Luminescent MOFs constructed by butterfly-like AIE ligands

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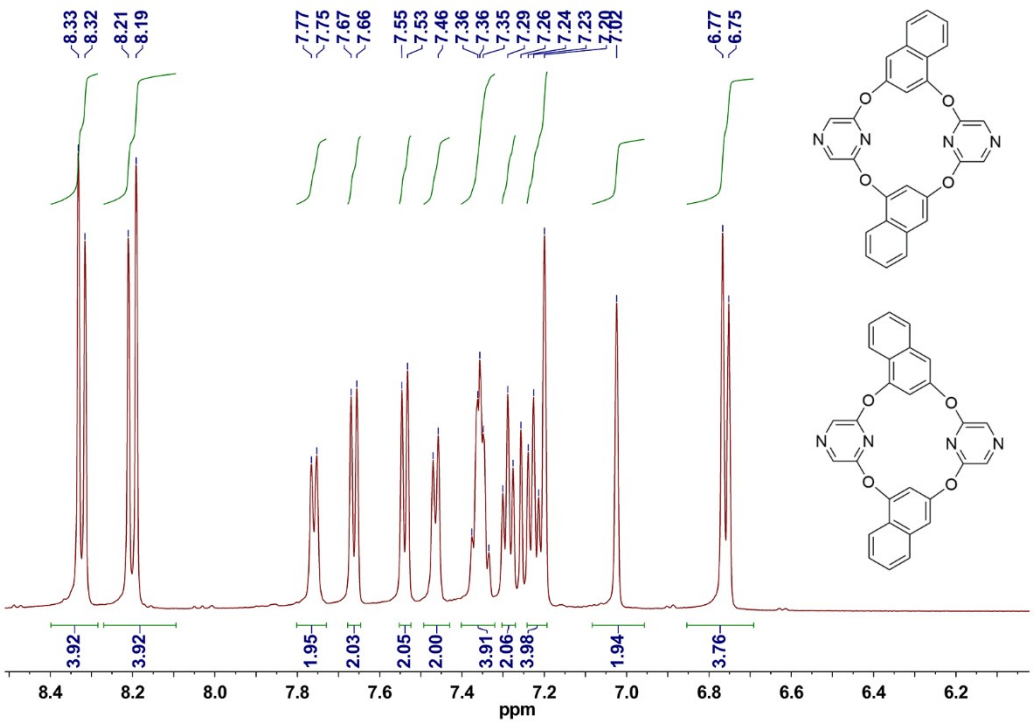

Figure S1. ^{1}H-NMR spectrum of **ONP-1**.

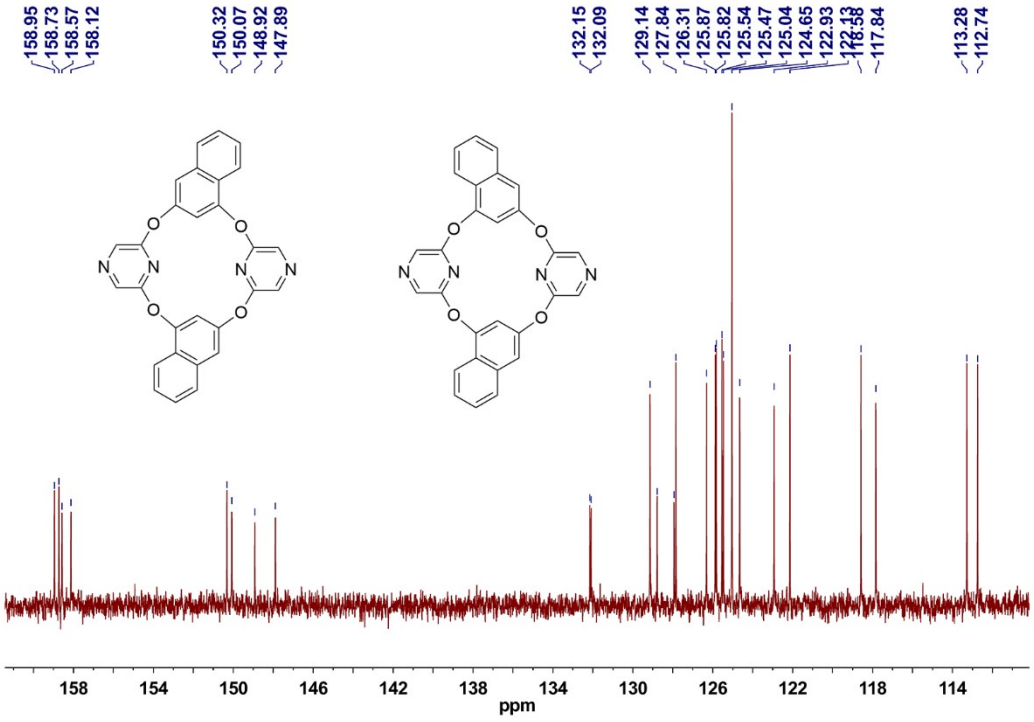

Figure S2. ^{13}C-NMR spectrum of **ONP-1**.

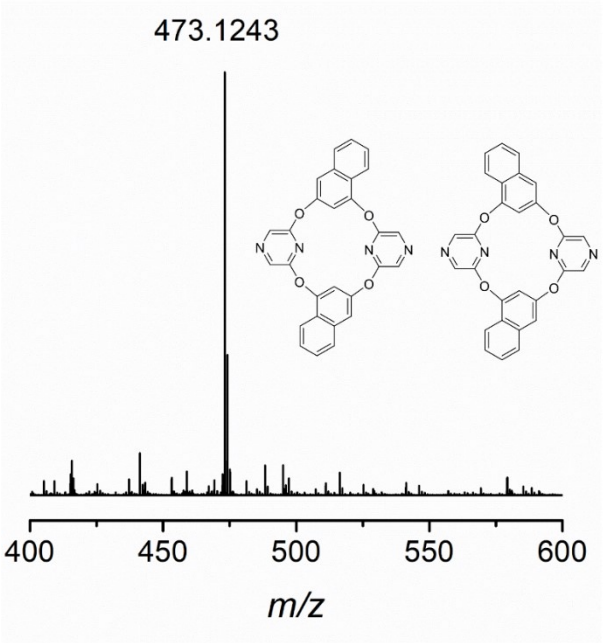

Figure S3. ESI-MS spectra of **ONP-1**.

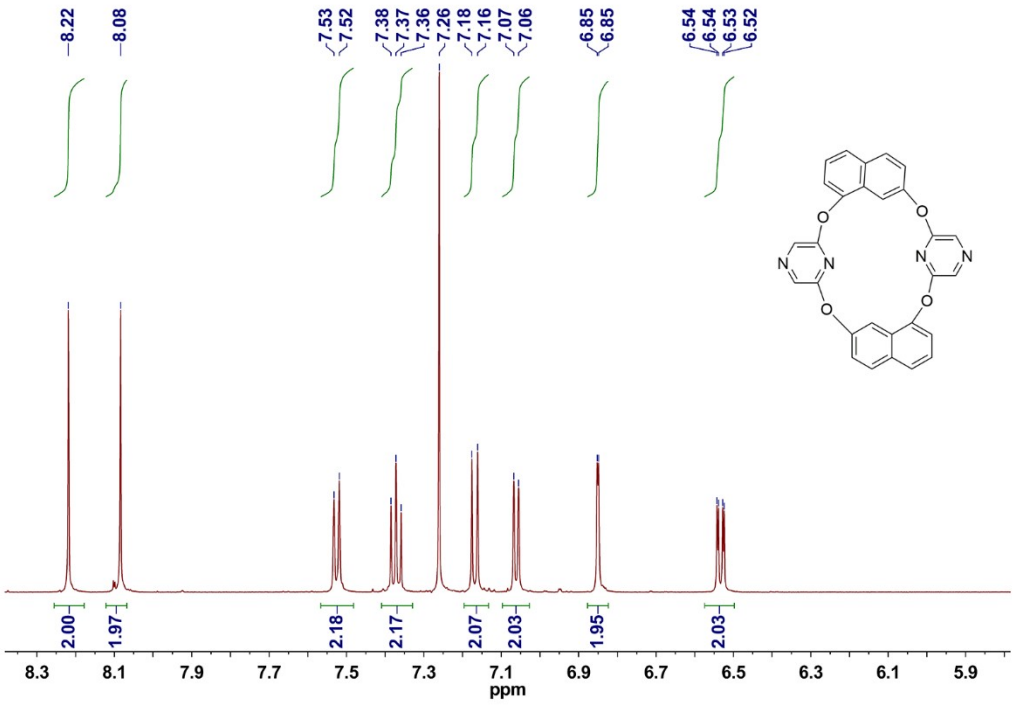

Figure S4. ^{1}H-NMR spectrum of **ONP-2**.

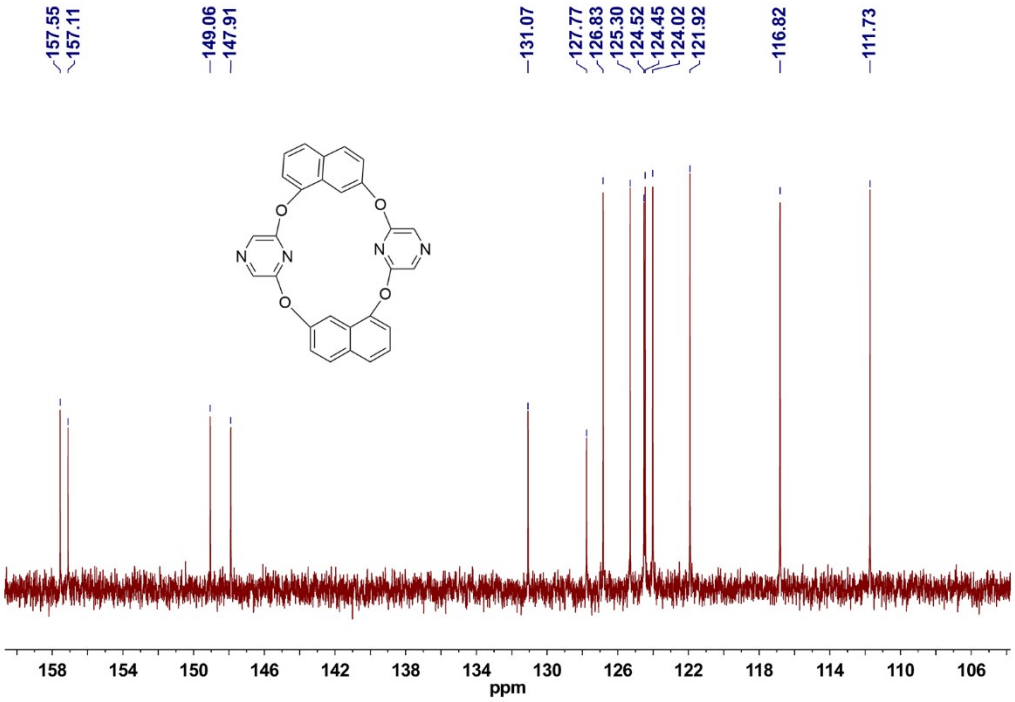

Figure S5. ^{13}C-NMR spectrum of **ONP-2**.

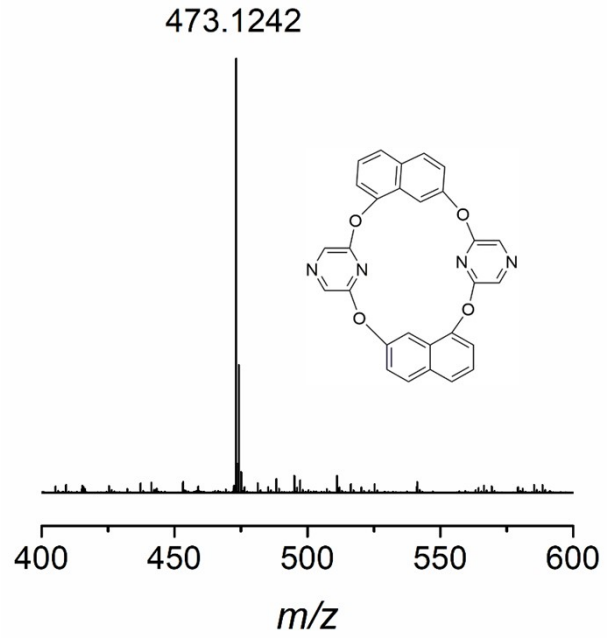

Figure S6. ESI-MS spectra of **ONP-2**.

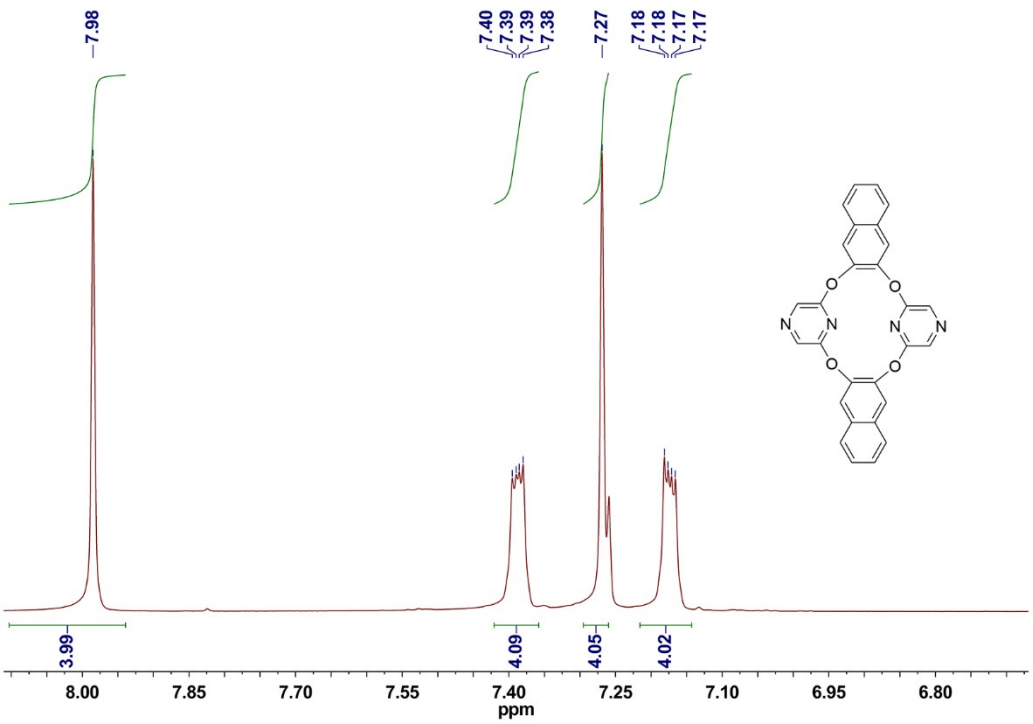

Figure S7. ^{1}H-NMR spectrum of **ONP-3**.

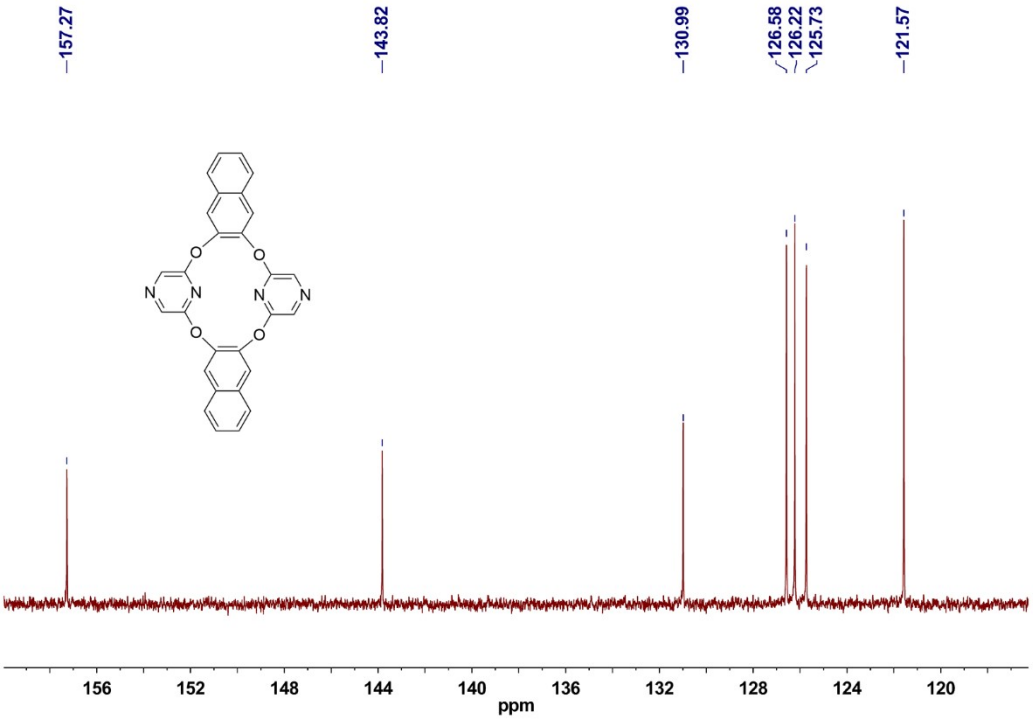

Figure S8. ^{13}C-NMR spectrum of **ONP-3**.

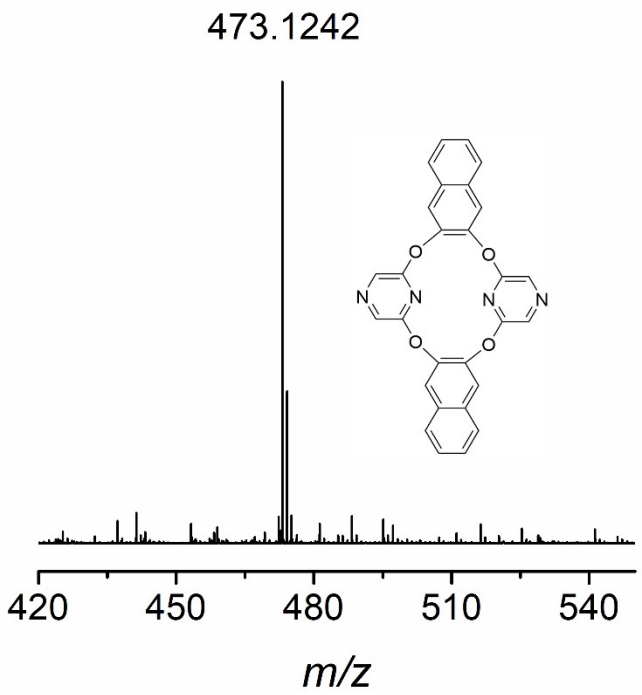

Figure S9. ESI-MS spectra of **ONP-3**.

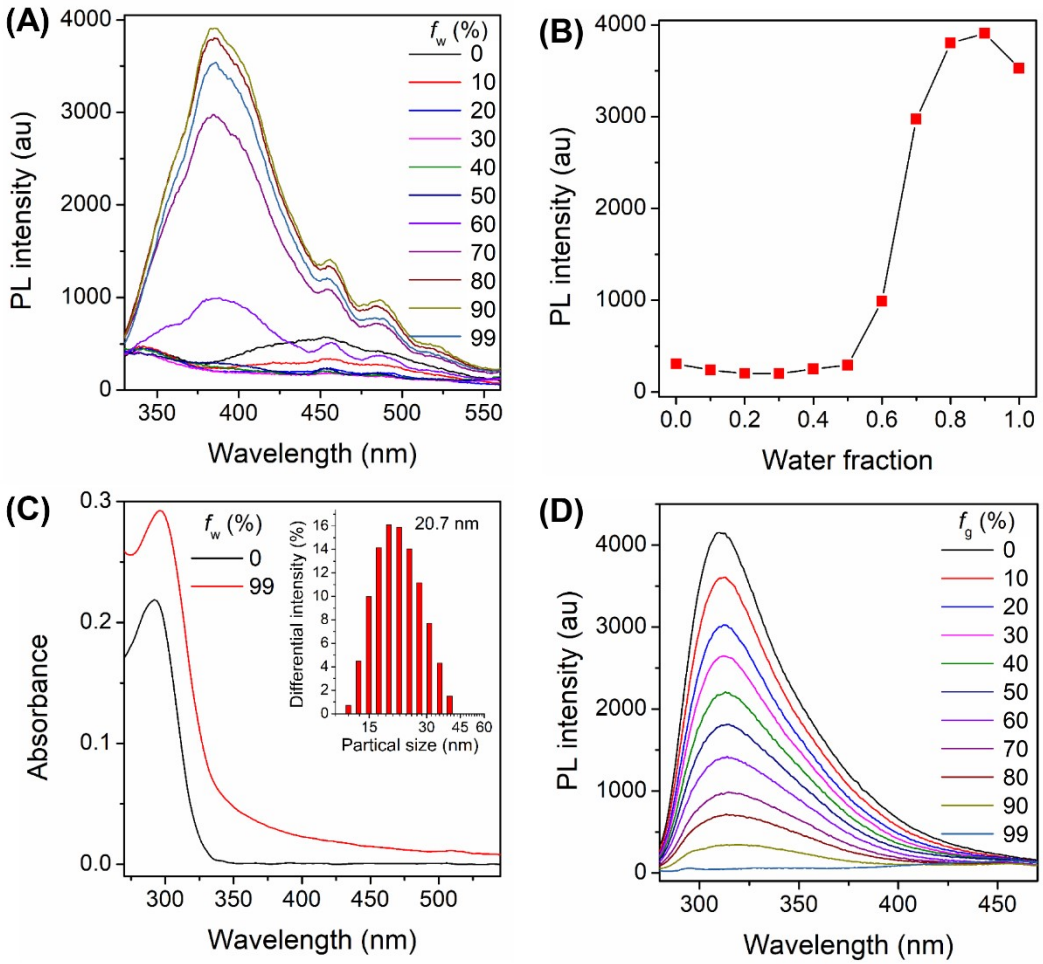

Figure S10. A) Luminescence spectra of **ONP-2** in water/DMSO mixtures with different f_w. B) Luminescence intensity of **ONP-2** at 398 nm as a function of f_w. C) Absorption spectra of **ONP-2** in water/DMSO mixtures with different f_w. Inset: DLS results of **ONP-2** in 99% water/DMSO mixture. D) Luminescence spectra of **ONP-2** in glycerol/DMSO mixtures with different f_g. Condition: [**ONP-2**] = 10 μmol/L.

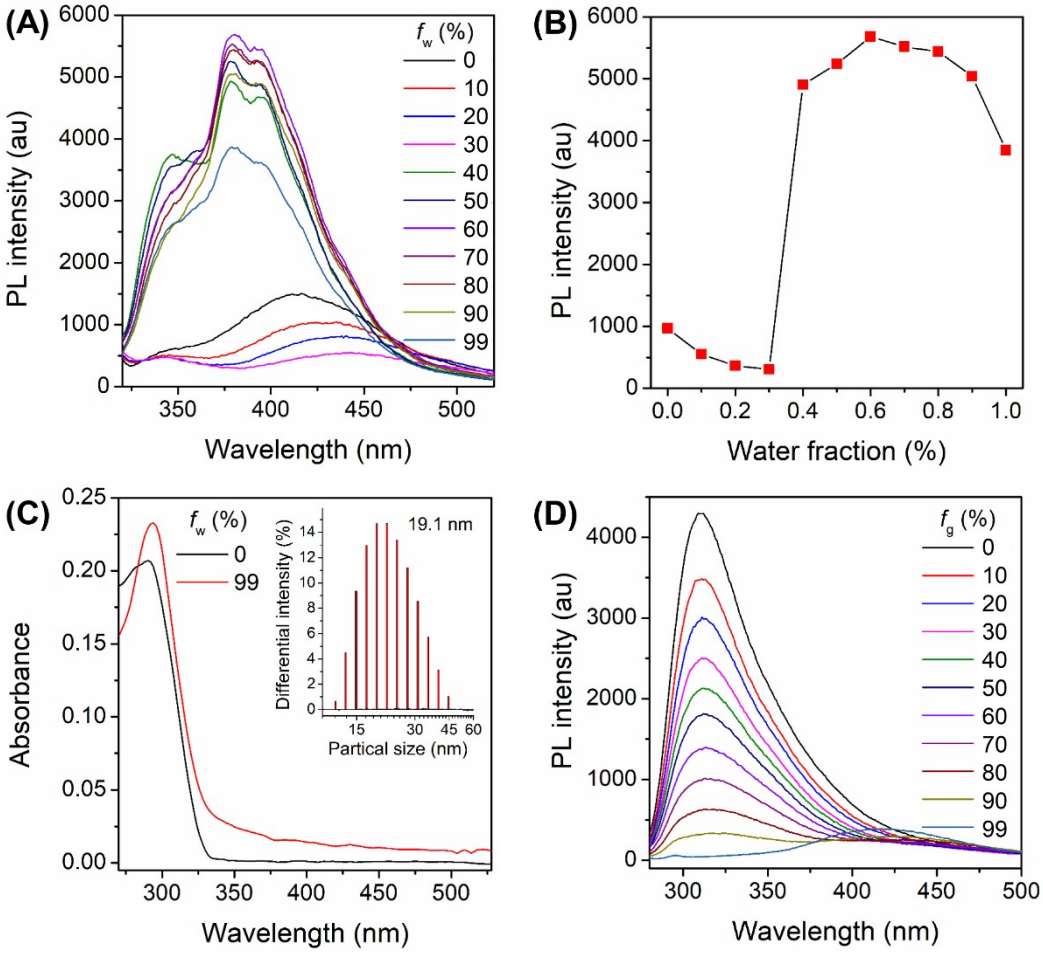

Figure S11. A) Luminescence spectra of **ONP-3** in water/DMSO mixtures with different f_w. B) Luminescence intensity of **ONP-3** at 381 nm as a function of f_w. C) Absorption spectra of **ONP-3** in water/DMSO mixtures with different f_w. Inset: DLS results of **ONP-3** in 99% water/DMSO mixture. D) Luminescence spectra of **ONP-3** in glycerol/DMSO mixtures with different f_g. Condition: [**ONP-3**] = 10 μmol/L.

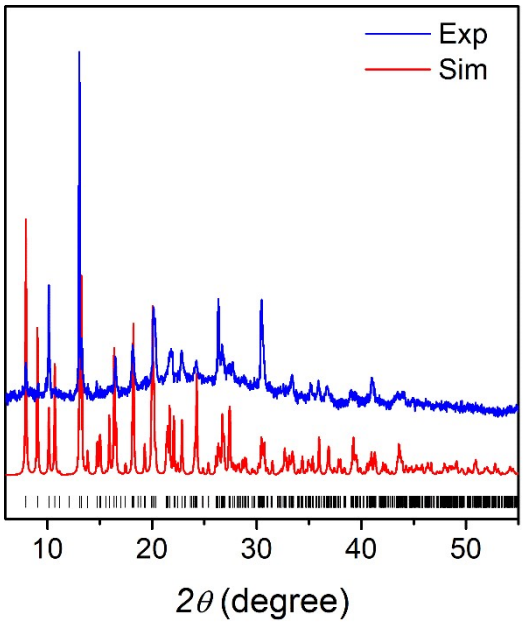

Figure S12. PXRD patterns of **MOF-1**.

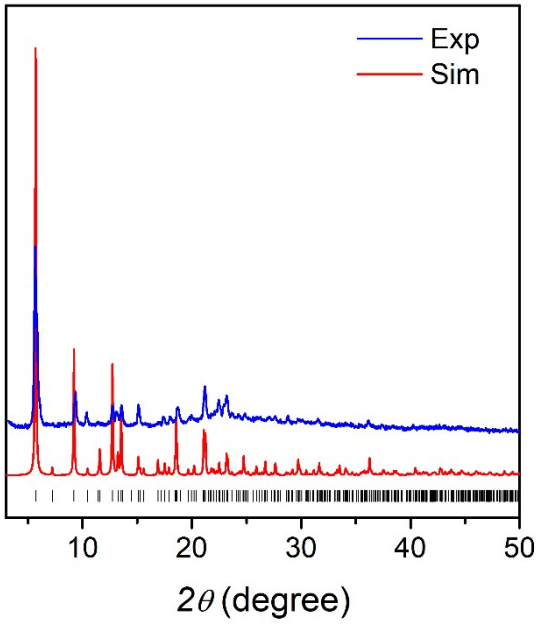

Figure S13. PXRD patterns of **MOF-2**.

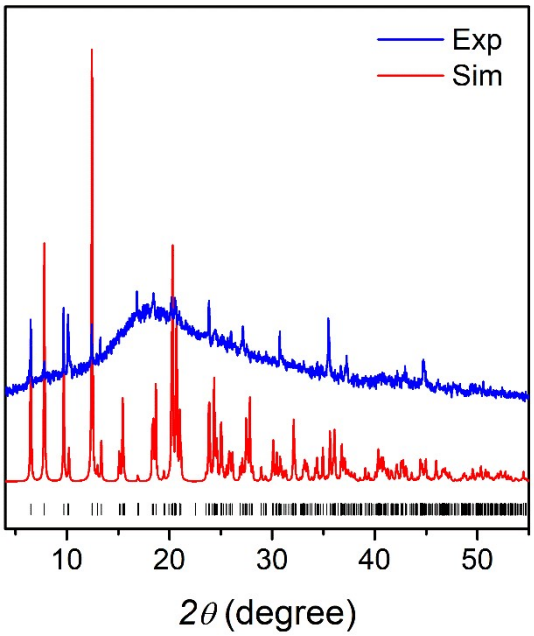

Figure S14. PXRD patterns of **MOF-3**.

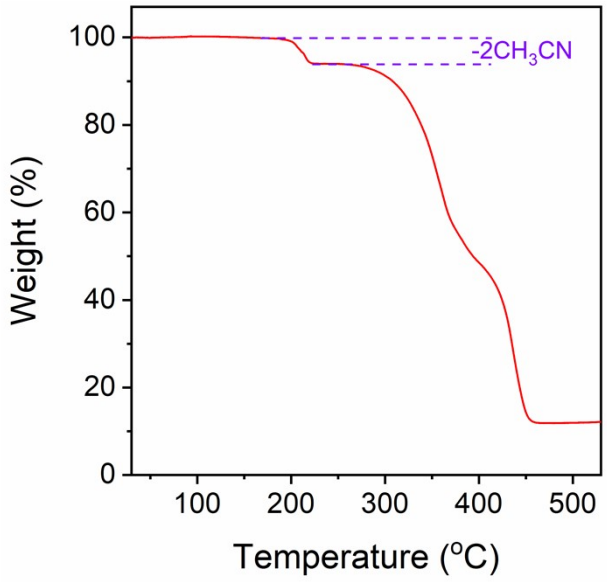

Figure S15. TGA curves of **MOF-1**.

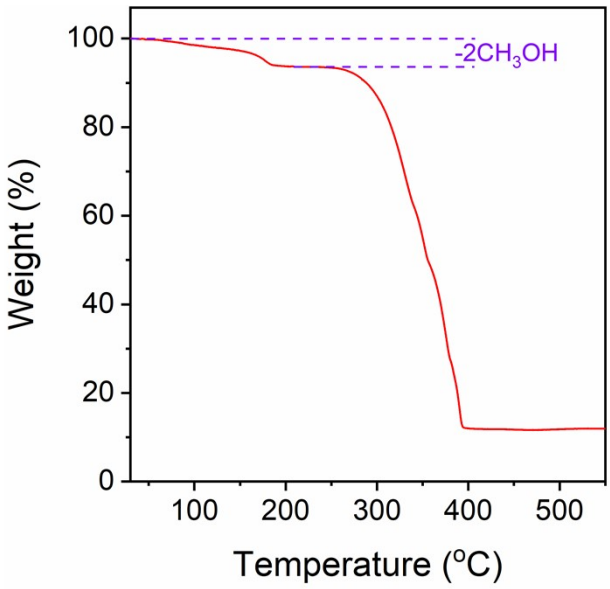

Figure S16. TGA curves of **MOF-2**.

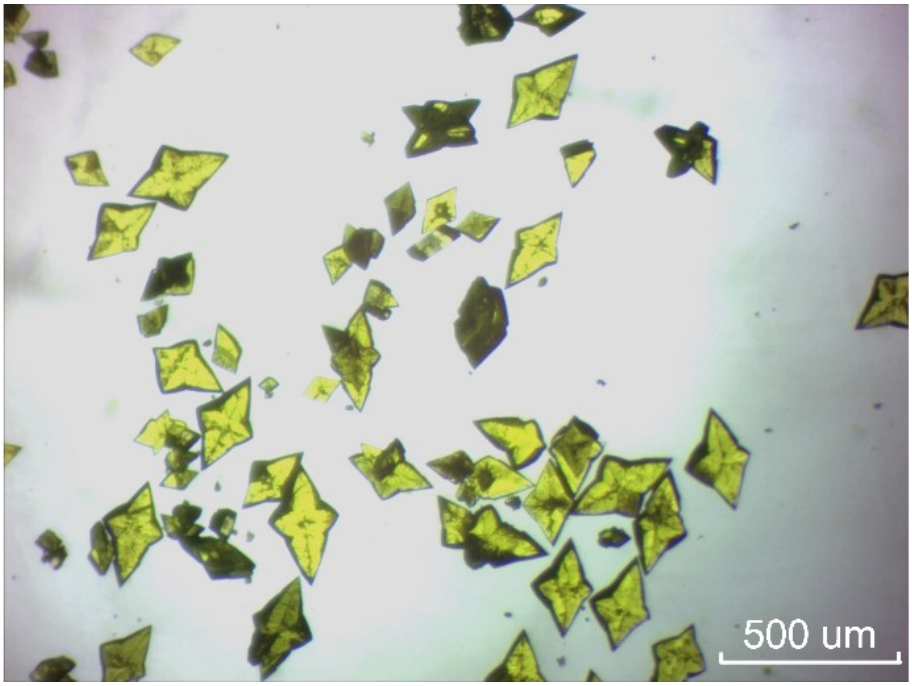

Figure S17. Photograph of **MOF-1**.

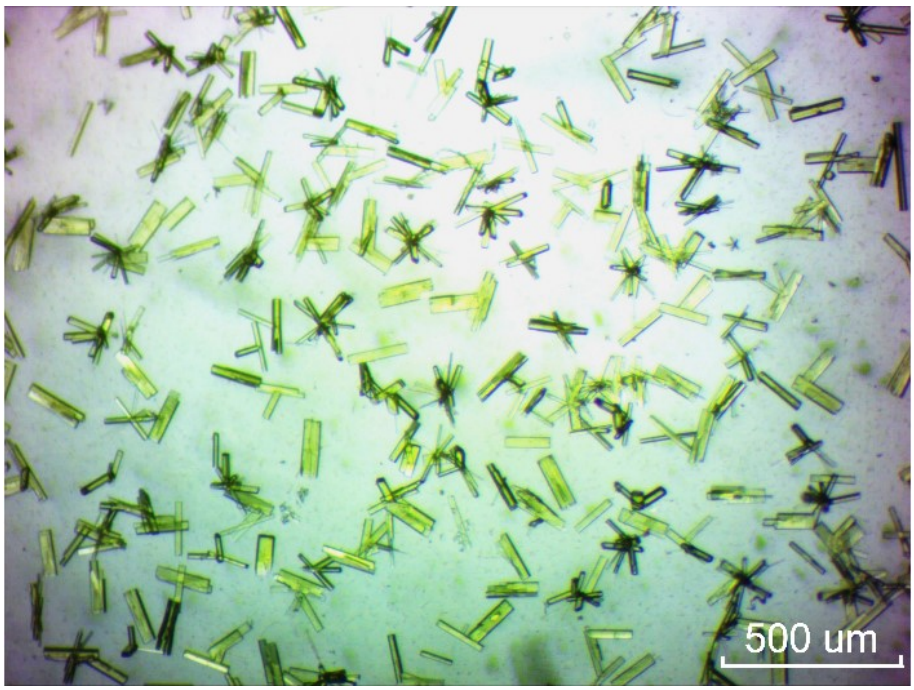

Figure S18. Photograph of **MOF-2**.

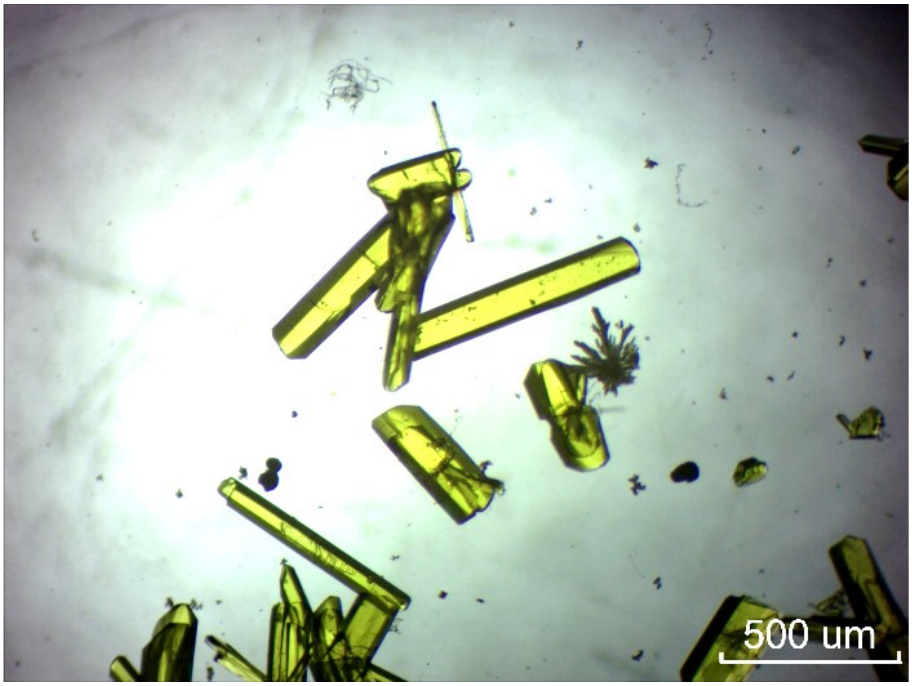

Figure S19. Photograph of **MOF-3**.

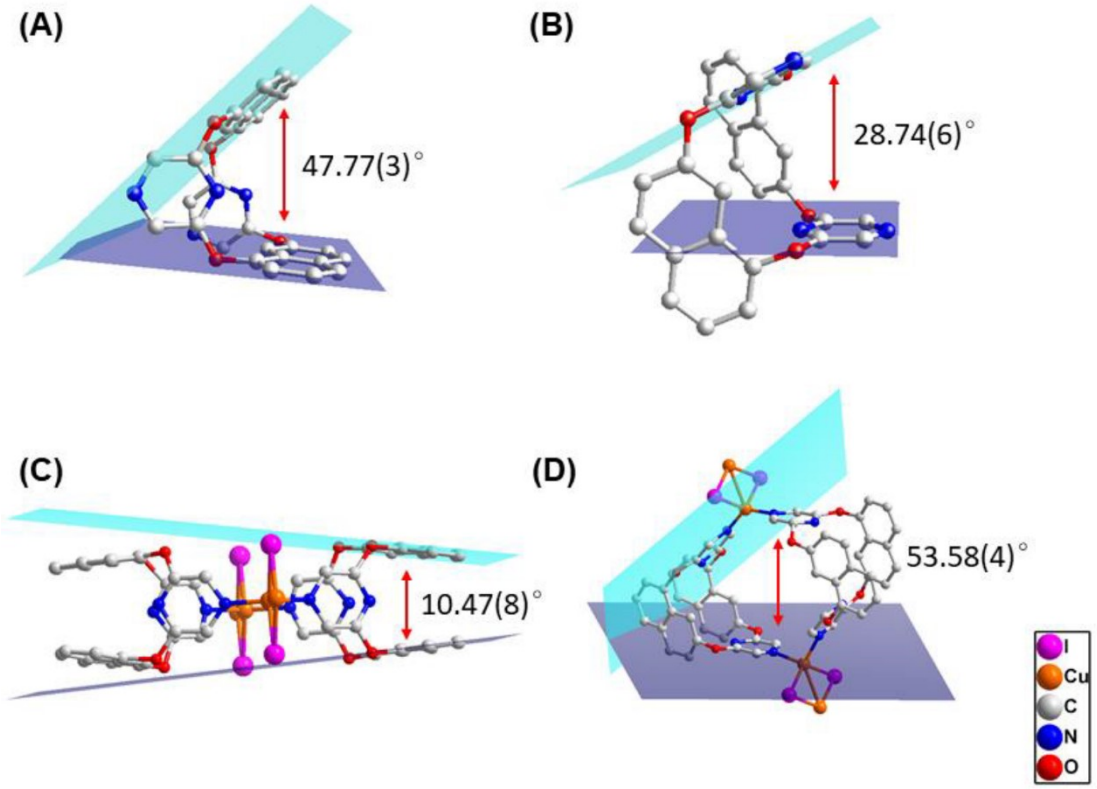

Figure S20. A) the dihedral angle between two naphthalene rings in free ligand. B) the dihedral angle between two pyrazine rings in free ligand. C) the dihedral angle between two naphthalene rings in **MOF-2**. D) the dihedral angle between two pyrazine rings in **MOF-2**.

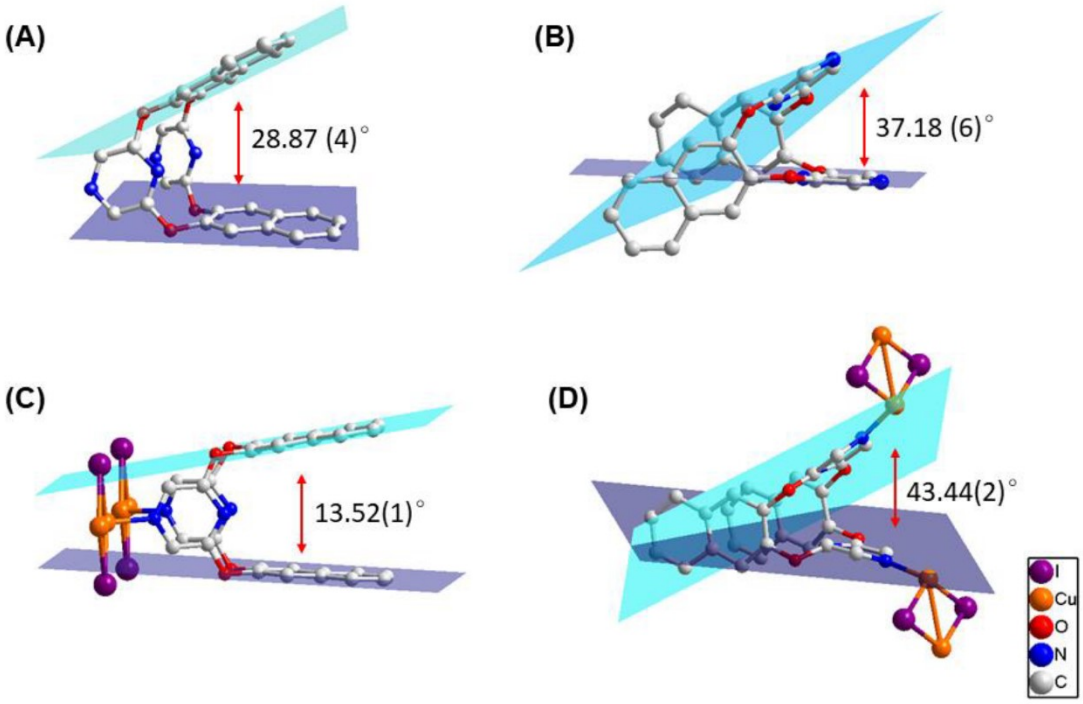

Figure S21. A) the dihedral angle between two naphthalene rings in free ligand. B) the dihedral angle between two pyrazine rings in free ligand. C) the dihedral angle between two naphthalene rings in **MOF-3**. D) the dihedral angle between two pyrazine rings in **MOF-3**.

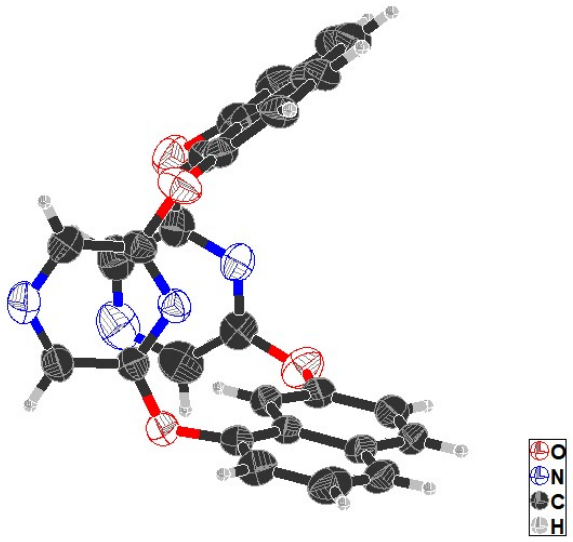

Figure S22. ADPs of compound **ONP-2**.

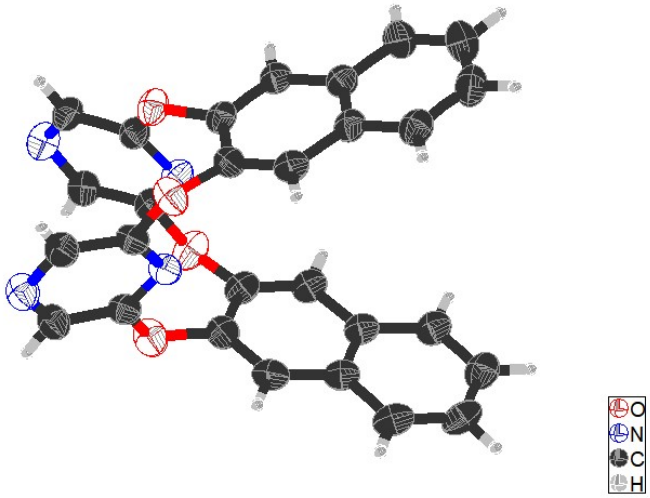

Figure S23. ADPs of compound **ONP-3**.

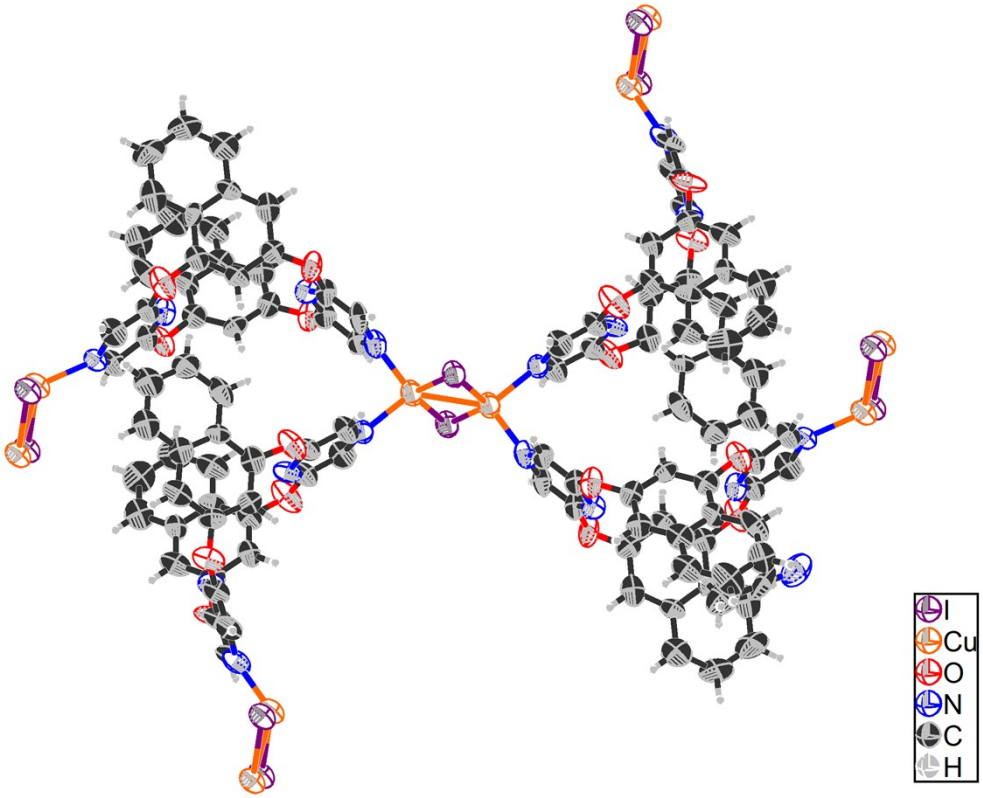

Figure S24. ADPs of compound **MOF-1**.

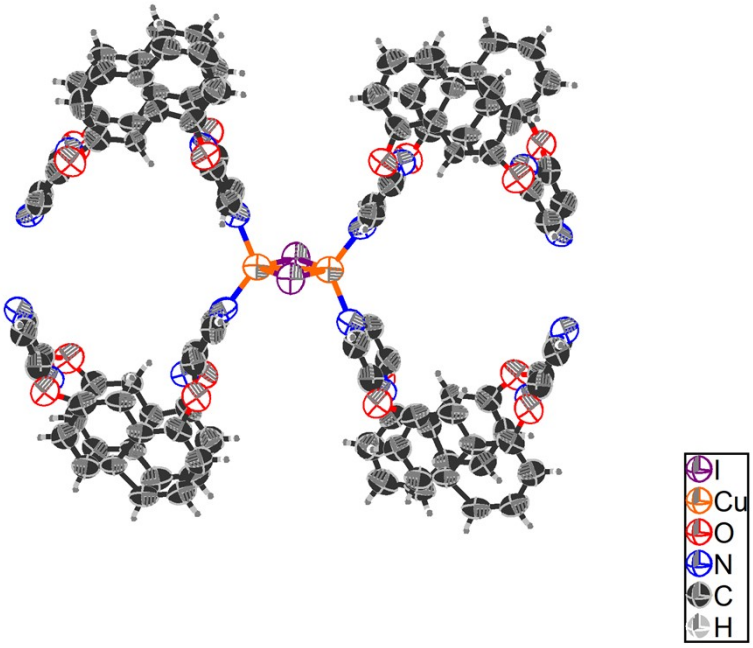

Figure S25. ADPs of compound **MOF-2**.

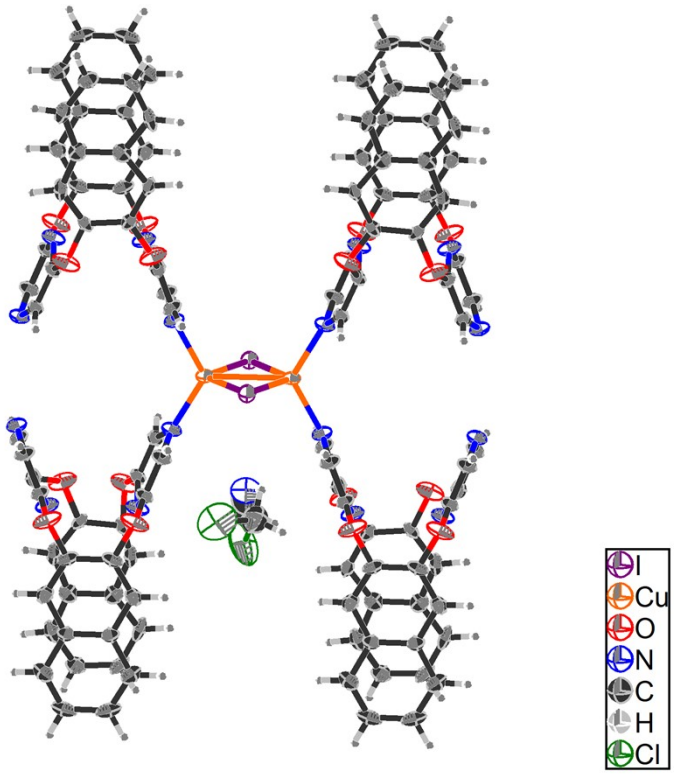

Figure S26. ADPs of compound **MOF-3**.

Table S1. Crystallographic data and structure refinement.

Compound	**ONP-2**	**ONP-3**
CCDCnumber	2211413	2157115
Empirical formula	$C_{28}H_{16}N_4O_4$	$C_{28}H_{16}N_4O_4$
Formula weight	472.45	472.45
Temperature/K	273.15	200.00
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	9.7538(16)	7.6216(3)
b/Å	11.407(2)	11.7920(5)
c/Å	11.4194(19)	13.0678(4)
α/°	103.712(7)	77.628(3)
β/°	113.415(6)	88.737(3)
γ/°	100.779(7)	71.633(4)
Volume/Å^3	1074.8(3)	1087.43(8)
Z	2	2
ρ_{calc}g/cm^3	1.460	1.443
μ/mm^{-1}	0.101	0.816
F(000)	488.0	488.0
Crystal size/mm^3	0.12 × 0.11 × 0.1	0.02 × 0.02 × 0.01
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	3.874 to 55.082	6.934 to 146.218
Index ranges	-12 ⩽ h ⩽ 12, -14 ⩽ k ⩽ 14, -14 ⩽ l ⩽ 14	-4 ⩽ h ⩽ 9, -14 ⩽ k ⩽ 14, -15 ⩽ l ⩽ 16
Reflections collected	28784	10319
Independent reflections	4938[R_{int} = 0.0540, R_{sigma} = 0.0327]	4192 [R_{int} = 0.0464, R_{sigma} = 0.0558]
Data/restraints/parameters	4938/0/325	4192/0/326
Goodness-of-fit on F^2	1.030	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.0953	R_1 = 0.0597, wR_2 = 0.1668
Final R indexes [all data]	R_1 = 0.0697, wR_2 = 0.1090	R_1 = 0.0722, wR_2 = 0.1802

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

Table S2. Crystallographic data and structure refinement.

Compound	**MOF-1**	**MOF-2**	**MOF-3**
CCDC number	2211414	2211415	2211417
Empirical formula	$Cu_2I_2(C_{28}H_{16}N_4O_4)_2 \cdot 2CH_3CN$	$Cu_2I_2(C_{28}H_{16}N_4O_4)_2 \cdot 2CH_3OH$	$Cu_2I_2(C_{28}H_{16}N_4O_4)_2 \cdot 2CH_3CN \cdot 2CH_2Cl_2$
Formula weight	1407.88	1389.86	1577.73
Temperature/K	150	200	200
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pbam$	$C2/m$
a/Å	10.4836(4)	30.9478(5)	27.2643(2)
b/Å	13.4881(4)	8.7794(2)	9.67980(10)
c/Å	19.6808(5)	12.2189(3)	11.31850(10)
α/°	90	90	90
β/°	97.791(3)	90	90.5060(10)
γ/°	90	90	90
Volume/Å^3	2757.25(15)	3319.91(12)	2986.98(5)
Z	2	2	2
ρ_{calc}g/cm^3	1.696	1.326	1.754
μ/mm^{-1}	10.294	8.507	11.186
F(000)	1392.0	1304.0	1560.0
Crystal size/mm^3	0.1 × 0.05 × 0.03	0.15 × 0.06 × 0.03	0.1 × 0.04 × 0.03
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.97 to 146.592	7.234 to 132.962	6.484 to 146.99
Index ranges	$-12 \le h \le 10$, $-16 \le k \le 12$, $-24 \le l \le 20$	$-36 \le h \le 34$, $-10 \le k \le 10$, $-10 \le l \le 14$	$-33 \le h \le 32$, $-11 \le k \le 11$, $-14 \le l \le 13$
Reflections collected	13917	10684	7750
Independent reflections	5377 [R_{int} = 0.0264, R_{sigma} = 0.0312]	3085 [R_{int} = 0.0398, R_{sigma} = 0.0388]	3124 [R_{int} = 0.0343, R_{sigma} = 0.0329]
Data/restraints/parameters	5377/0/371	3085/400/283	3124/149/284
Goodness-of-fit on F^2	1.199	1.057	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0899, wR_2 = 0.2050	R_1 = 0.0512, wR_2 = 0.1486	R_1 = 0.0496, wR_2 = 0.1381
Final R indexes [all data]	R_1 = 0.1026, wR_2 = 0.2122	R_1 = 0.0602, wR_2 = 0.1565	R_1 = 0.0501, wR_2 = 0.1386

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

Table S3. The main bond lenghs (Å) of **MOF-1**.

Atom	Atom	Length/Å
I1	Cu1	2.6094(18)
I1	Cu1[1]	2.6151(19)
Cu1	Cu1[1]	2.525(3)
Cu1	N1	2.070(10)
Cu1	N4[2]	2.083(8)

Symmetry codes: [1]1-X,2-Y,1-Z; [2]1/2-X, 1/2+Y,3/2-Z

Table S4. The main bond lenghs (Å) of **MOF-2**.

Atom	Atom	Length/Å
I1	Cu1[1]	2.6585(8)
I1	Cu1	2.6585(8)
I1	Cu2	2.629(11)
I1	Cu2[1]	2.630(10)
Cu1	Cu1[1]	2.664(3)
Cu1	N1	2.125(10)
Cu2	Cu2[1]	2.55(2)

Symmetry codes: [1]1-X,-Y,-Z

Table S5. The main bond lenghs (Å) of **MOF-3**.

Atom	Atom	Length/Å
I1	Cu1	2.6716(5)
I1	Cu1[1]	2.6716(5)
Cu1	Cu1[1]	2.7489(18)
Cu1	N1[2]	2.050(3)
Cu1	N1	2.051(3)

Symmetry codes: [1]1-X,-Y,-Z; [2]1-X,+Y,-Z; [3]+X,1-Y,+Z; [4]1-X,-Y,1-Z; [5]1-X,+Y,1-Z

Table S6. The main bond angles (º) of **MOF-1**.

Atom	Atom	Atom	Angle/˚
Cu1	I1	Cu1[1]	57.80(6)
I1	Cu1	I1[1]	122.20(6)
Cu1[1]	Cu1	I1	61.21(7)
Cu1[1]	Cu1	I1[1]	60.99(7)
N1	Cu1	I1	108.6 (3)
N1	Cu1	I1[1]	110.1(3)
N1	Cu1	Cu1[1]	133.2(3)
N1	Cu1	N4[2]	96.3(3)
N4[2]	Cu1	I1	108.3(3)
N4[2]	Cu1	I1[1]	108.3(3)
N4[2]	Cu1	Cu1[1]	130.5(3)

Symmetry codes:[1]1-X,2-Y,1-Z; [2]1/2-X, 1/2+Y,3/2-Z; [3]1/2-X, -1/2+Y,3/2-Z

Table S7. The main bond angles (º) of **MOF-2**.

Atom	Atom	Atom	Angle/˚
Cu1[1]	I1	Cu1	60.13(5)
Cu2	I1	Cu2[1]	57.9(5)
I1	Cu1	I1[1]	119.87(5)
I1	Cu1	Cu1[1]	59.93(3)
I1[1]	Cu1	Cu1[1]	59.93(3)
N1	Cu1	I1[1]	107.0(3)
N1	Cu1	I1	103.6(3)
N1	Cu1	Cu1[1]	121.7(4)
I1	Cu2	I1[1]	122.1(5)
Cu2[1]	Cu2	I1	61.1(4)
N1	Cu1	N1	116.52(4)°

Symmetry codes:[1]1-X,-Y,-Z

Table S8. The main bond angles (º) of **MOF-3**.

Atom	Atom	Atom	Angle/˚
Cu1	I1	Cu1[1]	61.92(3)
I1	Cu1	I1[1]	118.08(3)
I1	Cu1	Cu1[1]	59.038(17)
I1[1]	Cu1	Cu1[1]	59.038(17)
N1[2]	Cu1	I1	104.41(10)
N1	Cu1	I1	105.13(10)
N1[2]	Cu1	I1[1]	105.13(10)
N1	Cu1	I1[1]	104.40(10)
N1	Cu1	Cu1[1]	119.70(11)
N1[2]	Cu1	Cu1[1]	119.70(11)
N1[2]	Cu1	N1	120.6(2)

Symmetry codes: [1]1-X,-Y,-Z; [2]1-X,+Y,-Z; [3]+X,1-Y,+Z; [4]1-X,+Y,1-Z; [5]1-X,-Y,1-Z