Electronic Supplementary Information (ESI)

Two solvent-induced porous hydrogen-bonded organic frameworks: Solvent-effect on structure and functionality

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S1. Experimental Section

General Remarks. All reagents and solvents have been purchased from commercial suppliers and utilized directly without further purification. The building block, DAT-TPE, has been prepared according to the reported literature.[1] NMR spectrum was recorded on a Varian INOVA 500 MHz spectrometer at room temperature. Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50 thermogravimetric analyzer under N_2 atmosphere with a heating rate of 3 ^oC/min. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV diffractometer which was operated at 40 kV for CuKa (λ = 0.1543 nm) radiation. UV-vis absorption spectra were collected on a Cary 5000 UV-vis-NIR spectrophotometer, and diffused reflectance spectra were recorded on the same spectrophotometer using KBr as reflectance standard at room temperature. Room-temperature solid-state fluorescence spectroscopic studies were performed on an F4500 (Hitachi) spectrofluorometer. Energy-dispersive X-ray spectroscopy (EDX) analyses were performed on a SIRION-100 instrument which was performed on a dried powder sample. X-ray photoelectron spectroscopy (XPS) measurements to confirm the presence of Ag(I) were performed on a combined VG ESCALAB MARK II instrument. Gas sorption isotherms of activated HOFs were measured on a Micromeritics ASAP 2020 surface area analyzer, and the measurement temperature was maintained at 77 K with liquid nitrogen, 196 K with a dry ice-acetone slurry, 273 K with an ice-water bath, and 296 K with a water bath in an air-conditioned 23 ^oC laboratory. FTIR spectra were performed at a Bruker Vector 22 infrared spectrometer at room temperature.

Syntheses of HOF-10 and HOF-5. Nearly colorless needle-shaped crystals of HOF-10 were obtained using the slow diffusion of THF vapor into a mixed DMF/DMSO (4 mL, v:v = 1:1) solution containing DAT-TPE (60~115 mg) at room temperature. While slightly pale yellowish block-shaped crystals of HOF-5 were prepared through the slow diffusion of THF vapor into a 6 mL DMF/DMSO (v:v = 2:1) solution

containing DAT-TPE 65 mg.[1]

Fluorescence Sensing of HOF-10 and HOF-5 towards Different Metals. The treated HOF-10 and HOF-5 samples were prepared by introducing HOF powder (about 25 mg) into a 40.0 mL THF/water (v:v = 100:1) solution of $M(NO_3)_x$ ($M = Na^+$, Ag^+, Ca^{2+}, Cd^{2+}; Co^{2+}, Cu^{2+}, Mn^{2+}; Ni^{2+}, and Zn^{2+}) with the concentration of 5.0 mM for two hours. These treated phases were isolated by filtration and directly used to measure the solid luminescence.

Activation of HOF-10 and HOF-5. The as-synthesized HOF-10 and HOF-5 crystals were exchanged with dry acetone for six times and then degassed to 6 μmmHg at room temperature to afford activated phases HOF-10a and HOF-5a, respectively.

X-ray Crystallographic Investigation of HOF-10 and HOF-5. Crystallographic data of HOF-10 and HOF-5 single crystals were collected on an Oxford Diffraction SuperNova diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100.00(16) K. The structure was solved based on the direct method (SHELXS-97) and refined utilizing full-matrix least-squares (SHELXL-97) on F^2.[2] In order to reveal the solvent effect on the crystal structure, we tried to resolve the solvent molecules in HOF-10 and HOF-5. However, because of the seriously disordered solvent molecules in the HOF-10 and HOF-5 pores, PLATON/SQUEEZE program still was utilized to remove these disordered molecules in the pores.[3] Selected crystallographic data and pertinent information for these two phases are summarized in Table S1. CCDC 1567204 and 1052040 for HOF-10 and HOF-5, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif**.**

S2. Characterizations and Properties Section

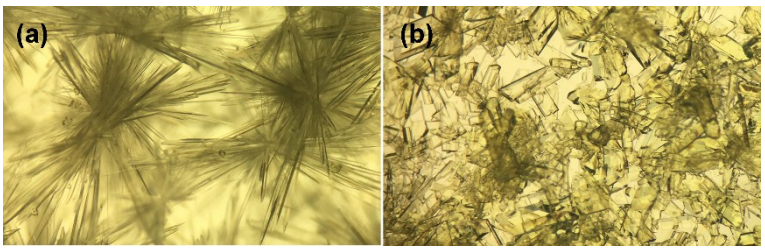


Figure S1. Crystal photos of HOF-10 (a) and HOF-5 (b).

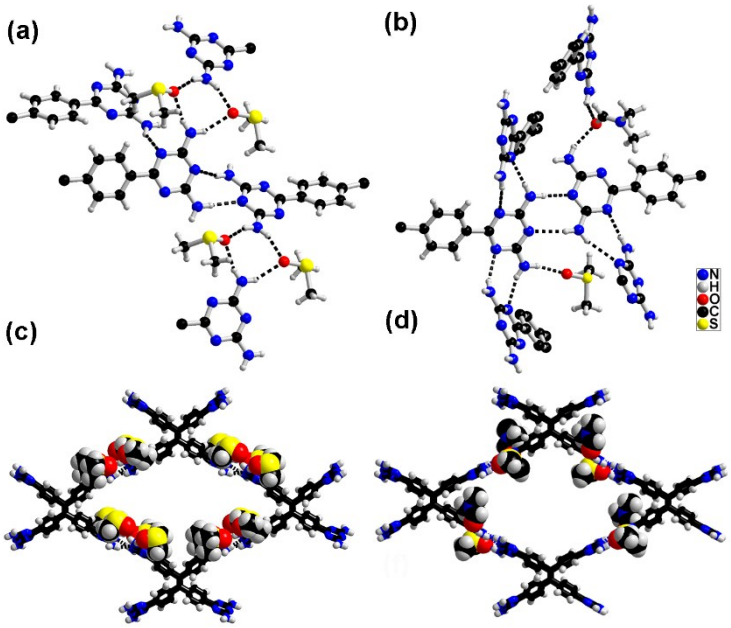


Figure S2. Crystal structures of HOF-10 and HOF-5 showing (a) neighboring DATs and DMSO molecules in HOF-10 connected through the hydrogen bonding; (b) neighboring DATs and solvent molecules in HOF-5 connected through the hydrogen bonding interactions; (c and d) hydrogen-bonded supramolecular grids in HOF-10 and HOF-5, respectively (carbon: black; hydrogen: white; nitrogen: blue; oxygen: red; sulfur: yellow; other solvent molecules are omitted for clarity)

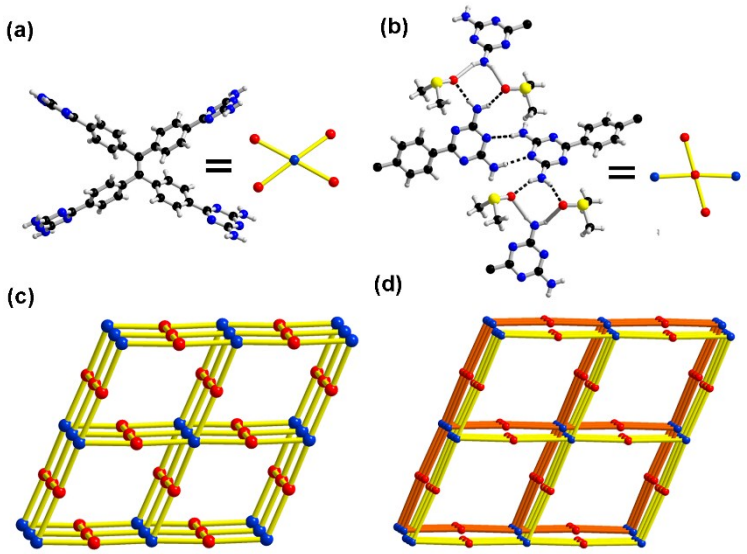


Figure S3. Crystal structure of HOF-10 showing (a) the organic building block acting as a 4-connected node (cyan ball); (b) DMSO-bridged neighboring DATs connected through the hydrogen bonding [the center acting as a 4-connected node (red ball)]; (c) a single binodal (4,4)-connected net; **(**d) a 2-fold interpenetrated topology.

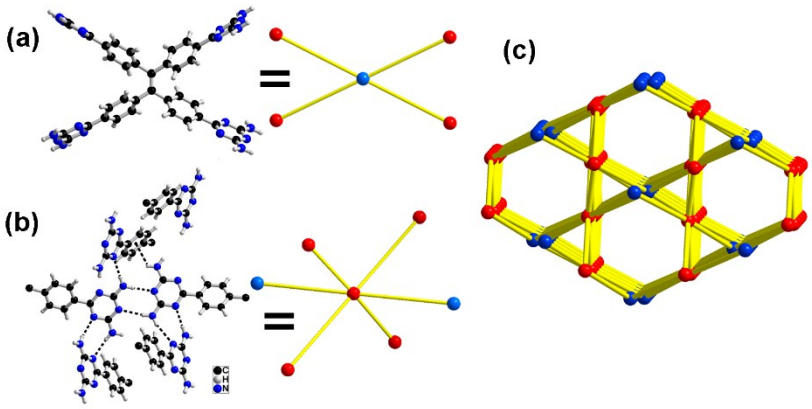


Figure S4. Crystal structure of HOF-5 showing (a) the organic building block acting as a 4-connected node (cyan ball); (b) six neighboring DATs connected through the hydrogen bonding and weak van der Waals interactions [the center acting as a 6-connected node (red ball)]; (c) a binodal (4,6)-connected net.

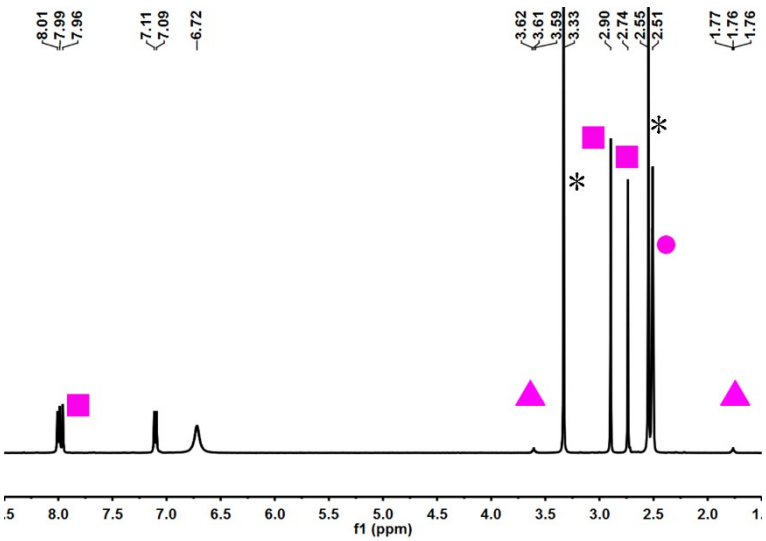


Figure S5. ^{1}H NMR spectrum of HOF-10 (DMF: square, THF: triangle, DMSO: circle). * denotes DMSO-d_6 solvent impurity.

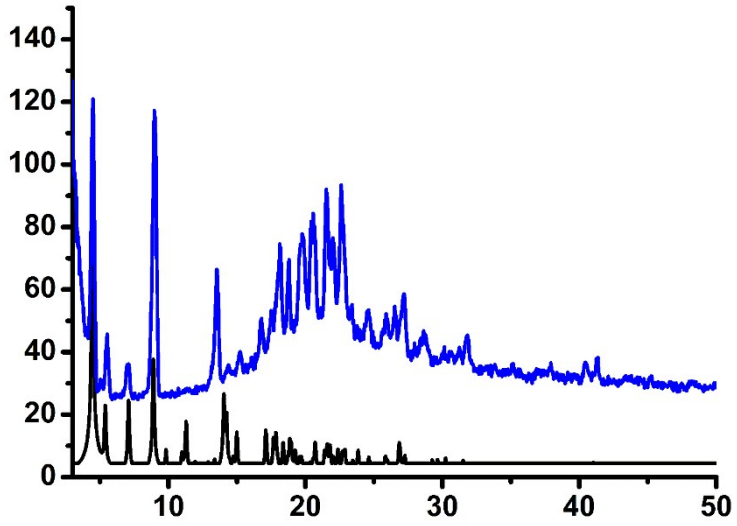


Figure S6. Powder X-ray diffraction profile of as-synthesized HOF-10 in the presence of mother liquid (blue line), in comparison with a simulated powder pattern based on the single-crystal HOF-10 structure (black line).

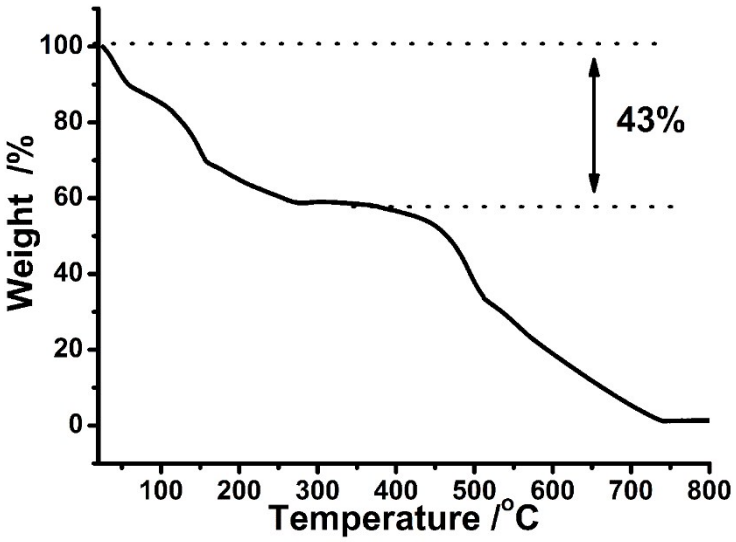


Figure S7. TGA curve of HOF-10 in the range of 25-800°C under N_2 atmosphere.

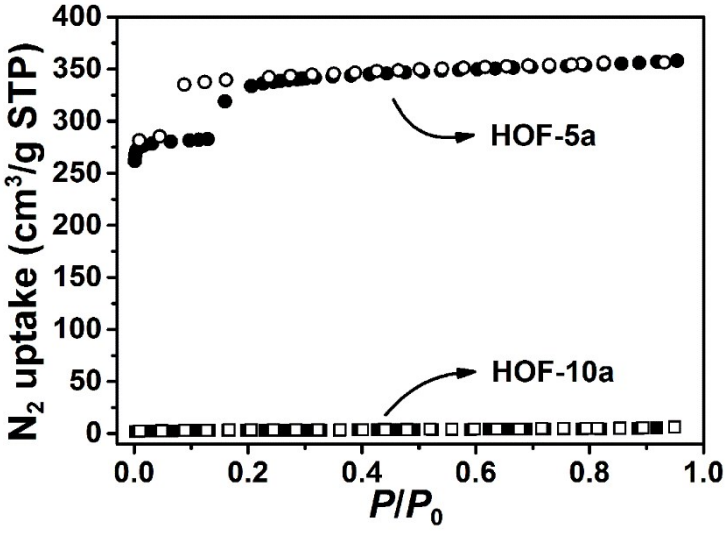


Figure S8. N_2 adsorption isotherms of HOF-10a and HOF-5a at 77 K (solid symbols: adsorption, open symbols: desorption).

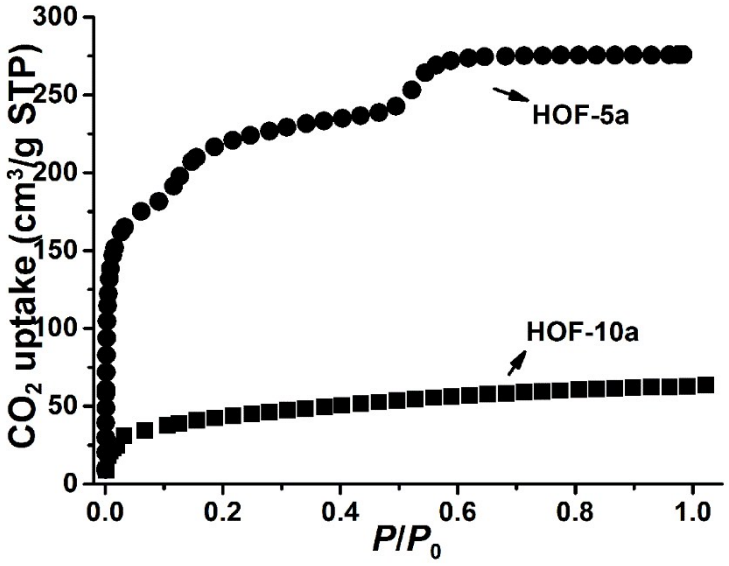


Figure S9. CO_2 adsorption isotherm of HOF-10 and HOF-5a at 196 K.

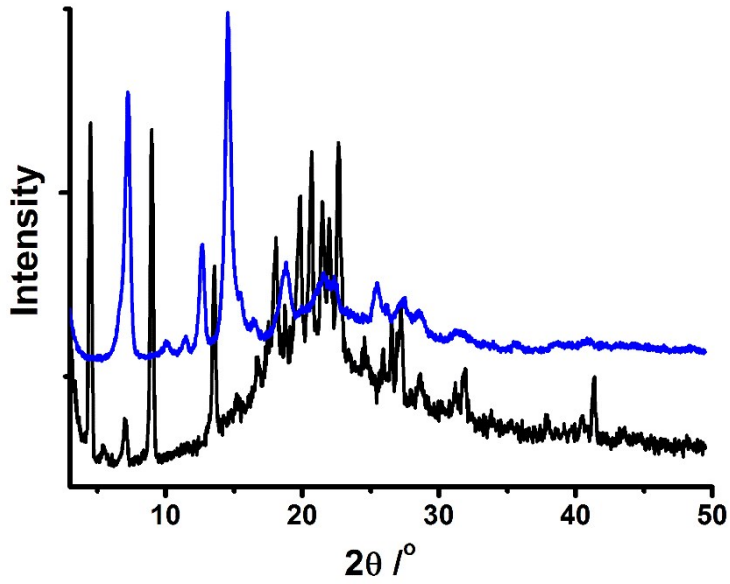


Figure S10. Powder X-ray diffraction profile of as-synthesized HOF-10a (blue line) in comparison with a powder pattern of as-synthesized HOF-10 (black line).

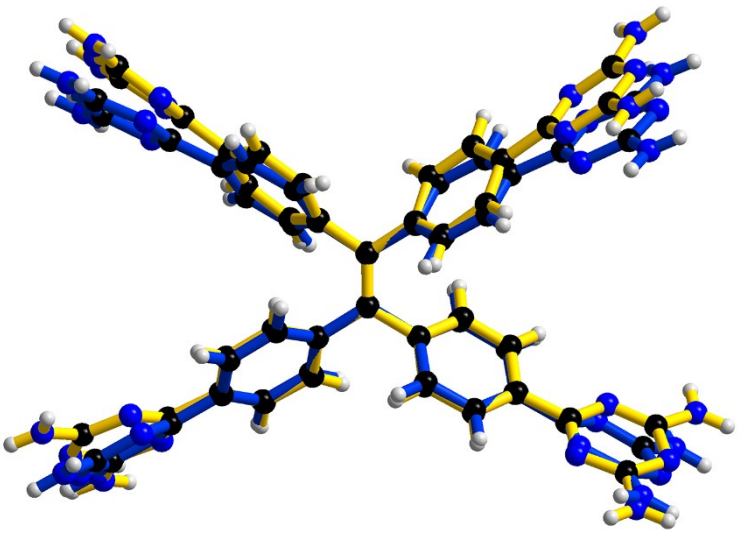


Figure S11. Comparison of DAT-TPE linkers in HOF-10 (yellow bond) and HOF-5 (blue bond) (carbon: black; hydrogen: white; nitrogen: blue).

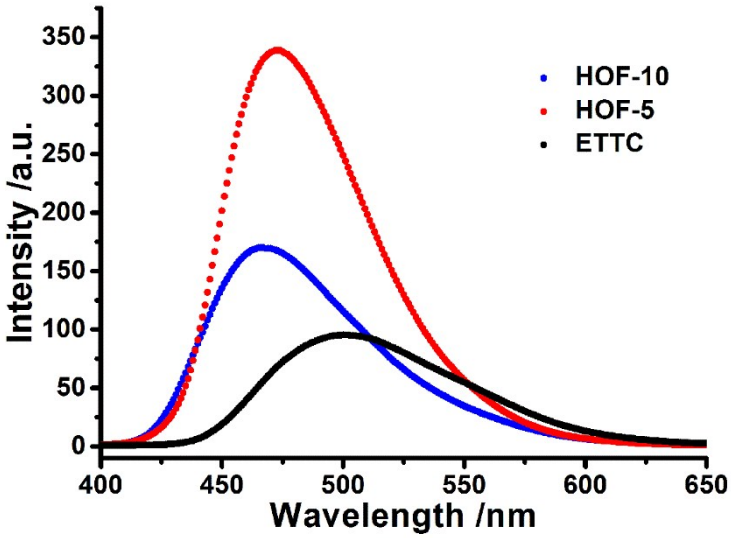


Figure S12. Fluorescence spectra of HOF-10, HOF-5, and ETTC at room temperature (excitation wavelength: 360 nm)

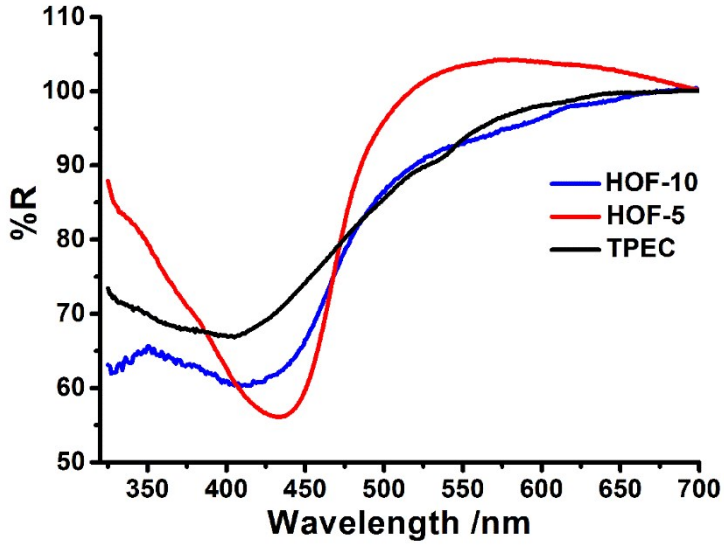


Figure S13. Diffused reflectance spectra of HOF-10, HOF-5, and ETTC at room temperature.

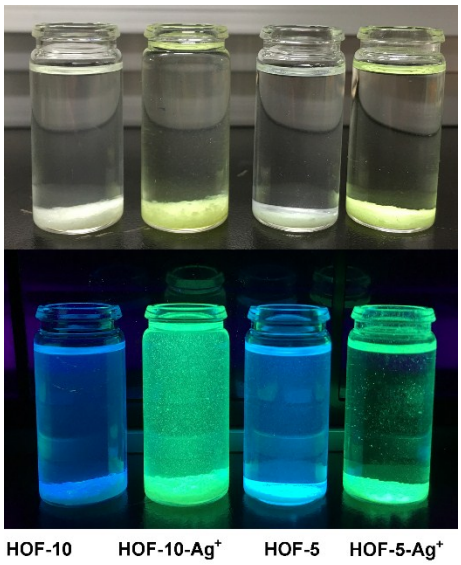


Figure S14. Digital photograph under sunlight (top) and UV irradiation at 365 nm (bottom).

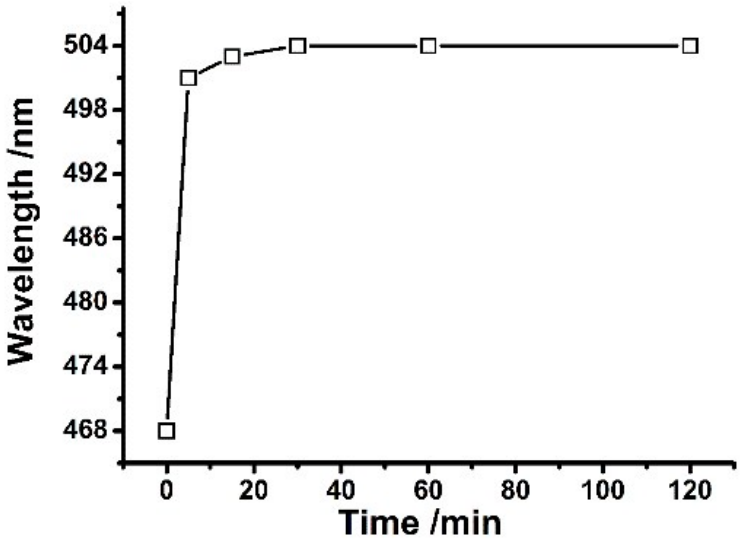


Figure S15. Maximum wavelength of emission peak of HOF-10 after immersion in Ag^+ solution for different time (excitation wavelength: 360 nm).

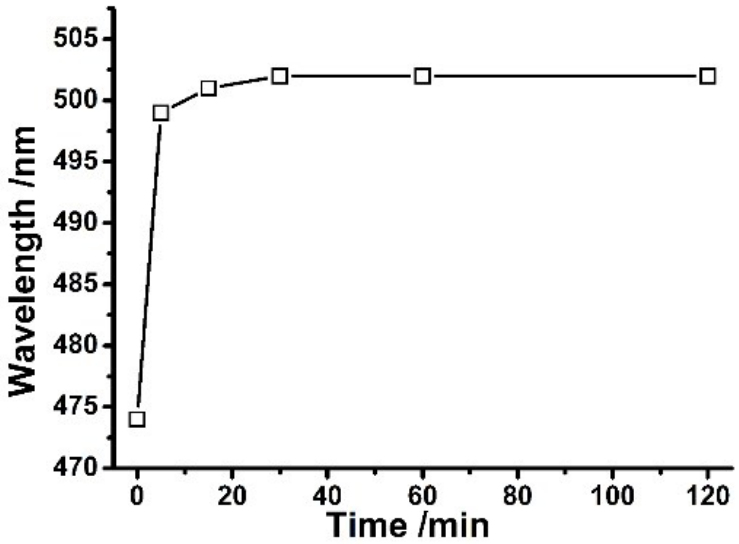


Figure S16. Maximum wavelength of emission peak of HOF-5 after immersion in Ag^+ solution for different time (excitation wavelength: 360 nm).

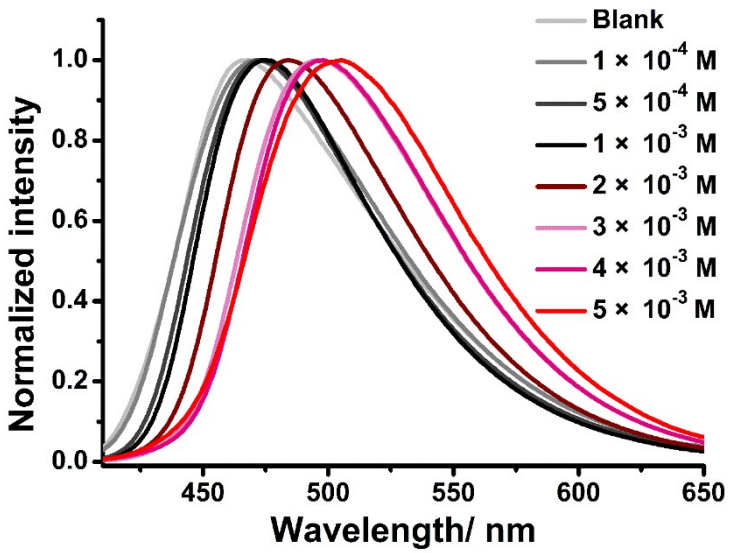


Figure S17. Emission spectra of HOF-10 after immersion in Ag^+ solution with different concentrations (excitation wavelength: 360 nm).

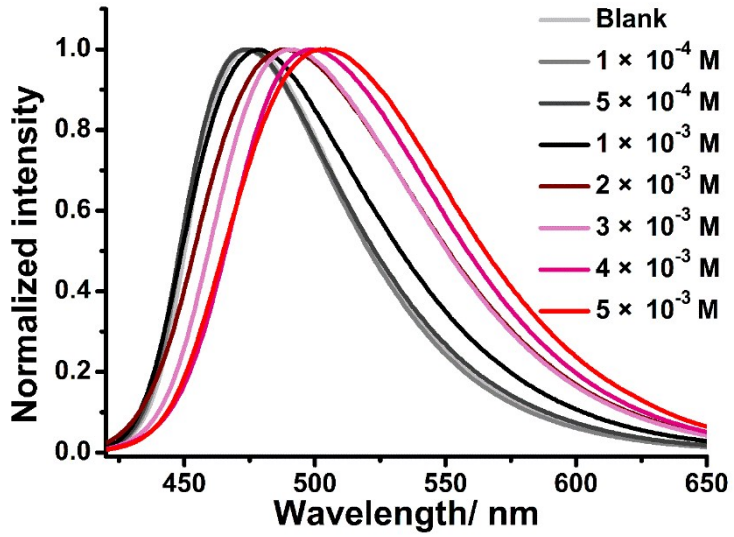


Figure S18. Emission spectra of HOF-5 after immersion in Ag^+ solution with different concentrations (excitation wavelength: 360 nm).

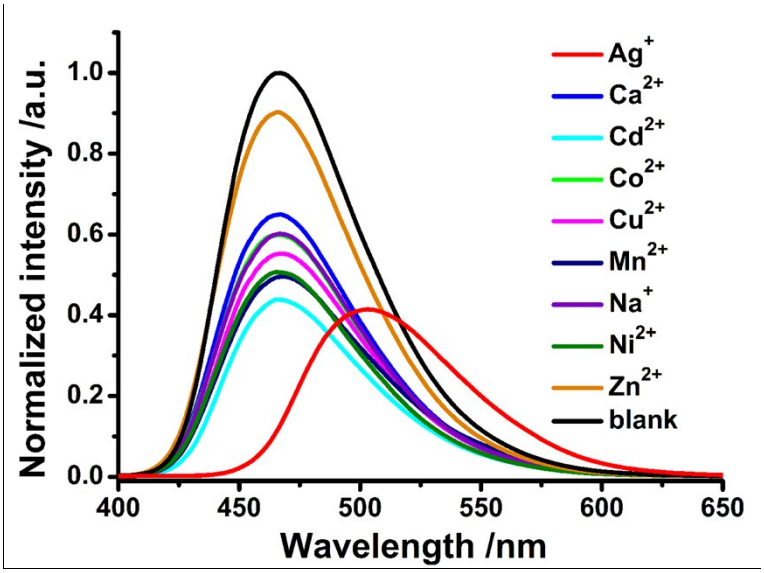


Figure S19. Fluorescence spectra (a) and digital photograph under UV irradiation (b) of as-made HOF-10 samples after treatment with THF/water solutions containing different metal ions.

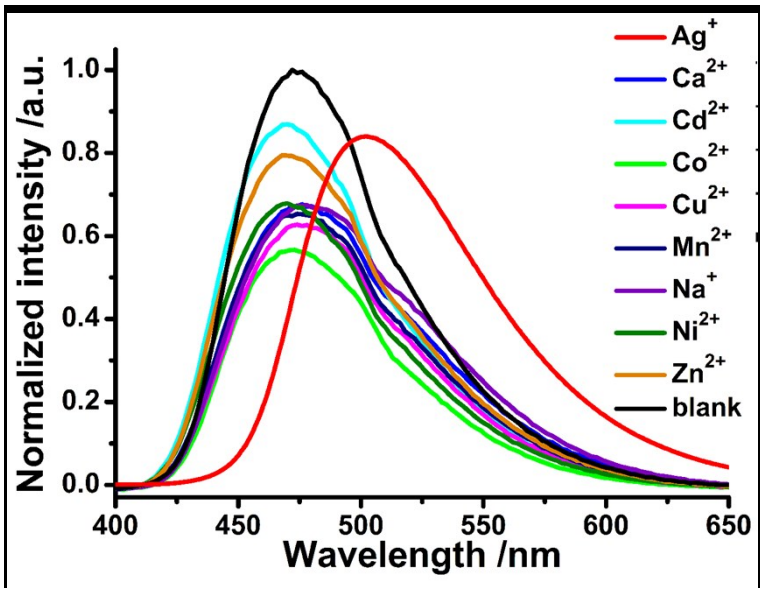


Figure S20. Fluorescence spectra (a) and digital photograph under UV irradiation (b) of as-made HOF-5 samples after treatment with THF/water solutions containing different metal ions.

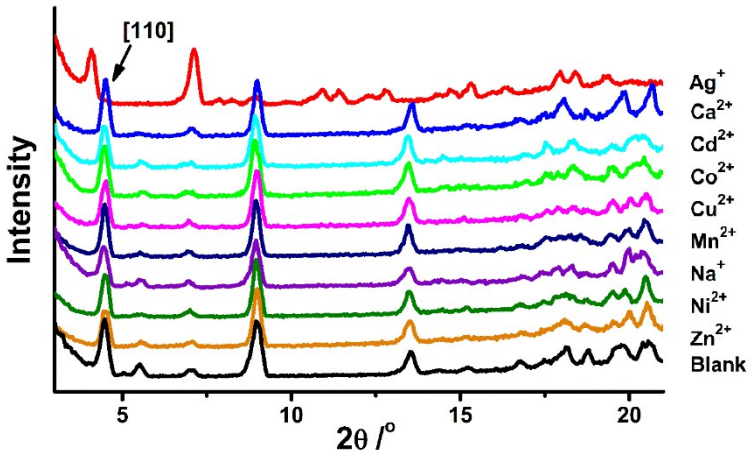


Figure S21. PXRD patterns of as-made HOF-10 samples after treatment with THF/water solutions containing different metal ions.

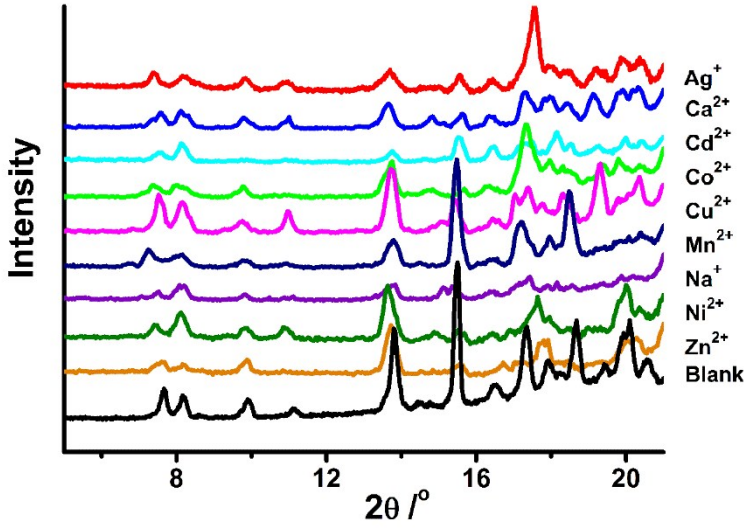


Figure S22. PXRD patterns of as-made HOF-5 samples after treatment with THF/water solutions containing different metal ions.

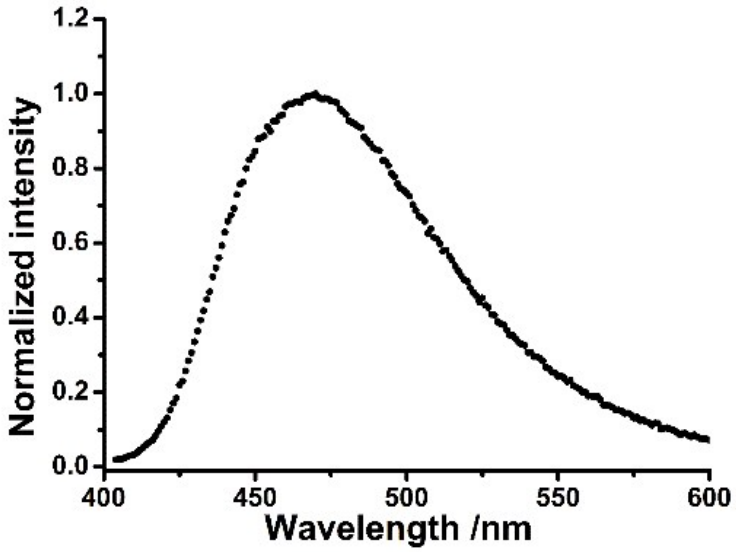
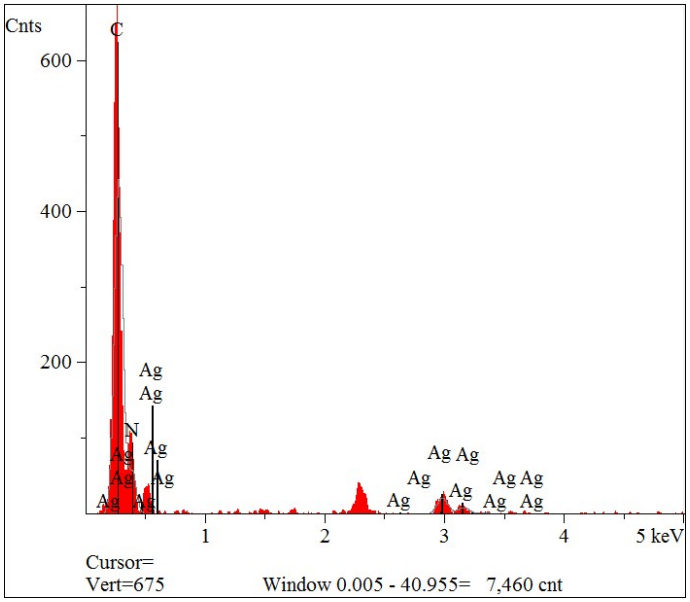
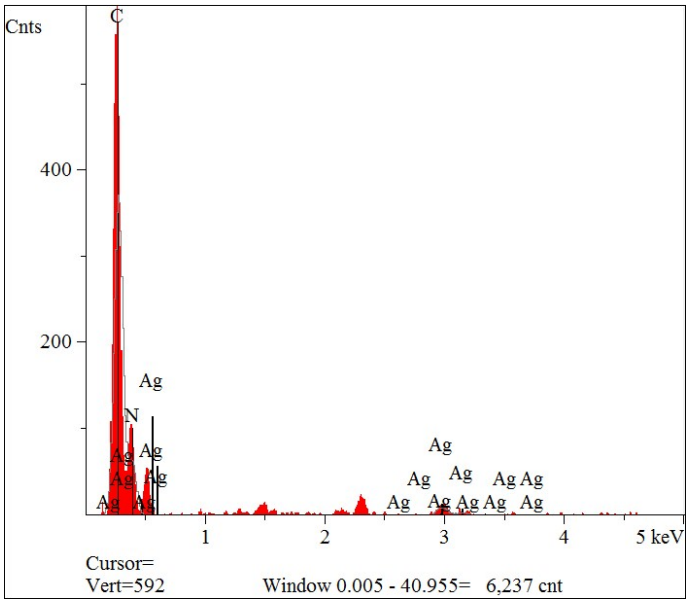


Figure S23. Fluorescence spectra of as-made HOF-5-Ag^+ sample after treatment with a THF/water solution containing KSCN (5.0 mM).



Element	Atomic %			
	1st	2nd	3rd	Average
C	53.246	49.559	50.504	51.103
N	42.955	45.647	46.490	45.031
Ag	3.799	4.793	3.005	3.866

Figure S24. Element Analysis for HOF-10-Ag^+ by EDX.



Element	Atomic %			
	1st	2nd	3rd	Average
C	52.531	52.683	48.000	51.071
N	46.123	46.338	50.253	47.571
Ag	1.346	0.979	1.747	1.358

Figure S25. Element Analysis for HOF-5-Ag^{+} by EDX.

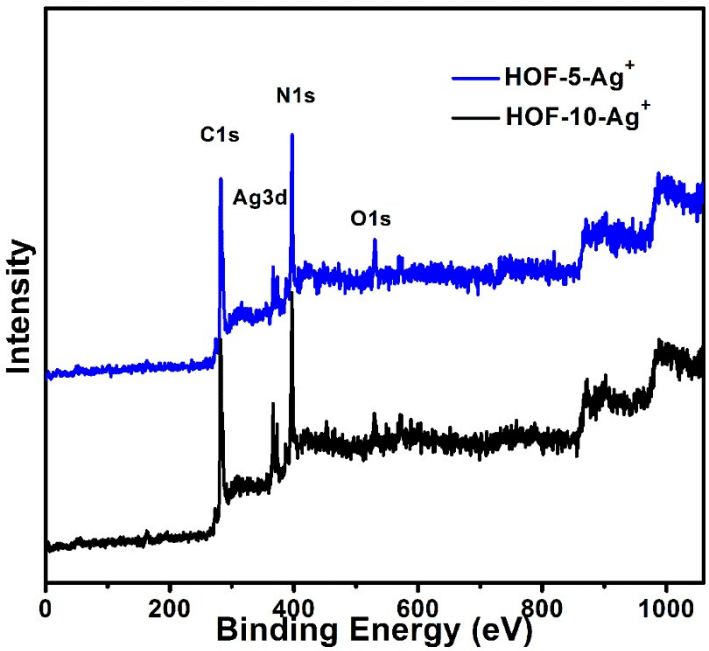


Figure S26. XPS spectra of Ag^{+}-incorporated HOFs.

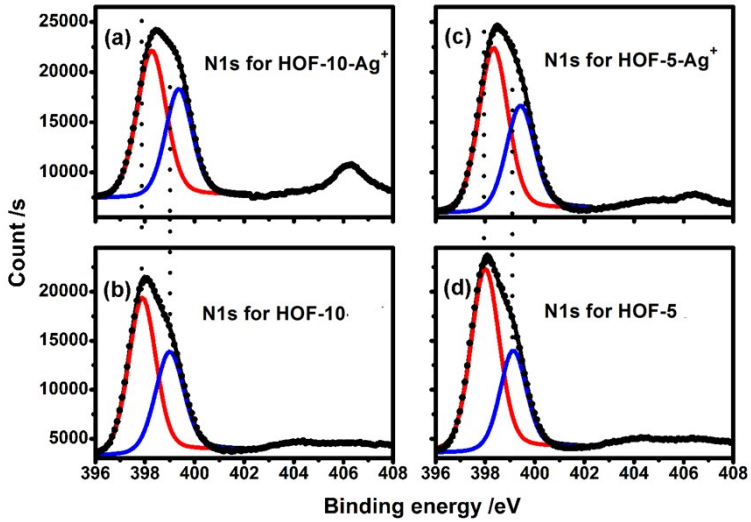


Figure S27. N1s XPS spectra of HOFs and Ag^+-treated HOFs (solid line represents fitting line, dotted straight line for comparison).

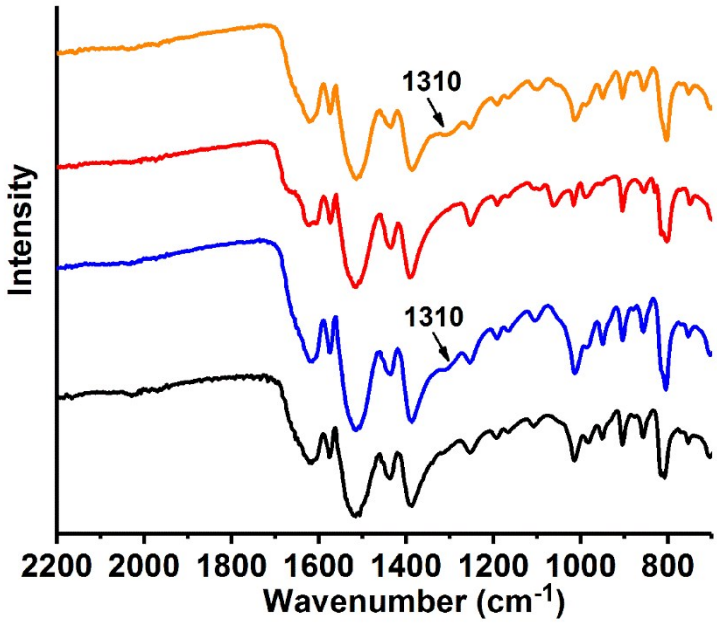


Figure S28. IR spectra of HOFs and Ag^+-treated HOFs (HOF-10: black, Ag^+-HOF-10: blue, HOF-5: red, Ag^+-HOF-10: yellow).

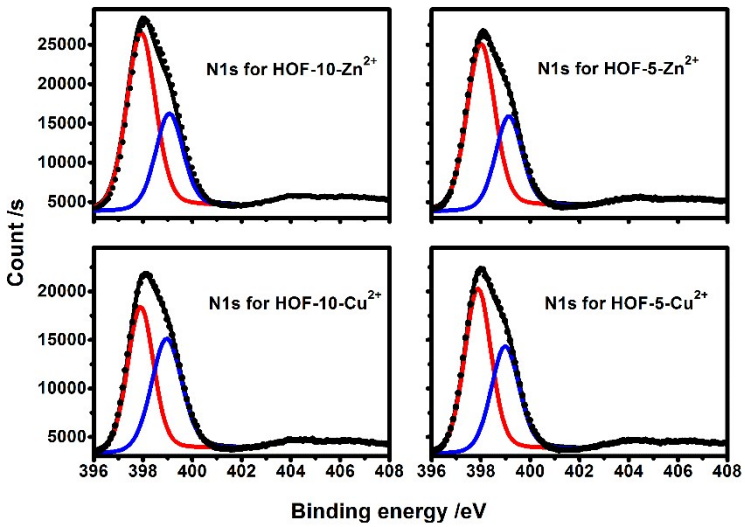


Figure S29. N1s XPS spectra of HOFs and metal-treated HOFs (solid line represents fitting line, dotted straight line for comparison).

Table S1. The crystallographic and refinement parameters for HOF-10 and HOF-5.

crystal data	HOF-10	HOF-5
system	monoclinic	monoclinic
space group	*C*2/c	*C*2/c
MF[a]	$C_{46}H_{56}N_{20}O_4S_4$	$C_{62}H_{84}N_{22}O_7S$
FW[a]	1081.35	1281.57
a /Å	34.2654(9)	21.6470(5)
b /Å	22.1261(9)	22.0832(5)
c /Å	9.8254(3)	14.1759(3)
α /°	90	90
β /°	105.358(2)	92.692(2)
γ /°	90	90
volume /Å^3	7183.2(4)	6769.1(3)
Z	4	4
density /g/cm^3	1.000	1.258
solvent-accessible[4] void space /%	55.2	56.6
theoretical pore volume /cm^3/g	0.78[b]	0.75[b]
refinement parameters	R_1 = 0.0819 [c] wR_2 = 0.2344[d]	R_1 = 0.1243 [c] wR_2 = 0.3846 [d]

[a] Molecular formula (MF) and formula weight (FW) were calculated based on the crystal structures after using the Platon/Squeeze program; [b]Calculated based on the HOF crystal structures using PLATON software; [c] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [d] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Comparison of the hydrogen bonding interactions and close contact in the crystal structures of HOFs and activated phases.

D-H···A	distance of D···A (Å)	angle of D-H···A (o)
HOF-10		
N1−H1A···O1#1	2.919	159.70
N1-H1B···O2#2	2.866	152.70
N2−H2A···N10#3	3.023	149.41
N2−H2B···N8#4	3.178	153.77
N6−H6A···O1#5	2.899	139.49
N6−H6B···O2#6	2.958	159.17
N7−H7A···N3#7	2.981	177.14
HOF-5		
N4-H4A···N7#1	2.924(4)	175.8
N4-H4B···N6#2	2.986(4)	176.3
N5-H5B···N3#3	3.030(5)	153.8
N9-H9A···N2#4	3.193(4)	166.8
N9-H9B···N1#2	3.385(4)	160.5
N10-H10B···O6	2.873(5)	144.0
N5-H5A···O7	2.856(8)	165.1

Symmetric code for HOF-10, #1: -x+1/2, y-1/2, -z+3/2, #2: -x+1/2, -y+1/2, #3: -z+1, -x+1, -y, -z+1, #4: x - 1/2, y - 1/2, z - 1, #5: -x+1, y, -z+3/2, #6: -x+1, -y+1, -z+1, #7: x+1/2, y+1/2, z+1. For HOF-5, #1: 1.5-x, 0.5+y, 1.5-z, #2: 1.5-x, 1.5-y, 1-z, #3: 1-x, y, 1.5-z, #4: 1.5-x, -0.5 +y, 1.5-z.

Reference:

(1) H. Wang, B. Li, H. Wu, T.-L. Hu, Z. Yao, W. Zhou, S. Xiang and B. Chen, *J. Am. Chem. Soc.,* 2015, **137**, 9963.

(2) G. M.Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*. 2008, A**64**, 112

(3) (a) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr*. 2009, **65**, 148; (b) A. L. Spek, *J. Appl. Crystallogr*. 2003, **36**, 7.

(4) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, the Netherlands, 2005.