

## Supporting information

### **Impact of intermolecular packing on separation of chlorinated cyclic hydrocarbons by flexible hydrogen-bonded organic frameworks**

Siwen Hu, He Zhao Meng Liang, Rui Wang, Jingjun Hao, Pengchong Xue\*

Tianjin Key Laboratory of Structure and Performance for Functional Molecules,  
College of Chemistry, Tianjin Normal University, No. 393, Binshui West Road,  
Tianjin 300387, P. R. China

E-mail: [xuepengchong@126.com](mailto:xuepengchong@126.com); [hxyxpc@tjnu.edu.cn](mailto:hxyxpc@tjnu.edu.cn)

## Experimental

### Materials and Instrumentation

All reagents and solvents used in synthetic studies were commercially available and used as supplied without further purification.  $^1\text{H}$  NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer at 400 MHz and in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ . UV–Vis spectra were obtained on a Mapada UV-1800pc spectrophotometer. Fluorescence emission spectra were obtained on a Hitachi F-4700 Luminescence Spectrophotometer. The thermal properties of crystals were evaluated using a thermogravimetric analysis (TGA) with a differential thermal analysis instrument (TA Instruments Q-50) over the temperature range from 20 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C  $\text{min}^{-1}$ . Powder XRD spectra were measured on a Bruker D8 Advance X-ray diffraction instrument equipped with graphite-monochromatized  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), by employing a scanning rate of 0.0261 ° $\text{s}^{-1}$  in the  $2\theta$  range from 5° to 30°.

### Theory calculation

Geometrical optimization was performed by density functional theory (DFT) calculations at the B3LYP/6-311G(d) level with the Gaussian 09W program package. Electronic transitions were carried out by TD-DFT calculations at the B3LYP/6-311G(d) level. Optimized PTTCN was used to calculate MPI, density maxima and minima, and areas of polar and nonpolar section in Multiwfn software (version 3.8).<sup>1</sup>The polar and nonpolar surface is the parts whose absolute value of electrostatic potential is greater than or less than 10 kcal/mol, and the non-polar surface area of molecules, that is, the part whose absolute value of electrostatic potential is less than 10 kcal/mol, is the non-polar surface. Hirshfeld surface and fingerprint plots and were obtained in CrystalExplorer17<sup>2</sup> and the cif file of X-HOF-6, X-HOF-6a, X-HOF-7 and X-HOF-7a was used to confirm the atomic coordinates. Intermolecular interaction energy was obtained at the B3LYP/6-31G(d,p) level in CrystalExplorer17. Adsorption energies of

CIBz and ClCy on the surface of X-HOF-6a were obtained in Materials Studio 2017. The (0 1 1) plane was selected the exposed plane to adsorb one molecule and adsorption locator was used to estimate adsorption location and adsorption energy. Compass II force field was used.

### **Gas chromatography**

GC measurements were carried out using an Agilent 7890B instrument configured with an FID detector and a 19091J-413 column (30 m × 320 μm × 0.25 μm). Samples were analyzed using headspace injections and were performed by incubating the sample at 55 °C for 3 min followed by sampling 100 μL of the headspace. Injection and detector temperature was 300 °C with nitrogen. Firstly, the gas chromatography analysis of mixtures containing CIBz and ClCy in varying proportions was conducted, followed by the construction of a calibration curve. Each sample underwent three replicates, from which an average value was obtained for accurate determination of CIBz content based on the established calibration curve.

### **Preparation and analysis of single crystals**

**X-HOF-6 and X-HOF-7:** PTTCN (10 mg) was firstly dissolved in CIBz or ClCy (2.0 mL) under heating, and then the solution was slowly cooled to room temperature and left for 12 hours to obtain X-HOF-6 or X-HOF-7.

**X-HOF-7a:** PTTCN (20 mg) was firstly dispersed in 0.3 mL of ClCy and the mixture was heated at 80 °C, and then yellow as-synthesized solids partially dissolved, and the remaining solids gradually transformed into large crystals, X-HOF-7a.

X-ray diffraction analysis was performed on a Bruker SMART APEX II CCD-based diffractometer with graphite-monochromated Mo K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and Cu K<sub>α</sub> ( $\lambda = 1.54184 \text{ \AA}$ ) using the  $\varphi$ - $\omega$  scan technique. Multi-scan absorption corrections were applied with the SADABS program. The structure was solved by ShelXT method and refined on F2 by fullmatrix least squares using the SHELXTL-2015 program<sup>3</sup> in Olex2.<sup>4</sup> CCDC 2323075, 2323074 and

2341368 contain the crystallographic data for X-HOF-6, X-HOF-7 and X-HOF-7a. Small crystals of X-HOF-6 were obtained by fast cooling of the hot dense ClBz solution, and small crystals of X-HOF-7 were gained after large X-HOF-7 crystals were treated in ultrasonic bath for 30 min.

#### **Adsorption experiment of X-HOF-6a and X-HOF-7a**

The small crystals (X-HOF-6 or X-HOF-7, 100 mg) in an open 5 mL weighted vial were firstly heated at 180 °C or 140 °C for 5 h to remove ClBz or ClCy, and NMR spectrum confirmed that the activated crystal did not contain ClBz or ClCy. The vial was weighted to obtain the mass of activated HOFs. Then, the small vial was placed in a sealed 20 mL vial containing 5 mL of ClBz, ClCy or ClBz/ClCy (V/V = 0.44/0.56) mixture. The sample was kept at 25 °C. After a period of fuming, the small vial was taken out of the large vial and weighed. After 24 hours of fuming, 2.0 mg of solid was taken out for the measurement of <sup>1</sup>H NMR and gas chromatography. Before measurements, the crystals were air-dried for 30 min to remove the surface-physically adsorbed molecules.

#### **Recycle experiment of X-HOF-6a**

After adsorbing for 24 h, 2.0 mg of solid was taken out for <sup>1</sup>H NMR spectroscopy, and then the remaining solid was heated at 180 °C for 5 hours and then exposed to vapor mixture. After 24 hours, the NMR and gas chromatography of fumed solid (2.0 mg) were measured again. This process is repeated several times to obtain reuse data for the samples.

#### **Reference**

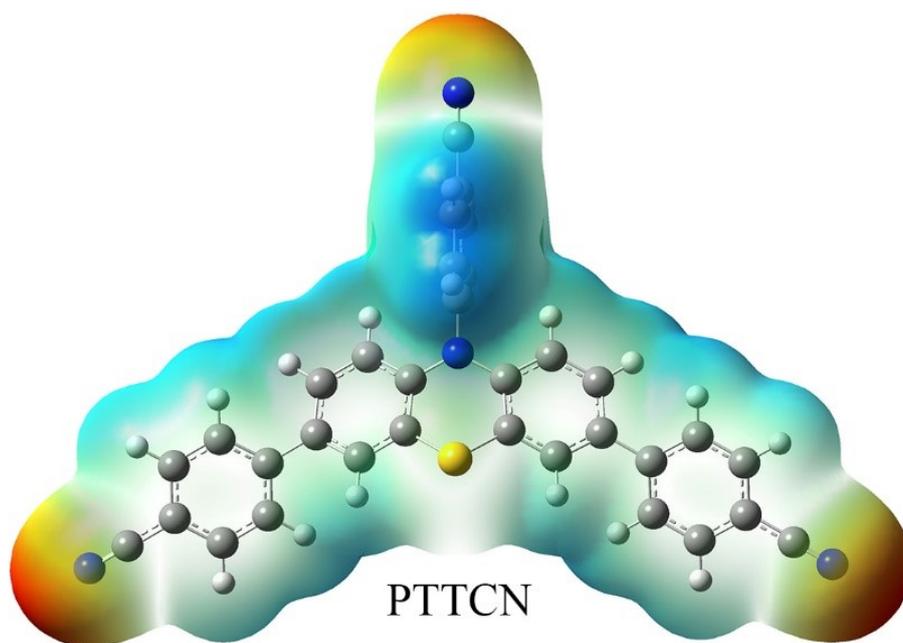
- 1 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.
- 2 P. R. Spackman, M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, D. Jayatilaka and M. A. Spackman, *J. Appl. Cryst.*, 2021, **54**, 1006–1011.
- 3 G. M. Sheldrick, *Acta Crystallogr. Sect. A.*, 2015, **71**, 3–8.
- 4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.



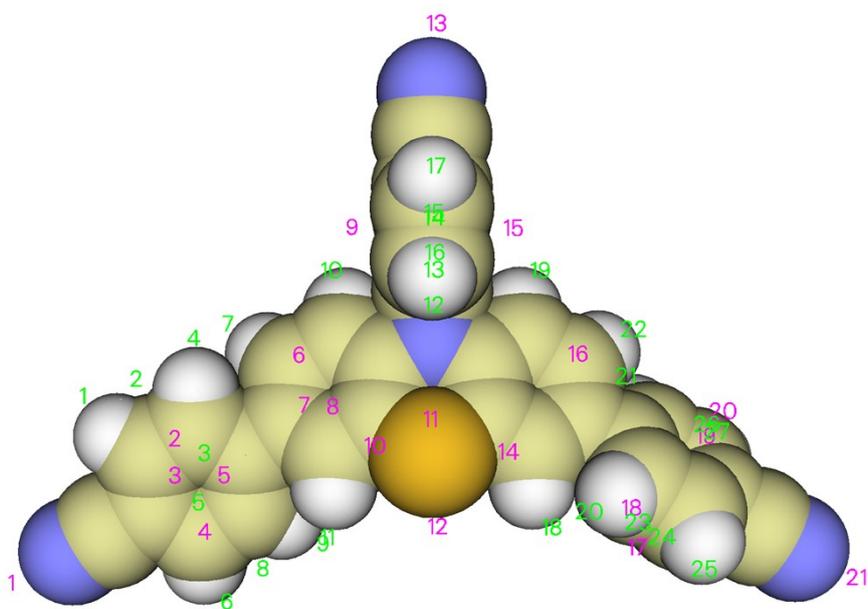
**Table S1.** Dipole moment, MPI and areas of nonpolar and polar sections.

	Dipole moment (Dedye)	MPI <sup>a</sup> (Kcal/mol)	A <sub>nonpolar</sub> (Å <sup>2</sup> ) (content) <sub>b</sub>	A <sub>nonpolar</sub> (Å <sup>2</sup> ) (content) <sup>c</sup>
ClCy	3.2450	9.48199	97.90 (60.17 %)	64.80 (39.83 %)
ClBz	2.4332	8.87832	84.31 (57.84 %)	61.44 (42.16 %)
PTTCN	2.982	13.44	312.47 (41.01%)	217.27 (58.99%)

<sup>a</sup> molecular polarity index, <sup>b</sup> the nonpolar and <sup>c</sup> polar surfaces are the parts whose absolute value of electrostatic potential is less than or greater than 10 kcal/mol.



**Figure S1.** Electrostatic potential of PTTCN.



**Figure S2.** PTTCN structure with density maxima (green) and minima (pink).

**Table S2.** Maximal and minimal density on the surface of PTTCN.

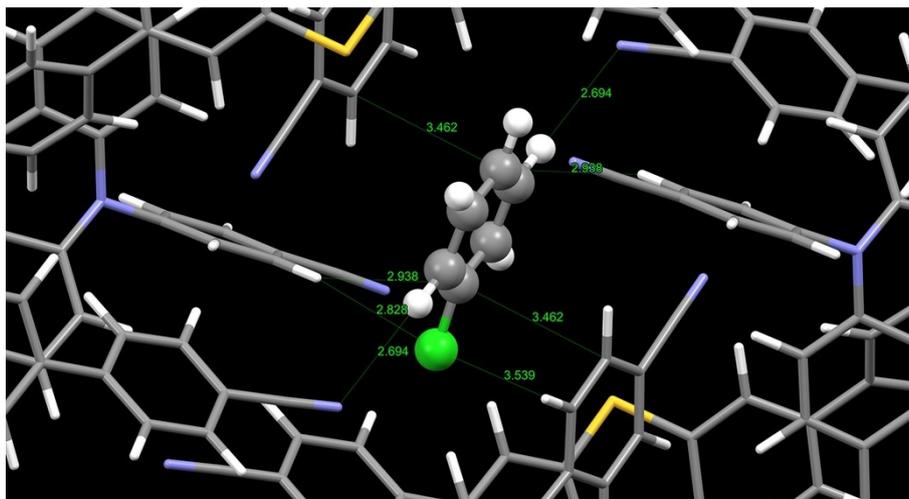
Position (blue)	Estimated density (Kcal/mol)	Position (red)	Estimated density (Kcal/mol)
1	<b>-38.429209</b>	1	23.341589
2	-0.789752	2	23.306615
3	-1.731053	3	0.708629
4	-1.086938	4	26.255836
5	-1.567105	5	0.512940
6	-0.304691	6	23.010211
7	-0.666946	7	26.388301
8	-0.759899	8	22.870712
9	9.292005	9	25.012284
10	-0.017959	10	26.841330
11	-7.284242	11	24.726741
12	-3.569282	12	32.419449
13	<b>-32.479343</b>	13	29.138542
14	-1.037084	14	29.997138
15	9.078254	15	31.609109
16	-1.174977	16	32.395048
17	-1.008992	17	29.971255
18	-1.623152	18	25.446469
19	-1.589698	19	26.915504
20	-0.798956	20	25.776333
21	<b>-38.342668</b>	21	26.609955
		22	26.452055
		23	0.608738
		24	23.075612
		25	23.154929
		26	0.736718
		27	23.522480

**Table S3.** Single crystal data of X-HOF-6.

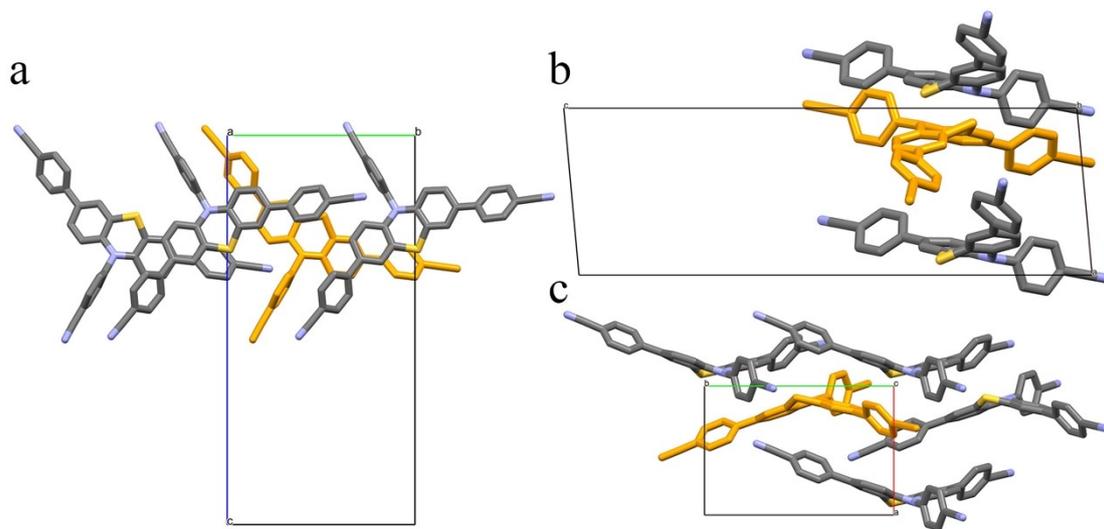
<b>Identification code</b>	X-HOF-6
<b>Empirical formula</b>	C <sub>72</sub> H <sub>41</sub> ClN <sub>8</sub> S <sub>2</sub>
<b>Formula weight</b>	1117.70
<b>Temperature/K</b>	298
<b>Crystal system</b>	monoclinic
<b>Space group</b>	P2 <sub>1</sub> /c
<b>a/Å</b>	8.6523(3)
<b>b/Å</b>	12.5805(4)
<b>c/Å</b>	26.3390(9)
<b>α/°</b>	90
<b>β/°</b>	95.197(3)
<b>γ/°</b>	90
<b>Volume/Å<sup>3</sup></b>	2855.22(17)
<b>Z</b>	2
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	1.300
<b>μ/mm<sup>-1</sup></b>	1.686
<b>F(000)</b>	1156.0
<b>Crystal size/mm<sup>3</sup></b>	0.23 × 0.21 × 0.2
<b>Radiation</b>	Cu K <sub>α</sub> (λ = 1.54184)
<b>2θ range for data collection/°</b>	6.74 to 146.174
<b>Index ranges</b>	-10 ≤ h ≤ 10, -15 ≤ k ≤ 10, -22 ≤ l ≤ 32
<b>Reflections collected</b>	10972
<b>Independent reflections</b>	5541 [R <sub>int</sub> = 0.0221, R <sub>sigma</sub> = 0.0281]
<b>Data/restraints/parameters</b>	5541/13/379
<b>Goodness-of-fit on F<sup>2</sup></b>	1.046
<b>Final R indexes [I ≥ 2σ (I)]</b>	R <sub>1</sub> = 0.0489, wR <sub>2</sub> = 0.1385
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0597, wR <sub>2</sub> = 0.1497
<b>Largest diff. peak/hole / e Å<sup>-3</sup></b>	0.47/-0.40

**Table S4.** Single-crystal data of X-HOF-7.

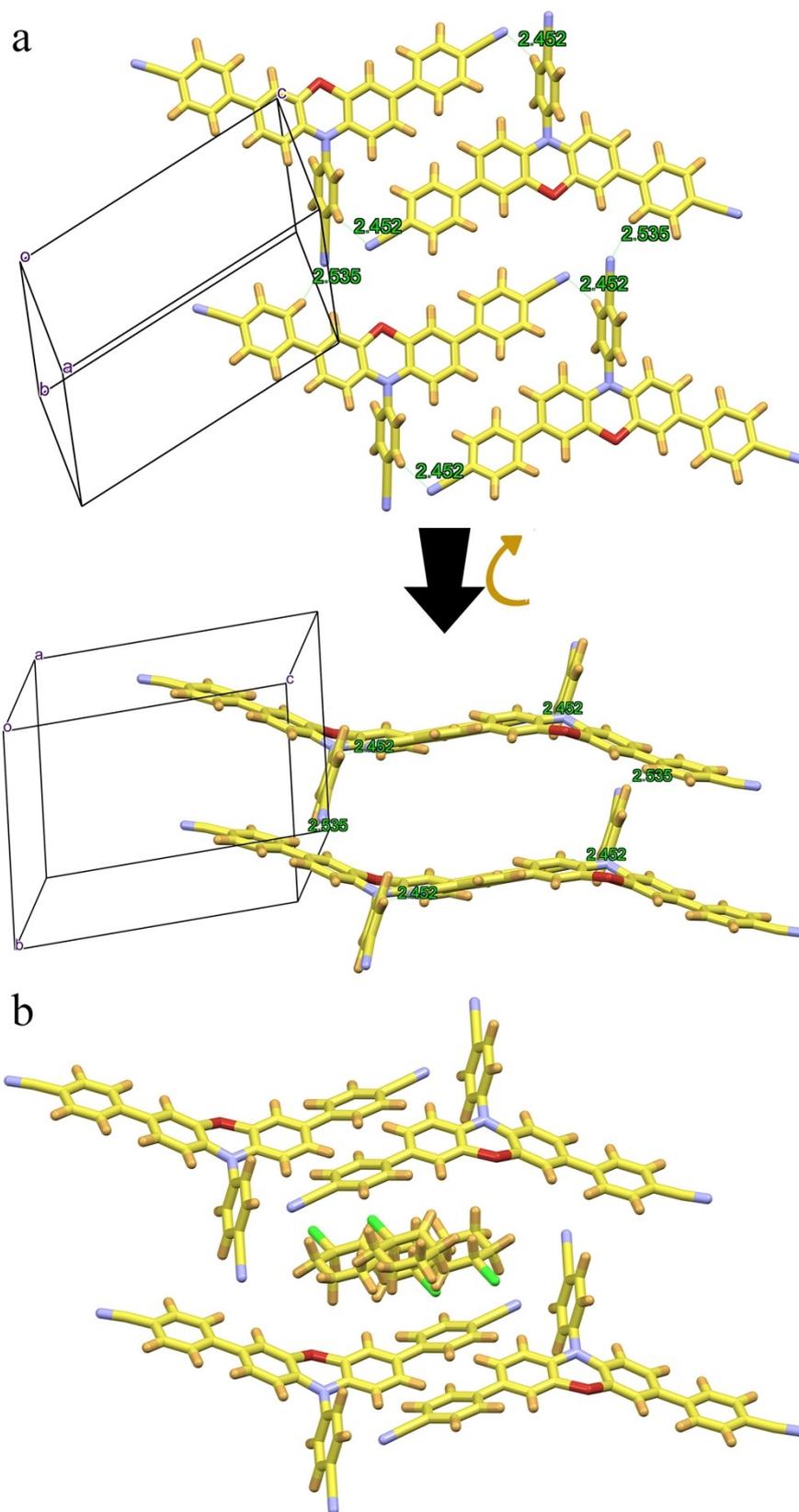
Identification code	X-HOF-7
Empirical formula	C <sub>39</sub> H <sub>28</sub> ClN <sub>4</sub> S
Formula weight	621.16
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	9.141(3)
b/Å	11.626(4)
c/Å	16.239(6)
α/°	102.613(6)
β/°	100.303(7)
γ/°	98.033(7)
Volume/Å <sup>3</sup>	1628.1(10)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.265
μ/mm <sup>-1</sup>	0.216
F(000)	646.0
Crystal size/mm <sup>3</sup>	0.34 × 0.24 × 0.21
Radiation	MoK <sub>α</sub> (λ = 0.71073)
2θ range for data collection/°	3.654 to 49.994
Index ranges	-10 ≤ h ≤ 9, -13 ≤ k ≤ 13, -19 ≤ l ≤ 18
Reflections collected	7117
Independent reflections	4988 [R <sub>int</sub> = 0.0691, R <sub>sigma</sub> = 0.1519]
Data/restraints/parameters	4988/270/346
Goodness-of-fit on F2	1.369
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.3440, wR <sub>2</sub> = 0.7106
Final R indexes [all data]	R <sub>1</sub> = 0.4079, wR <sub>2</sub> = 0.7254
Largest diff. peak/hole / e Å <sup>-3</sup>	1.66/-1.05



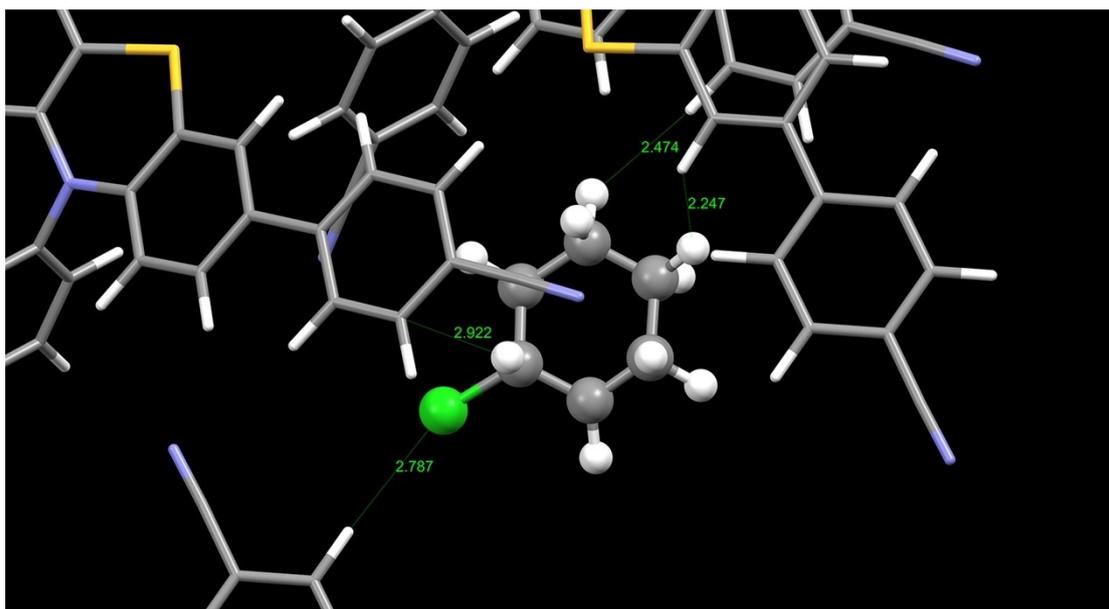
**Figure S3.** Intermolecular weak interactions between CIBz and PTTCN.



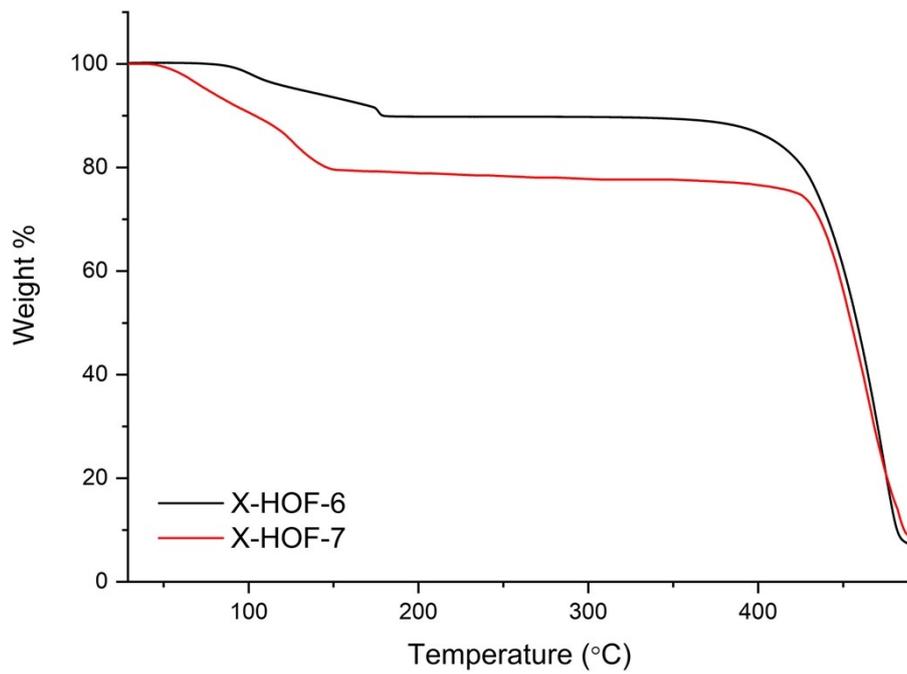
**Figure S4.** Intermolecular  $\pi$ -stacking in view of in X-HOF-6.



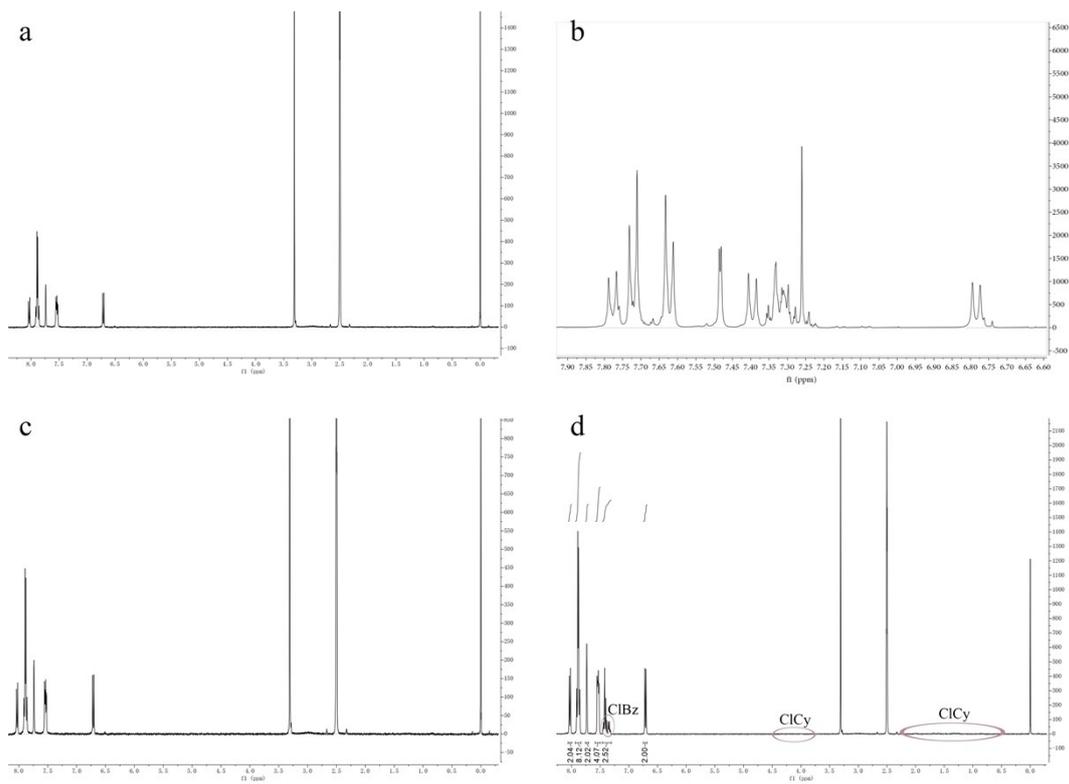
**Figure S5.** (a) Intermolecular packing with a pore, and (b) the pore with four ClCy molecules.



**Figure S6.** Intermolecular weak interactions between ClCy and PTTCN.



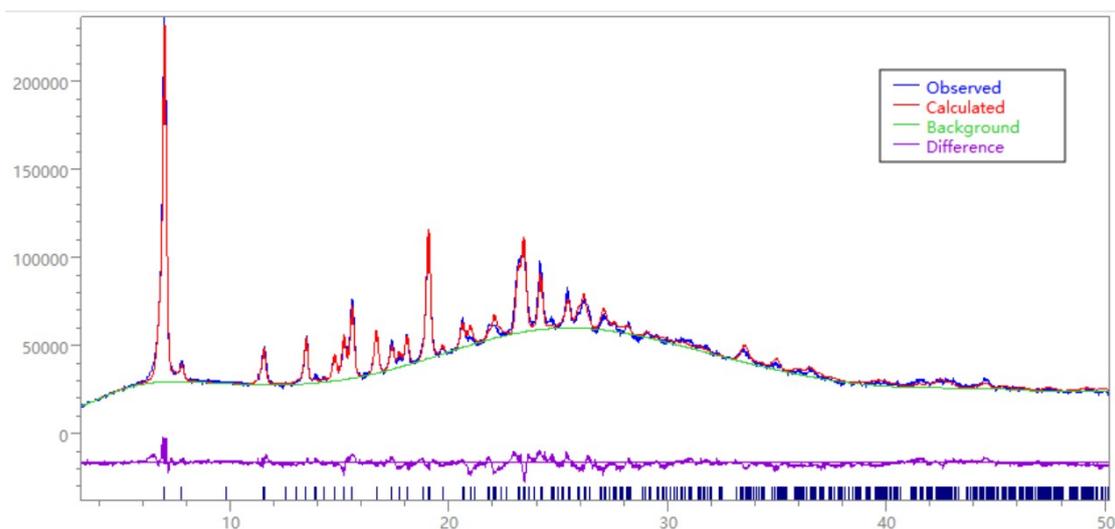
**Figure S7.** TG curves of X-HOF-6 and X-HOF-7.



**Figure S8.**  $^1\text{H}$  NMR spectra of (a) X-HOF-6a, X-HOF-6a upon exposure to (b) CIBz vapor, (c) ClCy vapor, and (d) the mixed vapors of CIBz and ClCy for 24 h.

### Structure solution of X-HOF-6a

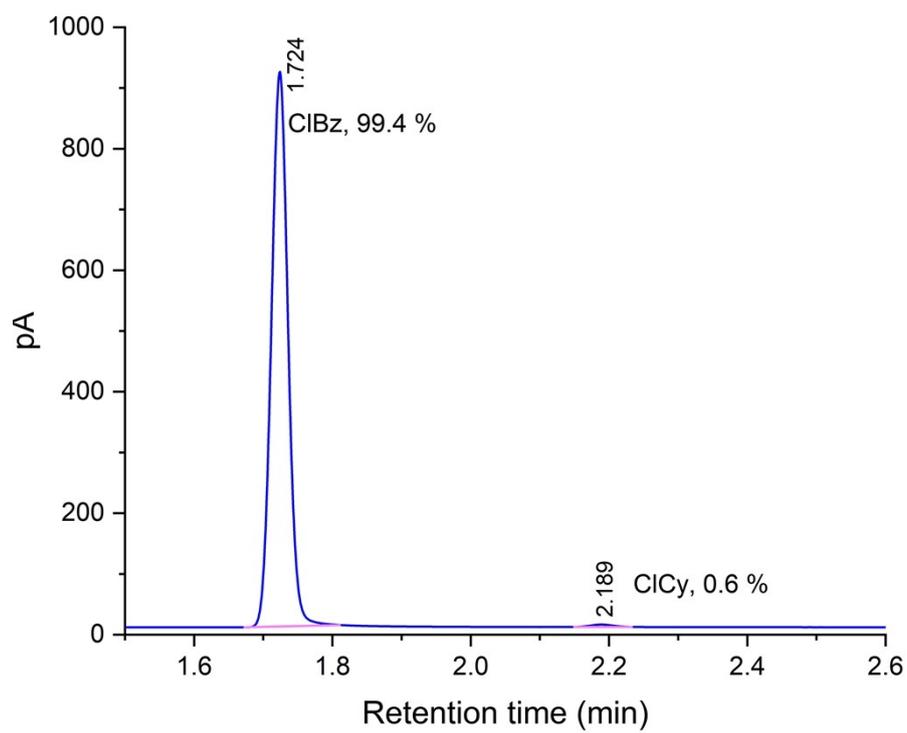
Structure solution was performed in EXPO2014. Structure determination is a four-step process. First step is indexing to determine the space system, and then the solution for packing was performed using a molecular conformation (torsion angles and bond angles could be adjusted during searching stacking model) in X-HOF-6. The method is simulated annealing, and times are 10 times. Finally, the structure was refined by Rietveld refinement. As a result, a best space group,  $P2_1/c$  was obtained after considering the molecular volume (a molecule has a volume of  $621.55 \text{ \AA}^3$ . The unit cell parameters are  $a = 8.03734 \text{ \AA}$ ,  $b = 12.75308 \text{ \AA}$ ,  $c = 26.59923 \text{ \AA}$ ,  $\beta = 107.451^\circ$ , cell volume is  $2600.961 \text{ \AA}^3$ . The simulated PXRD pattern is in good agreement with the experimental pattern (Figure S9,  $R_p = 3.24\%$ , and  $wR = 3.831\%$ ). The atom coordinates are listed in Table S8.



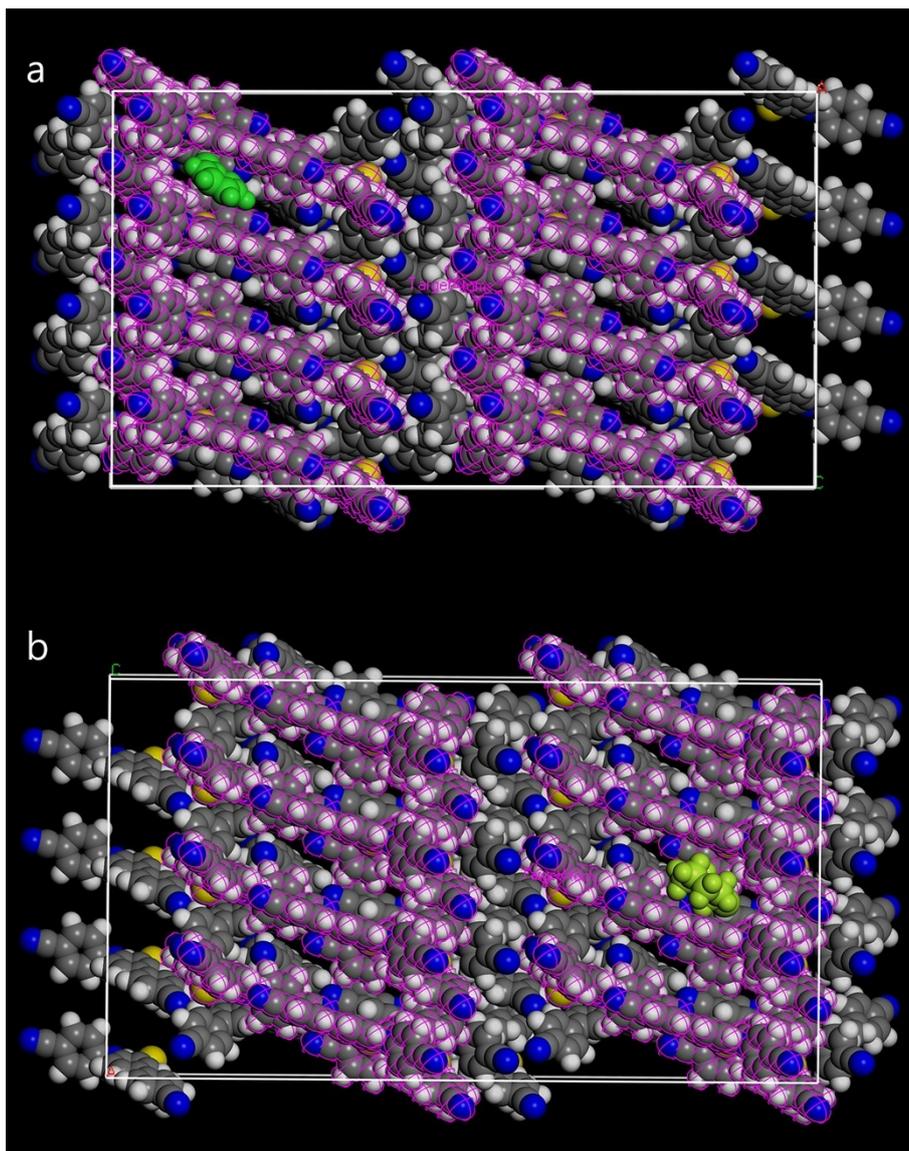
**Figure S9.** Experimental and simulated XRD patterns of X-HOF-6a.

**Table S5.** Atom coordinates in X-HOF-6a.

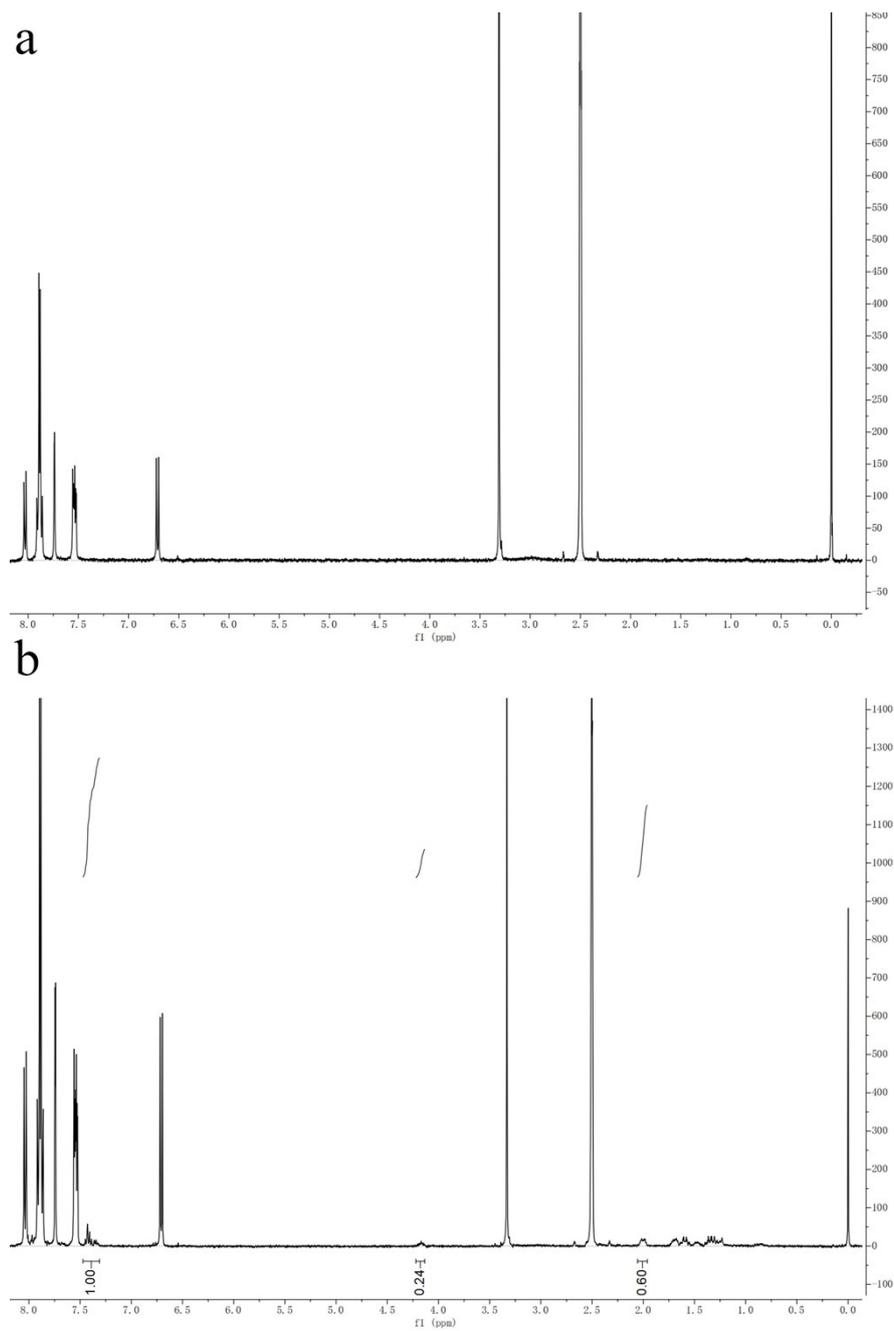
Atom	number	X	Y	Z
N	N1	0.5493	1.1254	0.3285
S	S1	0.0614	0.4114	0.1971
N	N2	0.1892	0.0206	0.5228
N	N3	0.25	-0.1714	-0.0413
C	C1	0.5092	1.0395	0.3267
N	N4	0.1442	0.2911	0.2994
C	C2	0.4621	0.9301	0.3252
C	C3	0.5259	0.8604	0.2951
C	C4	0.477	0.7566	0.2926
C	C5	0.3643	0.7198	0.3195
C	C6	0.3058	0.79	0.3507
C	C7	0.3539	0.8942	0.3533
C	C8	0.3037	0.6093	0.3135
C	C9	0.3176	0.5486	0.3579
C	C10	0.2678	0.4441	0.3537
C	C11	0.1982	0.3972	0.3048
C	C12	0.1785	0.4592	0.2599
C	C13	0.2352	0.5626	0.2646
C	C14	0.1229	0.2784	0.206
C	C15	0.1551	0.2315	0.2553
C	C16	0.196	0.1254	0.2598
C	C17	0.2038	0.0681	0.2165
C	C18	0.1735	0.114	0.1676
C	C19	0.1324	0.2206	0.1627
C	C20	0.1506	0.233	0.3464
C	C21	0.0006	0.2131	0.3603
C	C22	0.0099	0.1593	0.4062
C	C23	0.1712	0.1263	0.4385
C	C24	0.3212	0.1473	0.4248
C	C25	0.3109	0.2006	0.3786
C	C26	0.1818	0.0686	0.4862
C	C27	0.1827	0.0508	0.1217
C	C28	0.1663	0.0983	0.0737
C	C29	0.182	0.0407	0.0313
C	C30	0.2117	-0.0658	0.0365
C	C31	0.2285	-0.1144	0.0841
C	C32	0.2129	-0.0564	0.1261
C	C33	0.2311	-0.1254	-0.007



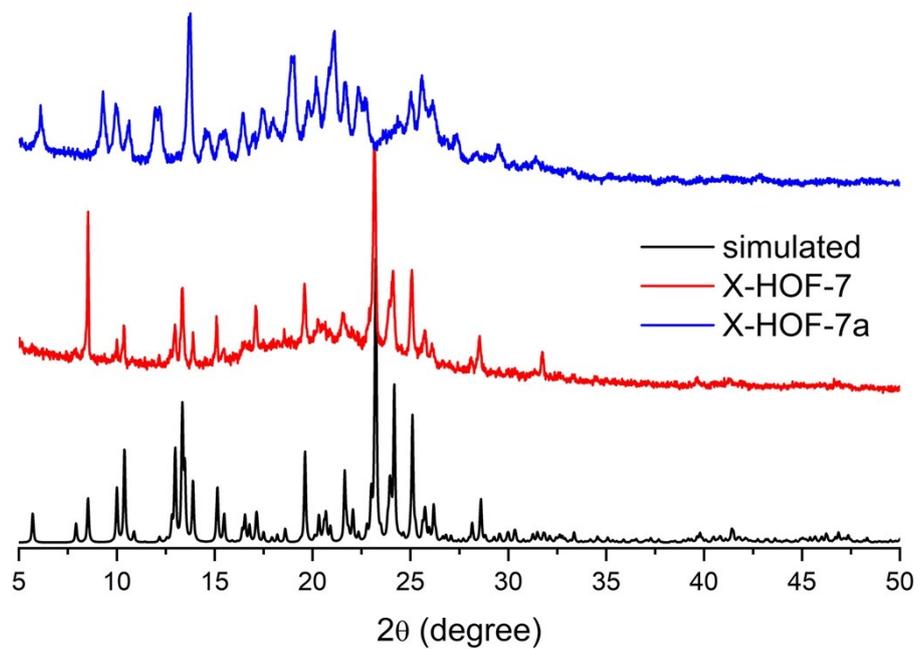
**Figure S10.** The gas chromatography of gas released by fumed X-HOF-6a after adsorbed for 24 h in 1:1 mixed vapor.



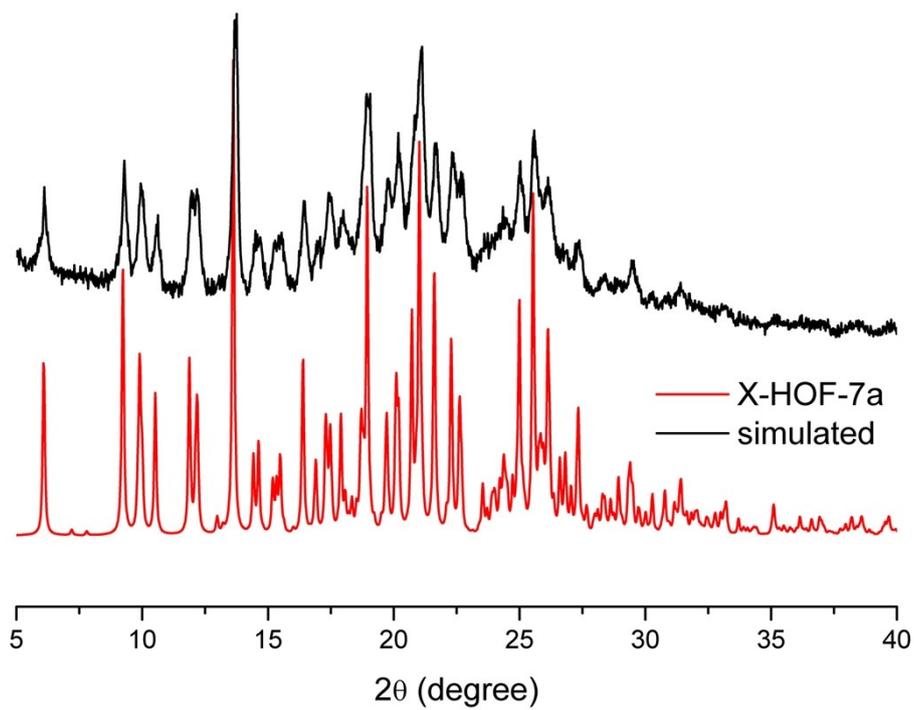
**Figure S11.** Intermolecular packing of cells with (a) ClBz and (b) ClCy. Cleaved surface is (0 1 1) because it has a largest exposure area. The adsorption energies for ClBz and ClCy are -21.57 and -21.73 Kcal/mol



**Figure S12.**  $^1\text{H}$  NMR spectra of X-HOF-7a (a) before and (b) after exposing the mixed vapor for 24 h.



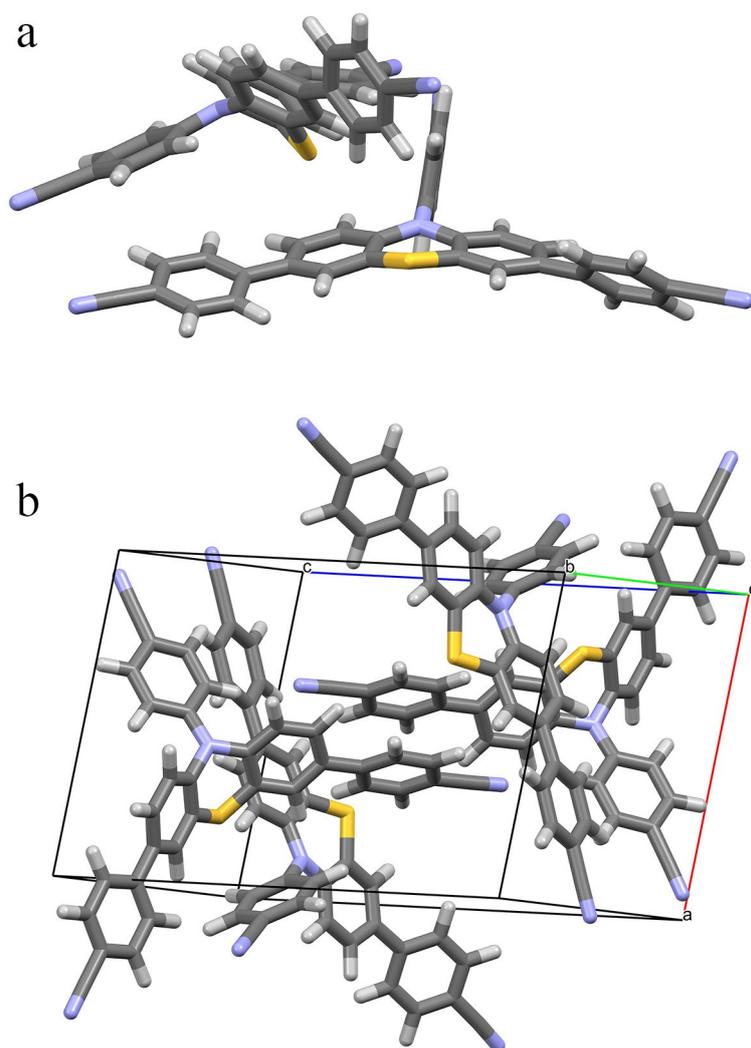
**Figure S13.** XRD patterns of X-HOF-7 and X-HOF-7a, and simulated XRD of X-HOF-7.



**Figure S14.** XRD pattern of X-HOF-7a and simulated XRD pattern of single crystals from ClCy at 80 °C.

**Table S6.** Single-crystal data of X-HOF-7a.

Identification code	X-HOF-7a
Empirical formula	C <sub>33</sub> H <sub>18</sub> N <sub>4</sub> S
Formula weight	484.68
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	11.468(5)
b/Å	15.320(7)
c/Å	15.391(8)
$\alpha$ /°	72.316(9)
$\beta$ /°	81.810(11)
$\gamma$ /°	86.230(10)
Volume/Å <sup>3</sup>	2549(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.263
$\mu/\text{mm}^{-1}$	0.155
F(000)	969.0
Crystal size/mm <sup>3</sup>	0.32 × 0.26 × 0.23
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	2.79 to 49
Index ranges	-13 ≤ h ≤ 12, -17 ≤ k ≤ 13, -16 ≤ l ≤ 17
Reflections collected	13139
Independent reflections	8211 [R <sub>int</sub> = 0.0639, R <sub>sigma</sub> = 0.1805]
Data/restraints/parameters	8211/0/685
Goodness-of-fit on F <sup>2</sup>	1.359
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.1732, wR <sub>2</sub> = 0.2199
Final R indexes [all data]	R <sub>1</sub> = 0.2555, wR <sub>2</sub> = 0.2392
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.26



**Figure S15.** Asymmetric unit of X-HOF-7a and intermolecular packing in one unit.