)		
N1-C19	1.471(3)	C6-C7	1.386(3)	C15-C16	1.386(3)		

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

Table S13. Bond angles (°) observed in as-synthesized IRH-**5**.

Type of bond	Angle/°	Type of bond	Angle/°
O4-Zn1-O41	180.0	C6-C5-C8	119.07(19)
N1[1]-Zn1-O41	91.95(7)	C7-C6-C5	120.21(19)
N1[1]-Zn1-O4	88.05(7)	C6-C7-C2	120.65(19)
N1-Zn1-O41	88.05(7)	C9-C8-C5	117.84(19)
N1-Zn1-O4	91.95(7)	C9-C8-C10[2]	117.98(19)
N1[1]-Zn1-N1	180.0	C10[2]-C8-C5	124.10(19)
N2-Zn1-O41	93.20(7)	C10-C9-C8	123.91(19)
N2-Zn1-O4	86.80(7)	C8[2]-C10-C11	124.70(18)
N2[1]-Zn1-O4	93.20(7)	C9-C10-C8[2]	118.11(19)
N2[1]-Zn1-O41	86.80(7)	C9-C10-C11	117.12(19)
N2[1]-Zn1-N1[1]	85.37(8)	C12-C11-C10	121.54(18)
N2-Zn1-N1[1]	94.63(8)	C12-C11-C16	118.39(19)
N2[1]-Zn1-N1	94.63(8)	C16-C11-C10	119.96(18)
N2-Zn1-N1	85.37(8)	C13-C12-C11	120.78(19)
N21-Zn1-N2	180.0	C12-C13-C14	120.48(19)
C17-O4-Zn1	123.51(13)	C13-C14-C17	119.81(18)
C19-N1-Zn1	104.68(14)	C15-C14-C13	119.15(19)
C19-N1-C20	114.39(19)	C15-C14-C17	120.98(18)
C20-N1-Zn1	114.00(15)	C16-C15-C14	120.39(19)
C18-N2-Zn1	105.08(14)	C15-C16-C11	120.80(19)
C18-N2-C22	113.58(19)	O3-C17-O4	124.56(19)
C22-N2-Zn1	115.99(15)	O3-C17-C14	118.37(18)
O1-C1-O2	124.57(19)	O4-C17-C14	116.98(17)
O1-C1-C2	122.0(2)	N2-C18-C19	109.46(18)
O2-C1-C2	113.47(18)	N1-C19-C18	109.24(19)
C3-C2-C1	121.49(19)	N1-C20-C21	112.08(19)
C3-C2-C7	119.55(19)	C20-C21-C22[1]	116.37(19)
C7-C2-C1	118.94(19)	N2-C22-C21[1]	111.78(19)
C2-C3-C4	119.84(19)	C1A-N1A-C2A	120.5(3)
C3-C4-C5	120.80(19)	C1A-N1A-C3A	120.3(3)
C4-C5-C6	118.94(19)	C2A-N1A-C3A	119.2(3)
C4-C5-C8	121.87(19)	O1A-C1A-N1A	126.6(3)

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

Table S14. Hydrogen bond geometry (Å, º) of as-synthesized IRH-**5**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2-H2-O3[1]	0.84	1.72	2.556(2)	175.3
N1-H1-O3	1.00	2.17	2.967(2)	135.3
N2-H2A-O1[2]	1.00	2.04	2.899(3)	142.7

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

Table S15. Bond lengths (Å) observed in solvent exchanged IRH-**5**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Zn1-O1	2.2039(11)	N1-C3	1.475(2)	C8-C9	1.389(2)	C16-C21	1.397(2)
Zn1-O1[1]	2.2039(11)	N1-C5	1.477(2)	C9-C10	1.395(2)	C17-C18	1.384(2)
Zn1-N1	2.1117(15)	N2-C1	1.477(2)	C10-C11	1.396(2)	C18-C19	1.389(2)
Zn1-N1[1]	2.1117(15)	N2-C4	1.475(2)	C10-C13	1.490(2)	C19-C20	1.398(2)
Zn1-N2	2.0853(14)	C1-C2	1.526(3)	C11-C12	1.389(2)	C19-C22	1.491(2)
Zn1-N2[1]	2.0854(14)	C2-C3	1.525(3)	C13-C14	1.395(2)	C20-C21	1.380(2)
O1-C6	1.256(2)	C4-C5[1]	1.516(3)	C13-C15[2]	1.407(2)		
O2-C6	1.260(2)	C6-C7	1.513(2)	C14-C15	1.397(2)		
O3-C22	1.211(2)	C7-C8	1.388(2)	C15-C16	1.488(2)		
O4-C22	1.328(2)	C7-C12	1.392(2)	C16-C17	1.400(2)		

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

Table S16. Bond angles (º) observed in solvent exchanged IRH-**5**.

Type of bond	Angle/˚	Type of bond	Angle/˚
O1[1]-Zn1-O1	180.00(4)	C8-C7-C6	120.65(14)
N1-Zn1-O11	88.45(5)	C8-C7-C12	119.28(14)
N11-Zn1-O1	88.45(5)	C12-C7-C6	120.01(15)
N11-Zn1-O11	91.55(5)	C7-C8-C9	120.57(15)
N1-Zn1-O1	91.55(5)	C8-C9-C10	120.60(15)
N11-Zn1-N1	180.0	C9-C10-C11	118.47(14)
N21-Zn1-O1	86.83(5)	C9-C10-C13	121.38(15)
N21-Zn1-O11	93.17(5)	C11-C10-C13	120.04(15)
N2-Zn1-O1	93.17(5)	C12-C11-C10	120.97(15)
N2-Zn1-O11	86.83(5)	C11-C12-C7	120.09(15)
N21-Zn1-N1	85.39(6)	C14-C13-C10	117.66(15)
N2-Zn1-N11	85.39(6)	C14-C13-C152	118.17(15)
N21-Zn1-N11	94.62(6)	C152-C13-C10	124.10(15)
N2-Zn1-N1	94.61(6)	C13-C14-C15	123.45(16)
N2-Zn1-N21	180.0	C132-C15-C16	123.60(14)
C6-O1-Zn1	124.72(10)	C14-C15-C132	118.37(15)
C3-N1-Zn1	114.39(11)	C14-C15-C16	117.95(15)
C3-N1-C5	114.56(15)	C17-C16-C15	121.21(15)
C5-N1-Zn1	104.50(11)	C21-C16-C15	120.38(15)
C1-N2-Zn1	116.03(12)	C21-C16-C17	118.32(15)
C4-N2-Zn1	105.30(11)	C18-C17-C16	120.82(16)
C4-N2-C1	114.17(14)	C17-C18-C19	120.49(15)
N2-C1-C2	112.56(14)	C18-C19-C20	119.06(15)
C3-C2-C1	116.52(16)	C18-C19-C22	122.31(15)
N1-C3-C2	111.63(15)	C20-C19-C22	118.63(15)
N2-C4-C51	109.39(14)	C21-C20-C19	120.42(16)
N1-C5-C41	109.57(15)	C20-C21-C16	120.88(15)
O1-C6-O2	124.93(14)	O3-C22-O4	124.29(15)
O1-C6-C7	116.94(14)	O3-C22-C19	122.63(15)
O2-C6-C7	118.00(14)	O4-C22-C19	113.07(14)

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

Table S17. Hydrogen bond geometry (Å, º) of solvent exchanged IRH-**5**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1-H1B-O1[1]	0.99	2.60	3.116(2)	112.7
C2-H2B-O2	0.99	2.59	3.391(2)	138.3
C3-H3A-O1[1]	0.99	2.56	3.117(2)	115.7
N2-H2-O3[2]	0.81(2)	2.23(2)	2.947(2)	148(2)
N1-H1-O2	0.84(2)	2.38(2)	3.0870(19)	143(2)
O4-H4-O2[3]	0.88(3)	1.69(3)	2.5708(16)	175(2)

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

Table S18. Bond lengths (Å) observed in activated IRH-**5**.

Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å	Type of bond	Length/Å
Zn1-O4	2.2061(19)	N1-C18	1.496(4)	C5-C8	1.487(4)	C14-C15	1.394(4)
Zn1-O4[1]	2.2061(19)	N1-C19	1.457(5)	C6-C7	1.384(4)	C14-C17	1.510(4)
Zn1-N1	2.086(2)	N2-C20	1.484(4)	C8-C9	1.393(4)	C15-C16	1.386(4)
Zn1-N1[1]	2.086(2)	N2-C21	1.465(4)	C8-C10[2]	1.412(4)	C18-C22[1]	1.512(6)
Zn1-N2	2.112(2)	C1-C2	1.496(4)	C9-C10	1.398(4)	C19-C20	1.517(5)
Zn1-N2[1]	2.112(2)	C2-C3	1.388(4)	C10-C11	1.488(4)	C21-C22	1.525(6)
O1-C1	1.216(3)	C2-C7	1.400(4)	C11-C12	1.395(4)	Cl1A-C1A	1.721(6)
O2-C1	1.318(3)	C3-C4	1.383(4)	C11-C16	1.399(4)	Cl2A-C1A	1.746(6)
O3-C17	1.259(3)	C4-C5	1.404(4)	C12-C13	1.387(4)		
O4-C17	1.257(3)	C5-C6	1.395(4)	C13-C14	1.393(4)		

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

Table S19. Bond angles (°) observed in activated IRH-**5**.

Type of bond	Angle/˚	Type of bond	Angle/˚
O41-Zn1-O4	180.0	C6-C5-C4	118.5(3)
N11-Zn1-O41	86.91(9)	C6-C5-C8	120.7(3)
N1-Zn1-O4	86.91(8)	C7-C6-C5	121.1(3)
N1-Zn1-O41	93.09(9)	C6-C7-C2	119.9(3)
N11-Zn1-O4	93.09(9)	C9-C8-C5	117.6(2)
N1-Zn1-N11	180.0	C9-C8-C10[2]	118.7(3)
N11-Zn1-N2	94.48(11)	C10[2]-C8-C5	123.5(2)
N11-Zn1-N21	85.52(11)	C8-C9-C10	123.4(3)
N1-Zn1-N21	94.48(11)	C8[2]-C10-C11	124.3(3)
N1-Zn1-N2	85.52(11)	C9-C10-C8[2]	117.9(3)
N2-Zn1-O4	91.16(9)	C9-C10-C11	117.5(2)
N2-Zn1-O41	88.84(9)	C12-C11-C10	121.4(3)
N21-Zn1-O41	91.16(9)	C12-C11-C16	118.5(3)
N21-Zn1-O4	88.84(9)	C16-C11-C10	119.8(3)
N2-Zn1-N21	180.00(15)	C13-C12-C11	120.7(3)
C17-O4-Zn1	124.82(18)	C12-C13-C14	120.4(3)
C18-N1-Zn1	115.5(2)	C13-C14-C15	119.1(2)
C19-N1-Zn1	105.6(2)	C13-C14-C17	120.9(2)
C19-N1-C18	114.3(3)	C15-C14-C17	119.9(2)
C20-N2-Zn1	103.6(2)	C16-C15-C14	120.3(3)
C21-N2-Zn1	114.4(2)	C15-C16-C11	120.8(3)
C21-N2-C20	114.7(3)	O3-C17-C14	118.0(2)
O1-C1-O2	124.6(3)	O4-C17-O3	125.0(2)
O1-C1-C2	122.2(3)	O4-C17-C14	116.9(2)
O2-C1-C2	113.2(2)	N1-C18-C22[1]	113.0(3)
C3-C2-C1	119.4(3)	N1-C19-C20	109.0(3)
C3-C2-C7	119.3(3)	N2-C20-C19	110.2(3)
C7-C2-C1	121.2(3)	N2-C21-C22	111.4(3)
C4-C3-C2	120.7(3)	C18[1]-C22-C21	116.4(3)
C3-C4-C5	120.4(3)	Cl1A-C1A-Cl2A	113.8(4)
C4-C5-C8	120.7(3)		

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

Table S20. Hydrogen bond geometry (Å, º) of activated IRH-**5**.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1-H1B -O11	0.99	2.60	3.116(2)	112.7
C2-H2B-O2	0.99	2.59	3.391(2)	138.3
C3-H3A-O11	0.99	2.56	3.117(2)	115.7
N2-H2-O32	0.81(2)	2.23(2)	2.947(2)	148(2)
N1-H1-O2	0.84(2)	2.38(2)	3.0870(19)	143(2)
O4-H4-O23	0.88(3)	1.69(3)	2.5708(16)	175(2)

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

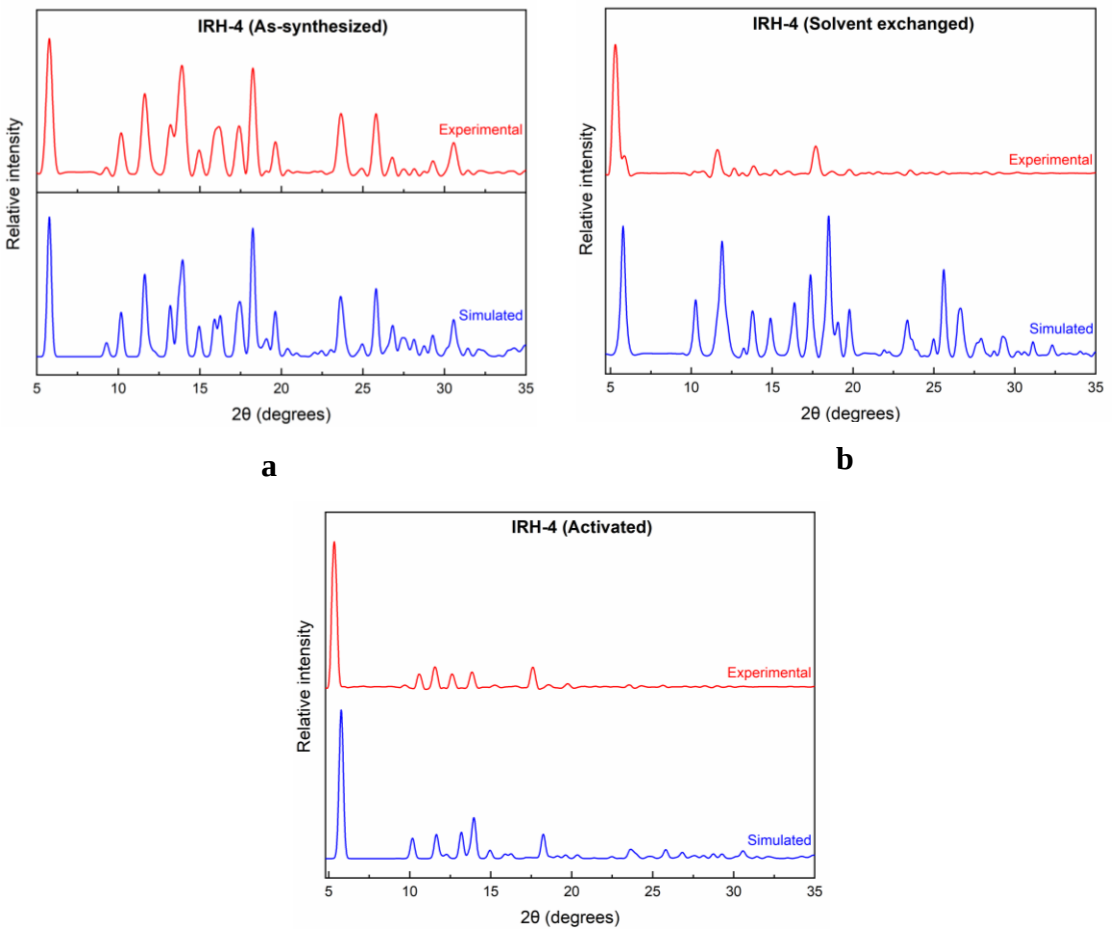

Figure S12. Comparison of the simulated from the SCXRD data and the experimental PXRD patterns. (a)-(c) as-synthesized, solvent exchanged and activated IRHs-**4** respectively.

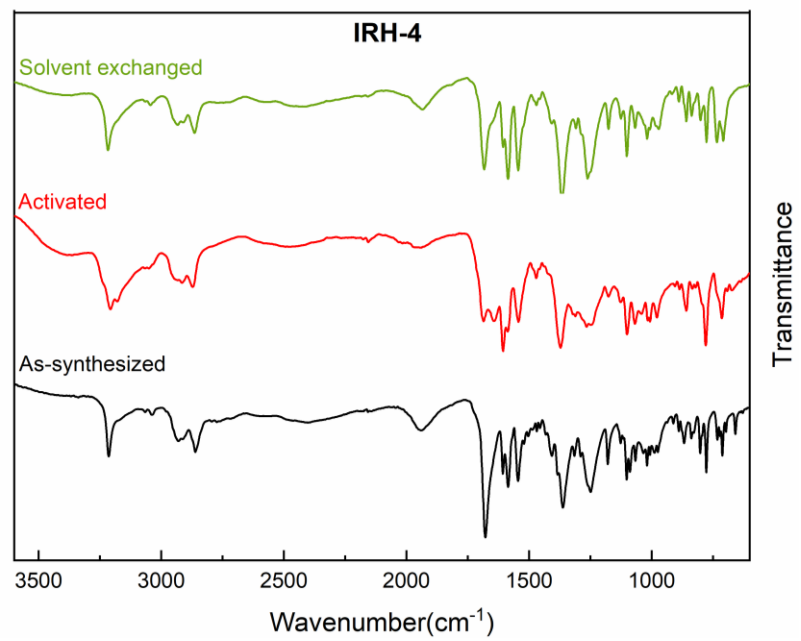

Figure S13. Comparison of FT-IR spectra of as-synthesized, solvent exchanged and activated IRHs-**4**.

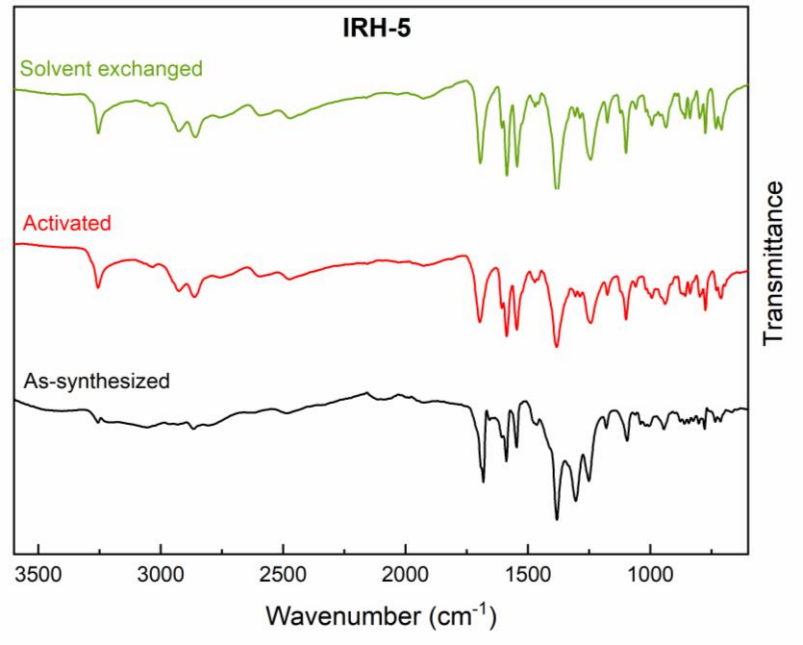

Figure S14. Comparison of FT-IR spectra of as-synthesized, solvent exchanged and activated IRHs-**5**.

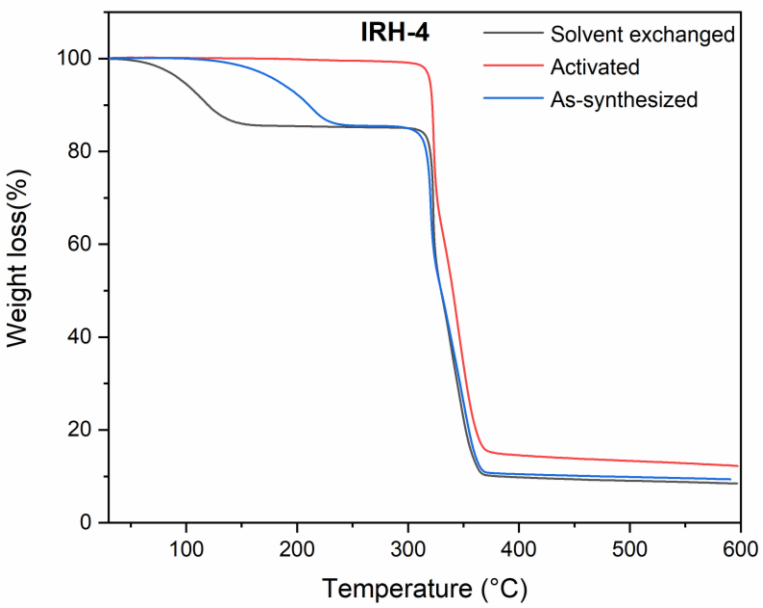

Figure S15. Thermogravimetric analysis curve of as-synthesized, solvent exchange and activated IRHs-**5**.

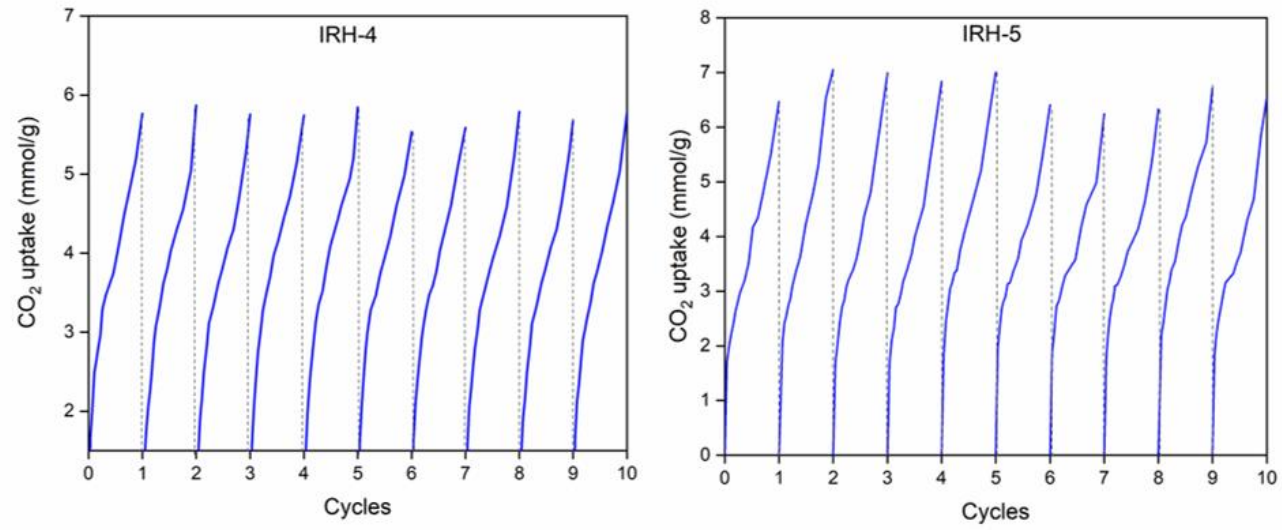

Figure S16. Cycles of adsorption-desorption of CO_2 for IRHs-(**4** and **5**) respectively.

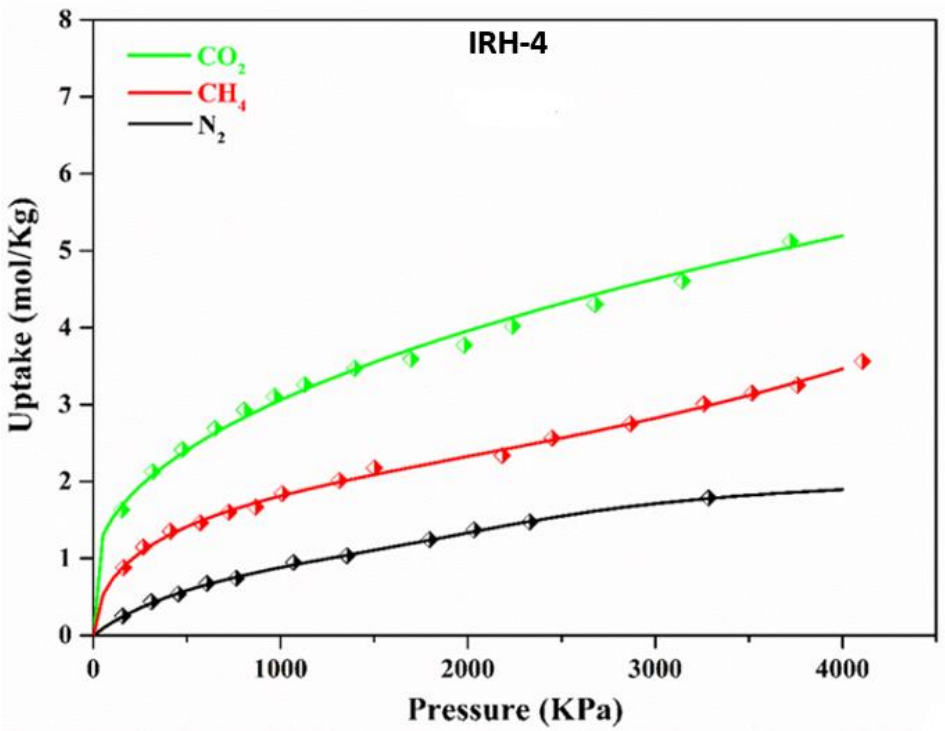

Figure S17 Pure gas isotherms data and dual-site Langmuir–Freundlich (DSLF) fitting models for IRH-**4**. DSLF fitting models are shown in lines, real data in Symbols.

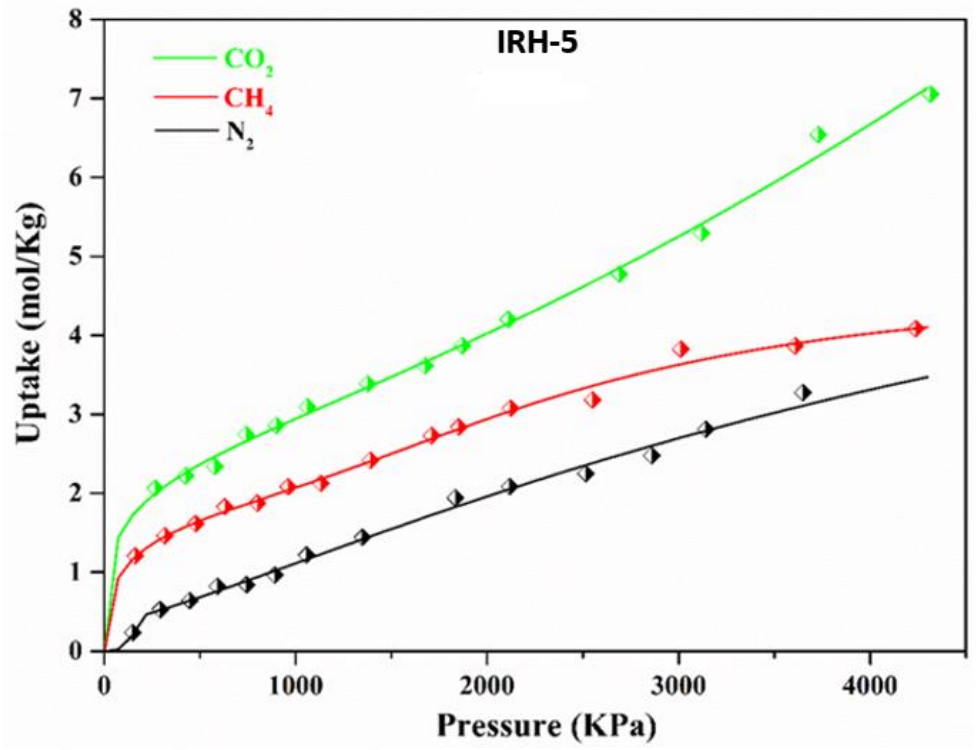

Figure S18. Pure gas isotherms data and dual-site Langmuir–Freundlich (DSLF) fitting models for IRH-**5**. DSLF fitting models are shown in lines, real data in Symbols.

Table S21. Dual-site Langmuir–Freundlich model parameters for real adsorption isotherms fitting of IRHs-(**4** and **5**).

Adsorbent	Adsorbate	q_1	k_1	n_1	q_2	k_2	n_2	R^2
IRH-**4**	CO_2	1.5774	0.0195	$3.2xe^{-5}$	72.3885	0.0001	0.4993	0.99846
	CH_4	23.9304	0.0082	3.0181	4.7535	0.0393	0.52768	0.99969
	N_2	0.4638	0.0426	4.8367	1.9805	0.0783	0.9198	0.99980
IRH-**5**	CO_2	150.1230	0.0028	1.7631	12.7272	0.0009	0.27895	0.99938
	CH_4	4.0377	0.0798	0.4205	1.8489	0.0430	2.8609	0.99924
	N_2	7.2334	0.0188	1.2717	0.3486	0.6637	15.9276	0.99855

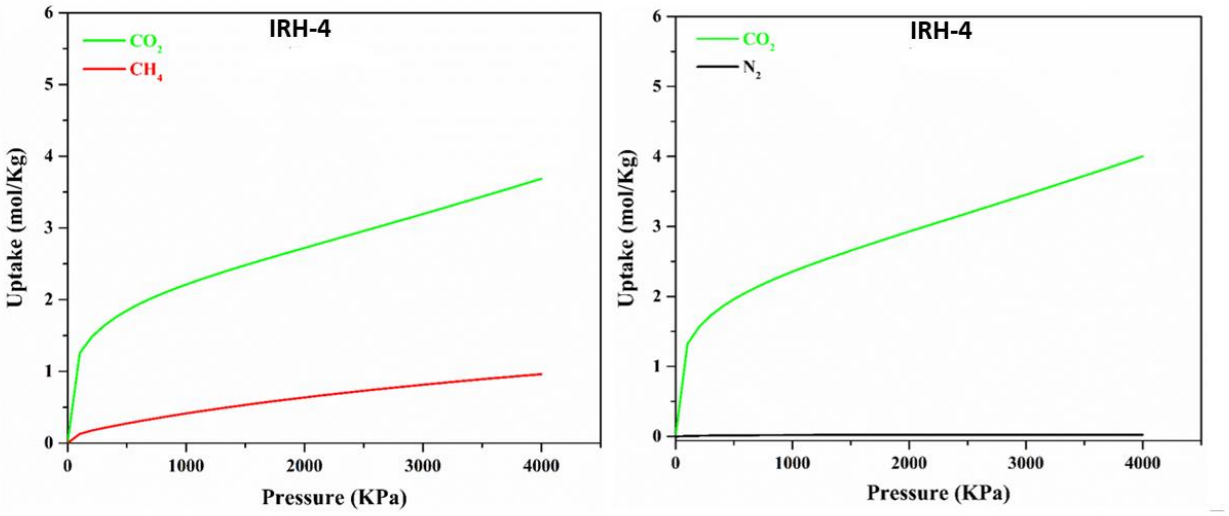

Figure S19. IAST simulated adsorption isotherms for the equimolar (a) CO_2/CH_4 and (b) CO_2/N_2 mixtures at 298 K from IAST for IRH-**4**.

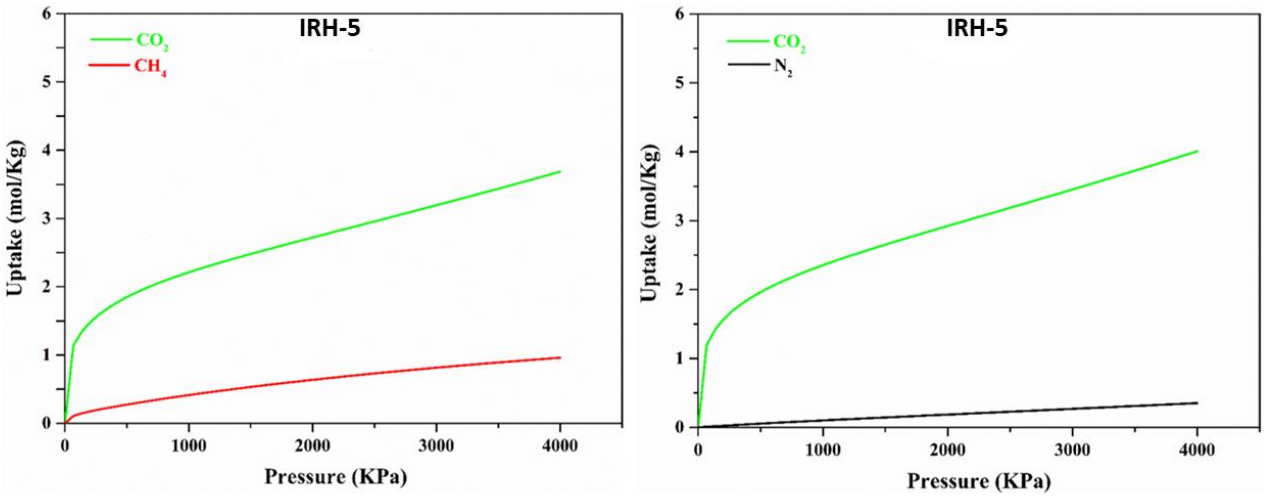

Figure S20. IAST simulated adsorption isotherms for the equimolar CO_2/CH_4 and CO_2/N_2 mixtures at 298 K for IRH-**5**.

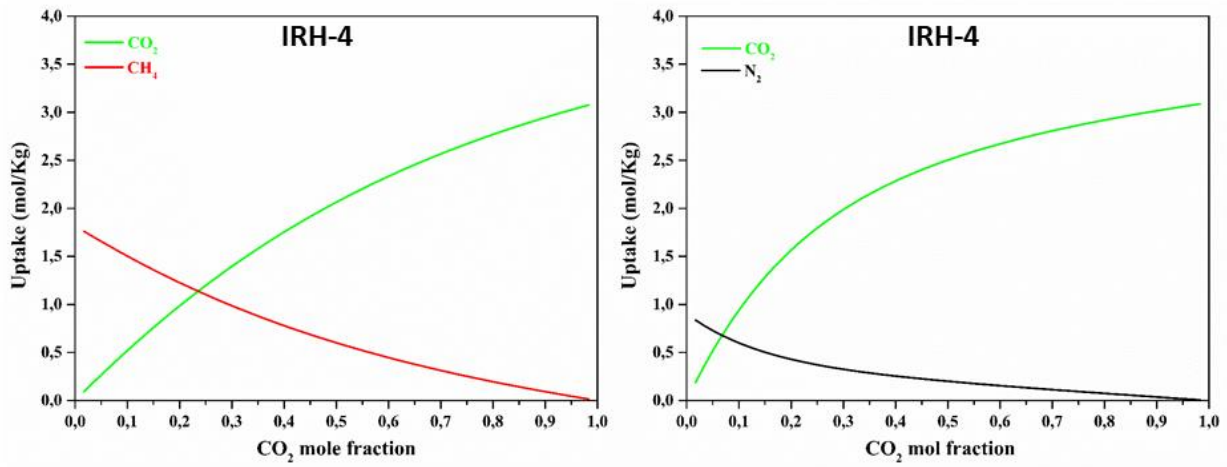

Figure S21. IAST simulated adsorption uptake of CO_2/CH_4 and CO_2/N_2 mixtures in IRH-**4** as a function of CO_2 mole fraction at 298 K and 1000 KPa.

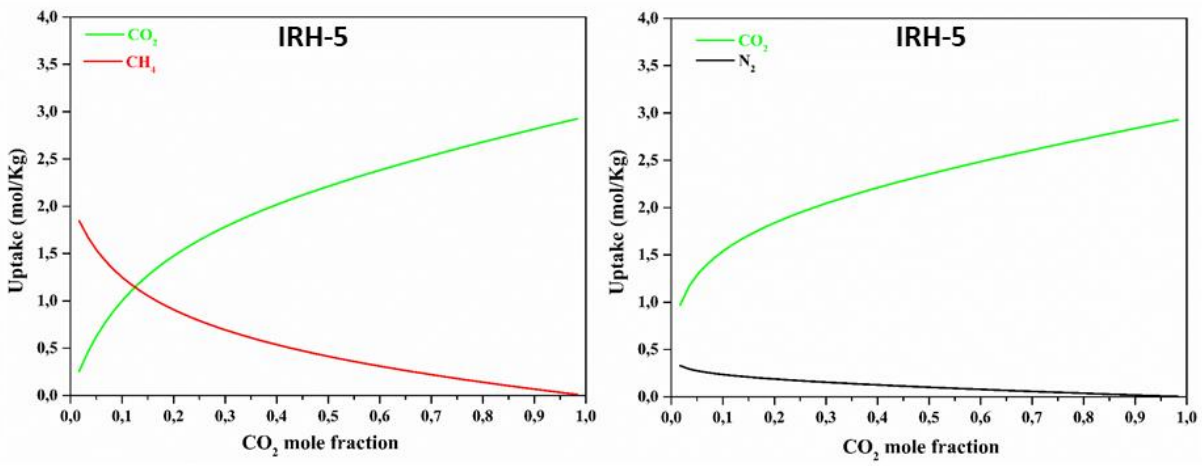

Figure S22. IAST simulated adsorption uptake of CO_2/CH_4 and CO_2/N_2 mixtures in IRH-**5** as a function of CO_2 mole fraction at 298 K and 1000 KPa.

References

1) A. L. Spek, *J. Appl. Crystallogr*., 2003, **36**, 7-13.

2) P. Van Der Sluis and A. L. Spek, *Acta Crystallogr*., 1990, **A46**, 194-201.