Supplementary Information

Breathing-induced high-temperature negative thermal quenching and room-temperature enhancement of luminescence in CuI-NCs based MOFs

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1. Figure

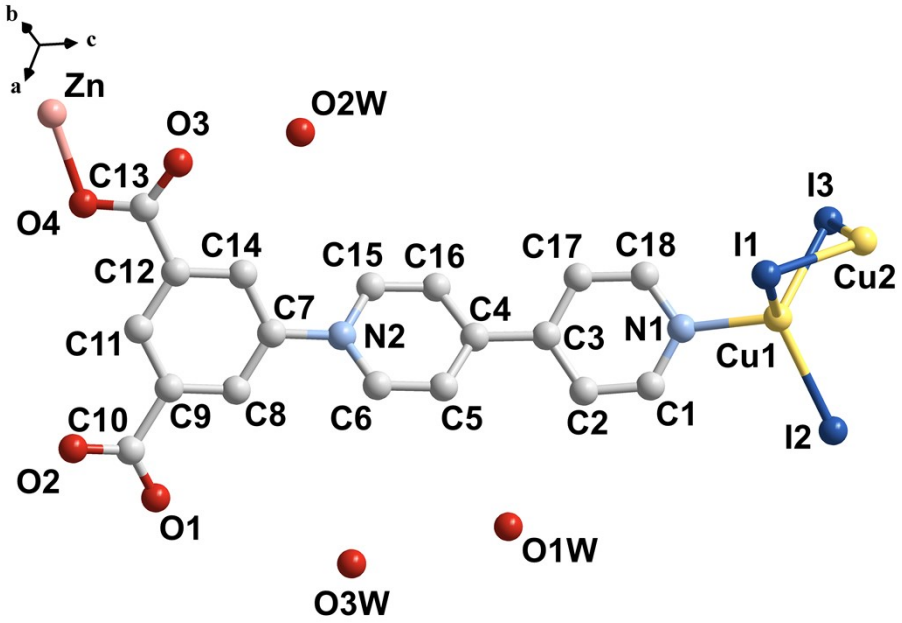

Figure S1. The asymmetric unit of **CuI-MOF**.

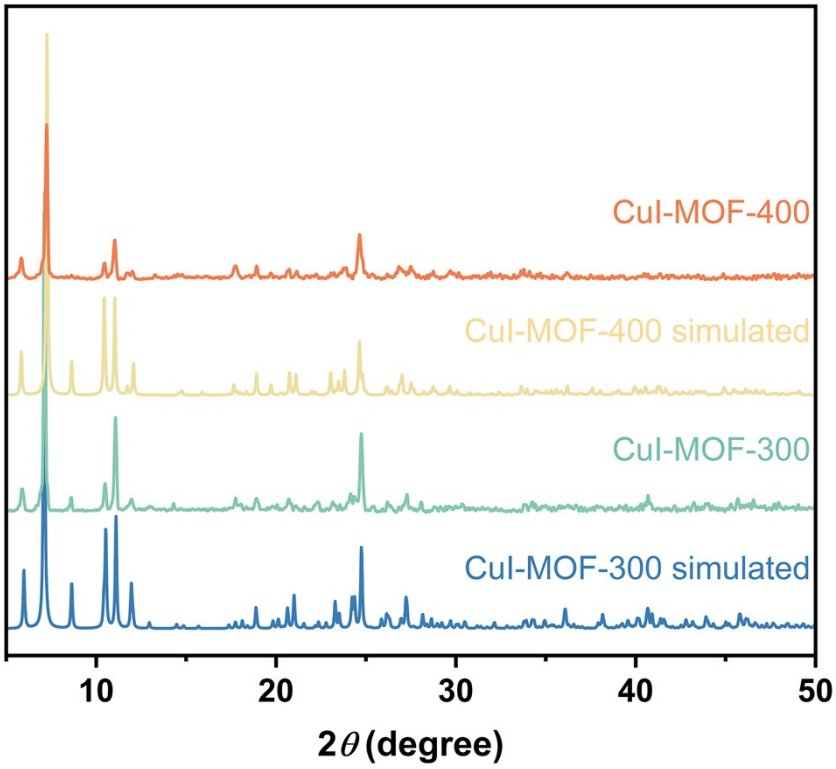

Figure S2. The experimental and simulated PXRD patterns of **CuI-MOF-300** and **CuI-MOF-400**.

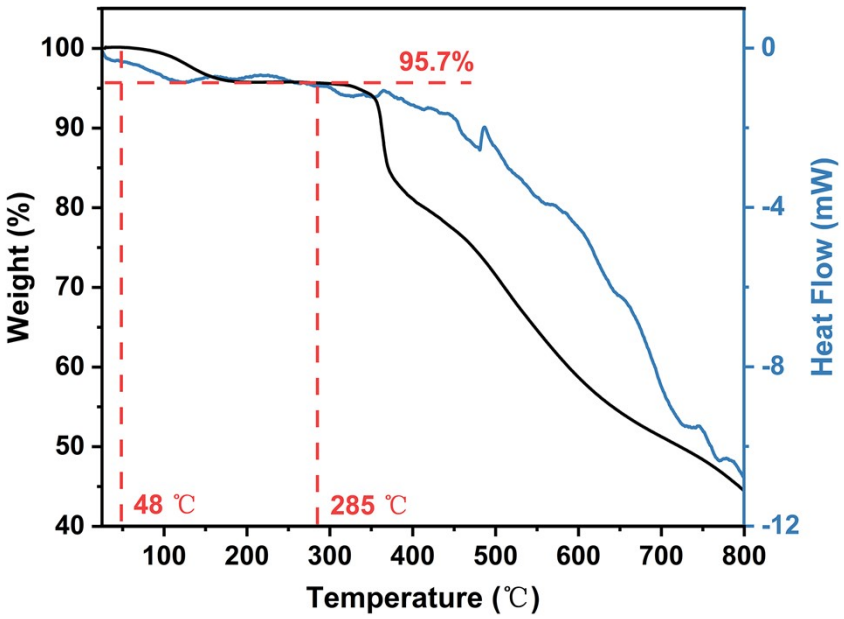

Figure S3. The TGA and DSC curves of **CuI-MOF**.

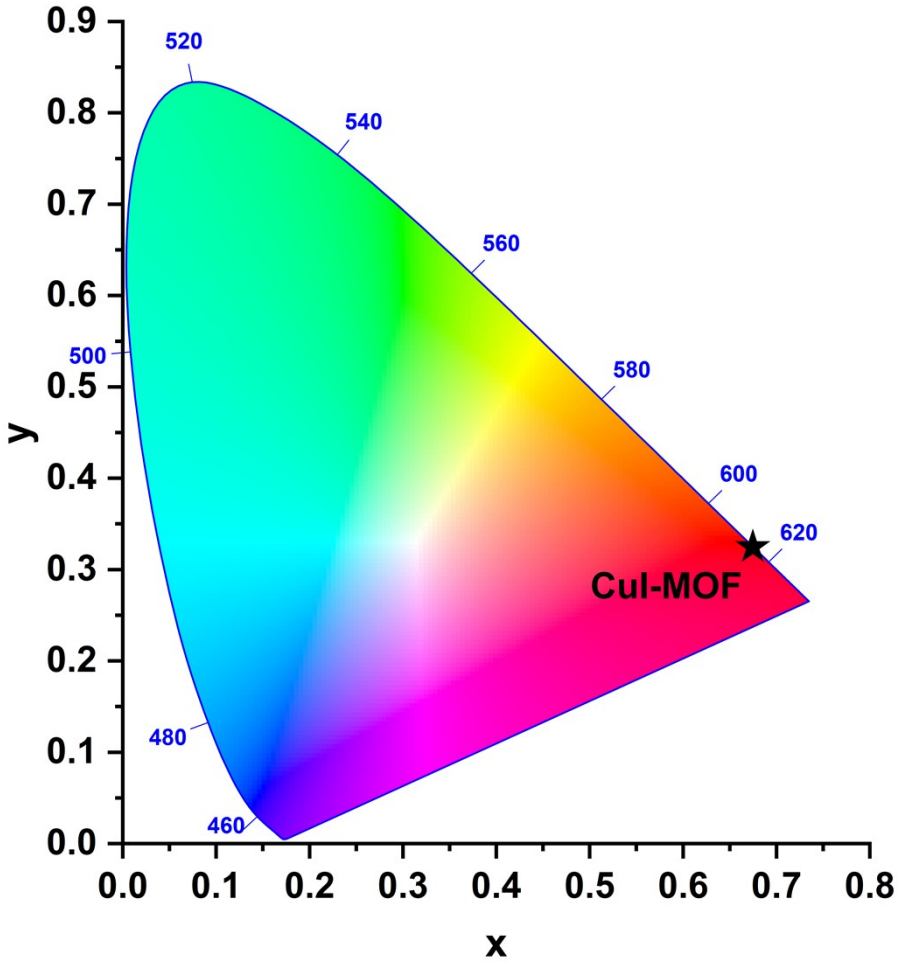

Figure S4. The CIE pattern of **CuI-MOF**.

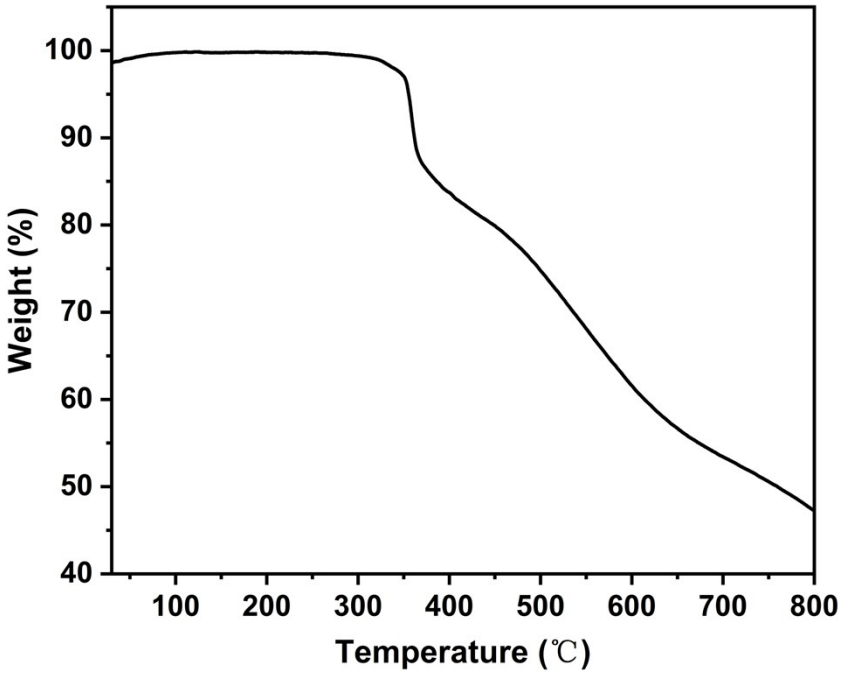

Figure S5. The TGA curve of **CuI-MOF-H**.

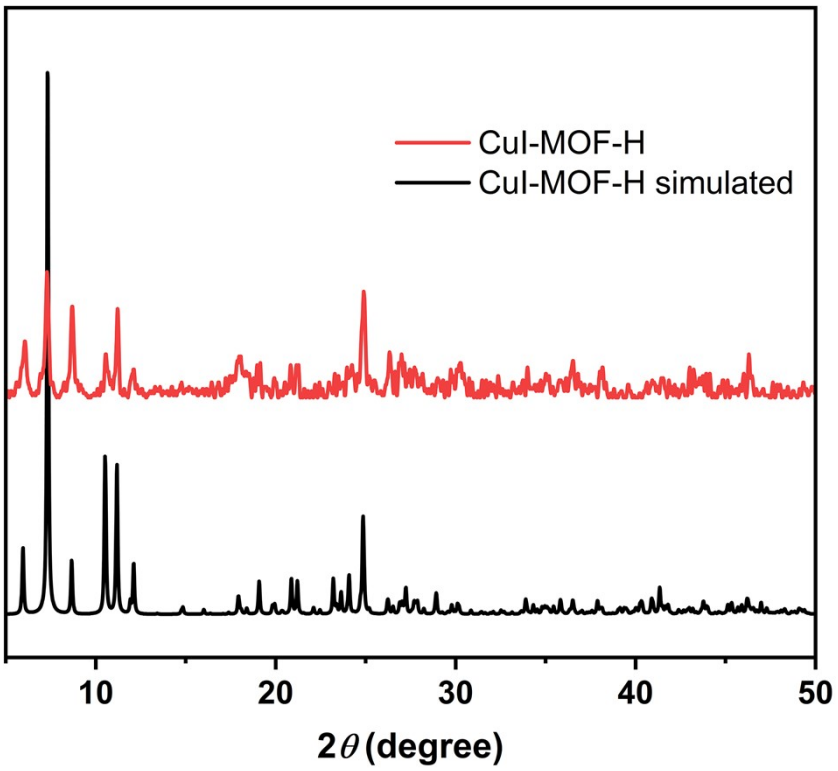

Figure S6. The experimental and simulated PXRD patterns of **CuI-MOF-H**.

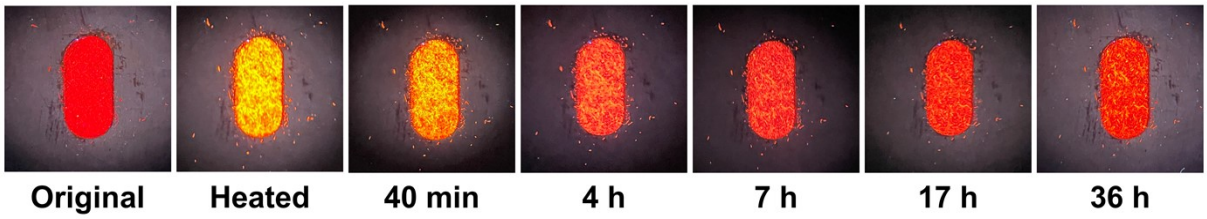

Figure S7. Photos of **CuI-MOF-H** under 365nm UV light at different times (room temperature, 54%RH).

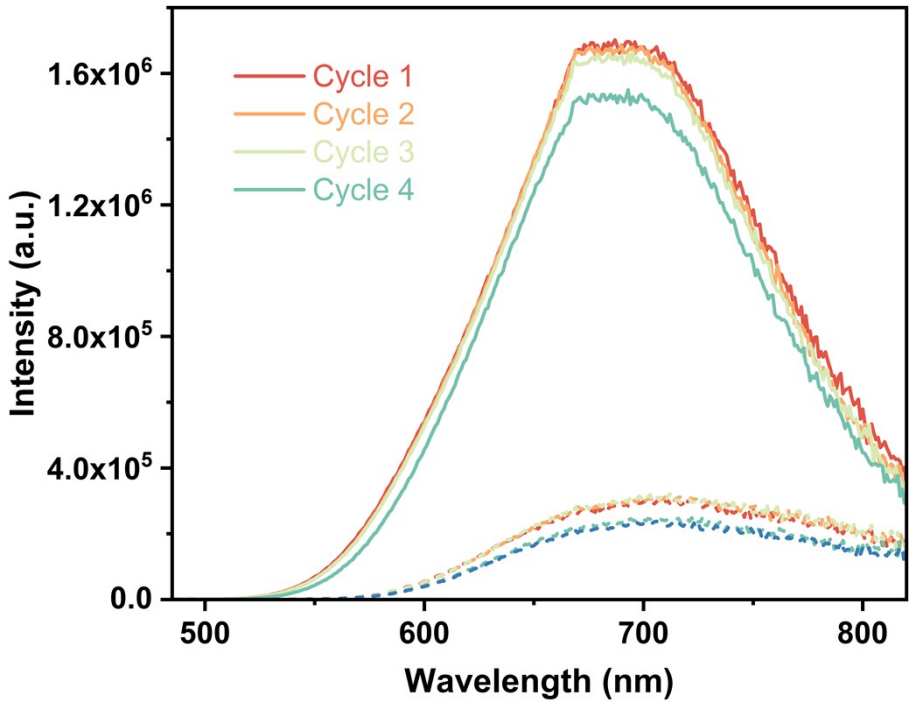

Figure S8. Recycle tests of **CuI-MOF** and **CuI-MOF-H** for four runs.

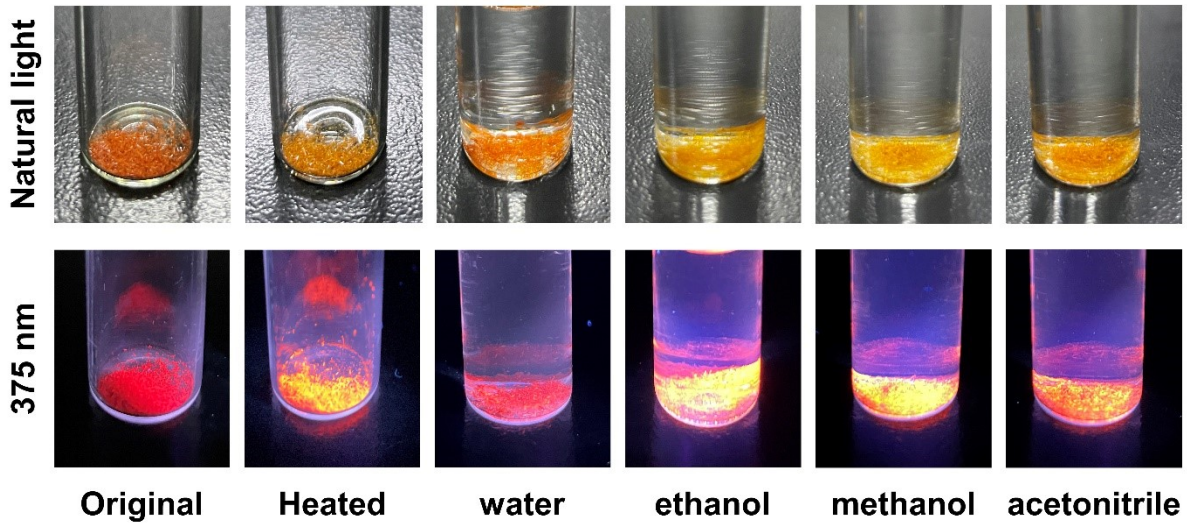

Figure S9. Photos of **CuI-MOF-H** after 3 days of water, anhydrous ethanol, methanol, and acetonitrile immersion.

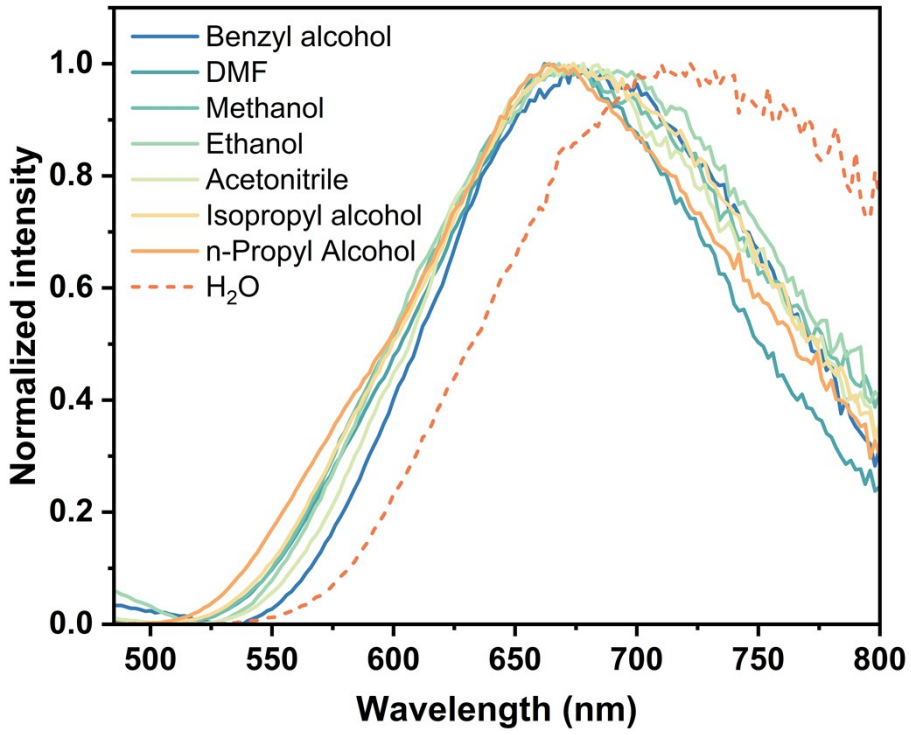

Figure S10. PL spectra of **CuI-MOF-H** after 3 days of water, methanol, ethanol, n-propyl alcohol, isopropyl alcohol, DMF, benzyl alcohol and acetonitrile immersion.

2. Table

Table S1. Crystal data and structural refinements for **CuI-MOF** after heating up from 300 to 400 K, cooling down to 300 K and reabsorbing water molecules.

Compound	**CuI-MOF-300**	**CuI-MOF-320**	**CuI-MOF-340**	**CuI-MOF-360**
Formula		$[Zn(Cu_3I_3)L_2]_n \cdot xnH_2O$		
Temperature/K	300	320	340	360
x	3	3	3	2.5
Fw	1329.31	1329.31	1329.31	1320.30
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*	*C*2/*m*
a /Å	13.7556(6)	13.7532(6)	13.7420(6)	13.6896(7)
b /Å	29.2549(13)	29.3445(12)	29.4318(12)	29.5886(14)
c /Å	10.2849(4)	10.2809(4)	10.2786(4)	10.2888(4)
α /°	90	90	90	90
β /°	98.676(4)	98.656(4)	98.672(4)	98.594(4)
γ /°	90	90	90	90
V /Å^3	4091.5(3)	4101.9(3)	4109.7(3)	4120.7(3)
Z	4	4	4	4
D_c /g.cm^{-3}	2.158	2.153	2.148	2.128
μ /mm^{-1}	4.444	4.433	4.424	4.411
Goodness-of-fit on F^2	1.062	1.034	1.061	1.056
R_1, wR_2 [$I > 2\sigma(I)$]	0.0273, 0.0802	0.0277, 0.0836	0.0298, 0.0890	0.0346, 0.1000
R_1, wR_2 (all data)	0.0316, 0.0831	0.0325, 0.0867	0.0354, 0.0923	0.0422, 0.1051
Compound	**CuI-MOF-380**	**CuI-MOF-400**	**CuI-MOF-H**	**CuI-MOF-300R**
Formula		$[Zn(Cu_3I_3)L_2]_n \cdot xnH_2O$		
Temperature/K	380	400	300	300
x	0.75	0	0	3

Fw	1288.78	1275.26	1275.26	1329.31
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*	*C*2/*m*
a /Å	13.5504(12)	13.3733(9)	13.3417(4)	13.6987(5)
b /Å	29.8545(16)	30.040(2)	29.6641(8)	29.2620(10)
c /Å	10.3019(5)	10.3062(6)	10.3124(3)	10.2928(3)
α /°	90	90	90	90
β /°	98.586(6)	98.857(6)	98.686(2)	98.490(3)
γ /°	90	90	90	90
V /Å^3	4120.8(5)	4090.9(5)	4034.5(2)	4080.7(2)
Z	4	4	4	4
D_c /g.cm^{-3}	2.077	2.071	2.100	2.164
μ /mm^{-1}	4.405	4.435	4.497	4.456
Goodness-of-fit on F^2	1.026	1.059	1.048	1.016
R_1, wR_2 [$I > 2\sigma(I)$]	0.0341, 0.0881	0.0309, 0.0807	0.0245, 0.0640	0.0329, 0.0927
R_1, wR_2 (all data)	0.0467, 0.0941	0.0392, 0.0850	0.0290, 0.0658	0.0400, 0.0983

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(\underline{F}_o)^2]^2\}^{1/2}$.

Table S2. The bond lengths (Å) in ligand at different temperature.

The bond lengths (Å) in **CuI-MOF-300**			
Zn1—O4^4	1.965(3)	C3—C4	1.490(5)
Zn1—O4	1.965(3)	C3—C17	1.381(5)
Zn1—O2^5	1.950(3)	C4—C5	1.385(5)
Zn1—O2^6	1.950(3)	C4—C16	1.389(6)
O3—C13	1.231(6)	C5—C6	1.373(5)
O4—C13	1.248(5)	C7—C8	1.387(5)
O1—C10	1.206(7)	C7—C14	1.381(5)
O2—C10	1.266(5)	C8—C9	1.393(5)

N1—C1	1.356(5)	C9—C10	1.514(6)
N1—C18	1.324(5)	C9—C11	1.381(6)
N2—C6	1.339(5)	C11—C12	1.394(6)
N2—C7	1.458(5)	C12—C13	1.517(6)
N2—C15	1.347(5)	C12—C14	1.384(5)
C1—C2	1.378(6)	C15—C16	1.372(5)
C2—C3	1.377(6)	C17—C18	1.369(5)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]2-X,+Y,-Z; [3]2-X,1-Y,-Z; [4]2-X,+Y,3-Z; [5]3/2-X,3/2-Y,3-Z; [6]1/2+X,3/2-Y,+Z.

The bond lengths (Å) in **CuI-MOF-320**

Zn1—O2[4]	1.951(3)	C3—C4	1.485(5)
Zn1—O2[5]	1.951(3)	C3—C17	1.379(5)
Zn1—O4	1.965(3)	C4—C5	1.388(5)
Zn1—O4[6]	1.965(3)	C4—C16	1.385(5)
O1—C10	1.211(6)	C5—C6	1.376(5)
O2—C10	1.258(5)	C7—C8	1.382(5)
O3—C13	1.234(6)	C7—C14	1.374(5)
O4—C13	1.256(5)	C8—C9	1.400(5)
N1—C1	1.358(5)	C9—C10	1.504(6)
N1—C18	1.311(5)	C9—C11	1.385(6)
N2—C6	1.344(5)	C11—C12	1.389(6)
N2—C7	1.459(4)	C12—C13	1.517(6)
N2—C15	1.347(5)	C12—C14	1.384(5)
C1—C2	1.370(6)	C15—C16	1.375(5)
C2—C3	1.382(6)	C17—C18	1.375(5)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]2-X,+Y,-Z; [3]2-X,1-Y,-Z; [4]3/2-X,3/2-Y,3-Z; [5]1/2+X,3/2-Y,+Z; [6]2-X,+Y,3-Z.

The bond lengths (Å) in **CuI-MOF-340**

Zn1—O2[4]	1.945(3)	C3—C4	1.486(5)
Zn1—O2[5]	1.945(3)	C3—C17	1.381(6)

Zn1—O4[6]	1.963(3)	C4—C5	1.385(6)
Zn1—O4	1.963(3)	C4—C16	1.387(6)
O1—C10	1.195(7)	C5—C6	1.373(6)
O2—C10	1.265(5)	C7—C8	1.384(6)
O3—C13	1.221(6)	C7—C14	1.370(6)
O4—C13	1.255(6)	C8—C9	1.398(5)
N1—C1	1.358(6)	C9—C10	1.508(6)
N1—C18	1.321(6)	C9—C11	1.382(6)
N2—C6	1.342(5)	C11—C12	1.390(6)
N2—C7	1.462(5)	C12—C13	1.516(6)
N2—C15	1.353(5)	C12—C14	1.388(6)
C1—C2	1.379(6)	C15—C16	1.370(6)
C2—C3	1.369(6)	C17—C18	1.379(6)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,1-Y,2-Z; [3]-X,+Y,2-Z; [4]-1/2+X,3/2-Y,+Z; [5]1/2-X,3/2-Y,-1-Z; [6]-X,+Y,-1-Z.

The bond lengths (Å) in **CuI-MOF-360**

Zn1—O2[4]	1.938(4)	C3—C4	1.483(6)
Zn1—O2[5]	1.938(4)	C3—C17	1.384(7)
Zn1—O4[6]	1.961(4)	C4—C5	1.394(7)
Zn1—O4	1.961(4)	C4—C16	1.396(7)
O1—C10	1.205(7)	C5—C6	1.388(6)
O2—C10	1.268(6)	C7—C8	1.369(7)
O3—C13	1.230(7)	C7—C14	1.373(7)
O4—C13	1.252(6)	C8—C9	1.407(6)
N1—C1	1.371(7)	C9—C10	1.508(7)
N1—C18	1.320(7)	C9—C11	1.382(7)
N2—C6	1.332(6)	C11—C12	1.397(7)
N2—C7	1.463(5)	C12—C13	1.511(7)
N2—C15	1.359(6)	C12—C14	1.396(6)
C1—C2	1.382(7)	C15—C16	1.370(7)

C2—C3	1.372(7)	C17—C18	1.372(6)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,1-Y,2-Z; [3]-X,+Y,2-Z; [4]-1/2+X,3/2-Y,+Z; [5]1/2-X,3/2-Y,-1-Z; [6]-X,+Y,-1-Z.

The bond lengths (Å) in **CuI-MOF-380**

Zn1—O2[4]	1.940(4)	C3—C4	1.494(6)
Zn1—O2[5]	1.940(4)	C3—C17	1.373(7)
Zn1—O4[6]	1.946(4)	C4—C5	1.383(7)
Zn1—O4	1.946(4)	C4—C16	1.386(7)
O1—C10	1.209(7)	C5—C6	1.374(6)
O2—C10	1.266(6)	C7—C8	1.381(7)
O3—C13	1.216(7)	C7—C14	1.375(7)
O4—C13	1.271(7)	C8—C9	1.401(6)
N1—C1	1.349(7)	C9—C10	1.509(7)
N1—C18	1.312(7)	C9—C11	1.388(7)
N2—C6	1.344(6)	C11—C12	1.387(7)
N2—C7	1.465(5)	C12—C13	1.535(7)
N2—C15	1.342(6)	C12—C14	1.393(6)
C1—C2	1.385(7)	C15—C16	1.364(7)
C2—C3	1.368(7)	C17—C18	1.371(7)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,1-Y,2-Z; [3]-X,+Y,2-Z; [4]-1/2+X,3/2-Y,+Z; [5]1/2-X,3/2-Y,-1-Z; [6]-X,+Y,-1-Z.

The bond lengths (Å) in **CuI-MOF-400**

Zn1—O2[4]	1.932(3)	C2—C3	1.355(6)
Zn1—O2[5]	1.932(3)	C3—C4	1.498(5)
Zn1—O4[6]	1.942(3)	C3—C17	1.374(6)
Zn1—O4	1.942(3)	C4—C5	1.378(6)
O1—C10	1.211(5)	C4—C16	1.378(6)
O2—C10	1.270(5)	C5—C6	1.374(5)
O3—C13	1.210(5)	C7—C8	1.385(5)
O4—C13	1.270(5)	C7—C14	1.370(5)

N1—C1	1.349(6)	C8—C9	1.399(5)
N1—C18	1.319(6)	C9—C10	1.506(6)
N2—C6	1.341(5)	C9—C11	1.374(5)
N2—C7	1.465(4)	C11—C12	1.386(5)
N2—C15	1.343(5)	C12—C14	1.393(5)
C13—C12	1.523(6)	C15—C16	1.375(5)
C1—C2	1.382(6)	C17—C18	1.375(5)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,1-Y,2-Z; [3]-X,+Y,2-Z; [4]1/2+X,3/2-Y,-1-Z; [5]-1/2-X,3/2-Y,+Z; [6]-X,+Y,-1-Z.

The bond lengths (Å) in **CuI-MOF-H**

Zn1—O2[4]	1.931(2)	C3—C4	1.494(4)
Zn1—O2[5]	1.931(2)	C3—C17	1.379(4)
Zn1—O4	1.949(2)	C4—C5	1.383(4)
Zn1—O4[6]	1.949(2)	C4—C16	1.377(5)
O1—C10	1.212(4)	C5—C6	1.371(4)
O2—C10	1.272(4)	C7—C8	1.384(4)
O3—C13	1.220(4)	C7—C14	1.378(4)
O4—C13	1.273(4)	C8—C9	1.402(4)
N1—C1	1.346(4)	C9—C10	1.517(4)
N1—C18	1.325(4)	C9—C11	1.374(4)
N2—C6	1.344(4)	C11—C12	1.394(4)
N2—C7	1.459(3)	C12—C13	1.517(4)
N2—C15	1.345(4)	C12—C14	1.384(4)
C1—C2	1.379(5)	C15—C16	1.377(4)
C2—C3	1.366(5)	C17—C18	1.380(4)

Symmetry transformations used to generate equivalent atoms: [1]+X,1-Y,+Z; [2]-X,1-Y,2-Z; [3]-X,+Y,2-Z; [4]-1/2+X,3/2-Y,+Z; [5]1/2-X,3/2-Y,-1-Z; [6]-X,+Y,-1-Z.

Table S3. Cu···Cu distances (Å) and Cu—I/N bonds lengths(Å) in **CuI-MOF** at different temperatures.

	CuI-MOF-300	**CuI-MOF-320**	**CuI-MOF-340**	**CuI-MOF-360**

Cu1···Cu1[1]	2.662	2.668	2.672	2.677
Cu1···Cu2	2.627	2.628	2.628	2.623
Cu1···Cu2[3]	2.533	2.534	2.535	2.537
Cu2···Cu2[2]	2.732	2.739	2.740	2.742
Cu1—I1	2.7668(7)	2.7670(7)	2.7692(8)	2.7757(9)
Cu1—I2	2.6637(6)	2.6650(6)	2.6652(7)	2.6697(8)
Cu1—I3	2.6579(6)	2.6576(6)	2.6573(6)	2.6561(8)
Cu2—I1	2.5125(11)	2.5119(10)	2.5112(11)	2.5087(13)
Cu2—I2[2]	2.5870(11)	2.5841(11)	2.5831(12)	2.5820(14)
Cu2—I3	2.7302(12)	2.7318(12)	2.7352(13)	2.7474(15)
Cu1—N1	2.036(3)	2.039(3)	2.029(4)	2.034(4)
	CuI-MOF-380	**CuI-MOF-400**	**CuI-MOF-H**	
Cu1···Cu1[1]	2.679	2.679	2.647	
Cu1···Cu2	2.628	2.641	2.616	
Cu1···Cu2[3]	2.532	2.525	2.512	
Cu2···Cu2[2]	2.753	2.749	2.722	
Cu1—I1	2.7873(10)	2.7882(8)	2.7814(6)	
Cu1—I2	2.6797(9)	2.6788(8)	2.6777(6)	
Cu1—I3	2.6526(8)	2.6489(7)	2.6357(5)	
Cu2—I1	2.5077(13)	2.5077(11)	2.5087(8)	
Cu2—I2[2]	2.5899(16)	2.5944(13)	2.5909(10)	
Cu2—I3	2.7537(16)	2.7522(13)	2.7428(10)	
Cu1—N1	2.037(4)	2.036(3)	2.026(3)	

Table S4. Hydrogen bonding in **CuI-MOF**.

Donor–H···Acceptor	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D–H···A**
O1W–H1W···O2	0.85	2.60	3.012(8)	111

O2W–H2W···O3	0.85	2.59	3.044(4)	114
O3W–H3WB···O1	0.85	2.65	3.014(5)	107
C8–H8···O1	0.93	2.48	3.241(6)	140
C14–H14···O2W	0.93	2.36	3.216(5)	153
C16–H16···O3	0.93	2.59	3.216(6)	125

Table S5 The selected dihedral angles (º) in **CuI-MOF** at different temperatures.

	CuI-MOF-300	**CuI-MOF-320**	**CuI-MOF-340**	**CuI-MOF-360**	**CuI-MOF-380**	**CuI-MOF-400**	**CuI-MOF-H**
θ1	25.0(6)	25.0(6)	25.3(6)	25.4(7)	27.2(8)	28.7(6)	28.9(5)
θ2	-39.3(5)	-39.8(5)	-40.0(5)	-39.9(6)	-41.7(6)	-41.8(5)	-41.5(4)

Table S6 The decay lifetimes of **CuI-MOF** at room temperature.

	τ_1 (ns)	**B_1 (%)**	**τ_2 (ns)**	**B_2 (%)**	**τ_{av} (ns)**
CuI-MOF	12.18	25.55	42.09	74.45	34.4

Table S7 The temperature-dependent PL decay lifetimes of **CuI-MOF**.

T (K)	**τ_1 (ns)**	**B_1 (%)**	**τ_2 (ns)**	**B_2 (%)**	**τ_3 (ns)**	**B_3 (%)**	**τ_{av} (ns)**
300	2.853	4.12	14.32	15.63	41.38	80.25	35.6
320	2.268	5.42	9.679	17.99	28.53	76.59	23.7
340	4.214	19.4	18.51	63.87	25.63	16.73	16.9
360	2.560	14.86	12.49	69.99	24.16	15.15	12.8
380	3.254	23.25	14.12	55.09	36.41	21.66	16.4
400	4.519	31.03	27.84	47.11	60.82	21.86	27.8
420	2.606	11.41	13.16	27.86	58.33	60.73	39.4

Table S8 The decay lifetimes of **CuI-MOF-H** at room temperature.

	τ_1 (ns)	**B_1 (%)**	**τ_2 (ns)**	**B_2 (%)**	**τ_3 (ns)**	**B_3 (%)**	**τ_{av} (ns)**

CuI-MOF-H	32.44	11.71	212.9	31.55	908.1	56.74	586.2