Supporting Information

Nanoporous In-MOF with Multiple One-Dimensional Pores

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Preparation of $(Et_2NH_2)[In(2,6\text{-}NDC)_2{\cdot}2H_2O{\cdot}DEF]$ (1)

$InCl_3$ (0.221 g, 1.0 mmol, Aldrich), 2,6-naphthalenedicarboxylic acid (0.432 g, 2.0 mmol, TCI), and 20 mL of *N*,*N*-diethylformamide (TCI) were sealed in a Teflon-lined high pressure bomb and heated at 130°C for 144 h. After slow cooling to room temperature, the colorless crystalline solids were retrieved by filtration and washed with diethylformamide. The as-made solids were immediately immersed in 20 mL of chloroform for the $CHCl_3$-exchanged sample. High quality colorless needles were chosen for the X-ray crystallography from the as-made sample.

X-ray Crystallography

The diffraction data for **1** were collected on a Bruker SMART AXS diffractometer using Mo Kα (λ = 0.71073 Å). The crystal was mounted on a glass fiber under epoxy. The CCD data were integrated and scaled using a Bruker SAINT, and the structures were

solved and refined using SHELXTL. Hydrogen atoms were located in the calculated positions. The crystallographic data are listed in Table S1. The selected bond lengths and angles are listed in Table S2. The CIF deposition number: CCDC 646877.

Physical Measurements

The N_2 sorption analysis was performed on a Belsorp-miniII at 77 K (BEL Japan). The samples were dried at 393 K under high vacuum for 2 h. Low-pressure hydrogen adsorption measurements were performed at 77 K on a Belsorp-miniII. The equipment was calibrated by using Cu-BTC (HKUST-1) as a reference material (S. S. -Y. Chui et al., *Science* 1999, **283**, 1148). The as-made HKUST-1 activated at 393 K under high vacuum for 2 h showed hydrogen uptake value of 2.23 wt% at 77 K and 1 bar. This value agrees well with the reported value (2.27 wt%) under the same condition (B. Xiao et al., *J. Am. Chem. Soc*., 2007, **129**, 1203). Powder X-ray diffraction patterns were obtained by using a Rigaku MiniFlex (30 kV, 15 mA). Thermogravimetric analysis was carried out on a TGA Q5000 (TA Instruments) under nitrogen atmosphere.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{33}\ H_{38}\ In\ N_2\ O_{11}$	
Formula weight	753.48	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4/n	
Unit cell dimensions	a = 31.745(3) Å	α = 90.00°
	b = 31.745(3) Å	β = 90.00°
	c = 8.2835(15) Å	γ = 90.00°
Volume	8347.9(19) $Å^3$	
Z	8	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.616 mm^{-1}	
F(000)	3064	
Crystal size	0.25 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.81 to 25.99	
Index ranges	$-39 \le h \le 28$, $-39 \le k \le 38$, $-10 \le l \le 9$	
Reflections collected	44090	
Independent reflections	8208 [R(int) = 0.1435]	
Completeness to theta = 25.99	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8208 / 0 / 418	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	$R_1 = 0.0998$, $wR_2 = 0.2668$	
R indices (all data)	$R_1 = 0.1460$, $wR_2 = 0.2812$	
Largest diff. peak and hole	1.521 and -2.405 e.$Å^{-3}$	

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

In(1)-O(14)	2.186(7)
In(1)-O(22)	2.234(7)
In(1)-O(23)	2.241(7)
In(1)-O(11)	2.242(7)
In(1)-O(12)	2.259(7)
In(1)-O(24)	2.286(7)
In(1)-O(21)	2.300(7)
In(1)-O(13)	2.397(7)
O(14)-In(1)-O(22)	89.9(3)
O(14)-In(1)-O(23)	141.5(3)
O(22)-In(1)-O(23)	85.2(3)
O(14)-In(1)-O(11)	86.0(3)
O(22)-In(1)-O(11)	164.3(3)
O(23)-In(1)-O(11)	88.6(2)
O(14)-In(1)-O(12)	86.5(3)
O(22)-In(1)-O(12)	137.1(3)
O(23)-In(1)-O(12)	121.9(3)
O(11)-In(1)-O(12)	57.8(3)
O(14)-In(1)-O(24)	160.7(3)
O(22)-In(1)-O(24)	88.1(3)
O(23)-In(1)-O(24)	57.4(3)
O(11)-In(1)-O(24)	100.6(3)
O(12)-In(1)-O(24)	82.0(3)
O(14)-In(1)-O(21)	80.7(3)
O(22)-In(1)-O(21)	57.2(3)
O(23)-In(1)-O(21)	126.1(3)
O(11)-In(1)-O(21)	136.5(3)
O(12)-In(1)-O(21)	80.1(3)
O(24)-In(1)-O(21)	82.1(3)
O(14)-In(1)-O(13)	56.6(3)
O(22)-In(1)-O(13)	79.7(3)
O(23)-In(1)-O(13)	85.0(3)
O(11)-In(1)-O(13)	85.4(3)
O(12)-In(1)-O(13)	130.4(3)
O(24)-In(1)-O(13)	141.4(2)
O(21)-In(1)-O(13)	119.2(2)

Table S3. The result of interpenetrating modes analyzed by TOPOS (Topos 4.0 Pro).

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####################
1:C33 H38 In N2 O11
####################
Topology for In1
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Atom In1 links by bridge ligands and has
Common vertex with                                  R(A-A)          f
In 1      0.8070      0.5346     -0.9031     ( 1 0-1)     12.988A          1
In 1      0.6930      0.9654      1.0969     ( 0 1 1)     12.988A          1
In 1      0.1930      0.4654     -0.0969     (-1 1 0)     13.128A          1
In 1      0.3070      1.0346     -0.0969     ( 1 0 0)     13.128A          1
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Structural group analysis
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Structural group No 1
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Structure consists of 3D framework with InO8C24H12
There are 4 interpenetrating nets
FIV: Full interpenetration vectors
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[0,0,1] (8.28A)
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PIC: [0,0,4][0,1,-2][1,1,0] (PICVR=4)

Zt=4; Zn=1
Class Ia    Z=4

Coordination sequences
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In1:    1    2    3    4     5     6     7     8     9    10
Num   4    9   18   32    48    67    92   120   150   185
Cum   5   14   32   64   112   179   271   391   541   726
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TD10=726

Vertex symbols for selected sublattice

In1 Point (Schläfli) symbol: {4^3.6^2.8}

Extended point symbol: [4.4.4.8(3).6.6]

Vertex symbol: [4.4.4.8(2).8.8]

All rings (up to 10): coincide with rings

All rings with types: [4b.4b.4a.8(2).8.8]

Point (Schläfli) symbol for net: {4^3.6^2.8}

4-c net; uninodal net

Topological type: gis Gismondine GIS; 4/4/t3; sqc2200 (topos&RCSR.ttd) {4^3.6^2.8} - VS [4.4.4.8(2).8.8] (66909 types in 9 databases)

Essential rings by homocrossing: 4a,4b,8

Inessential rings by homocrossing: none

Rings crossed by bonds: 8

Proper tiling cannot be constructed. Not all edges are shared.

Table S4. Binding energy of the hydrogen molecule onto various sites of **1** and MOF-5.

	Computational Method	Binding Energy (eV)
In-MOF with H_2 on site A	GGA	0.05
In-MOF with H_2 on site B	GGA	0.07
In-MOF with H_2 on site C	GGA	0.09
In-MOF with H_2 on site C	LDA	0.13
MOF-5 with H_2 near oxygen	GGA	0.02
MOF-5 with H_2 near oxygen	LDA	0.11

Figure S1. Coordination environment of the In(III) ion showing a T-motif.

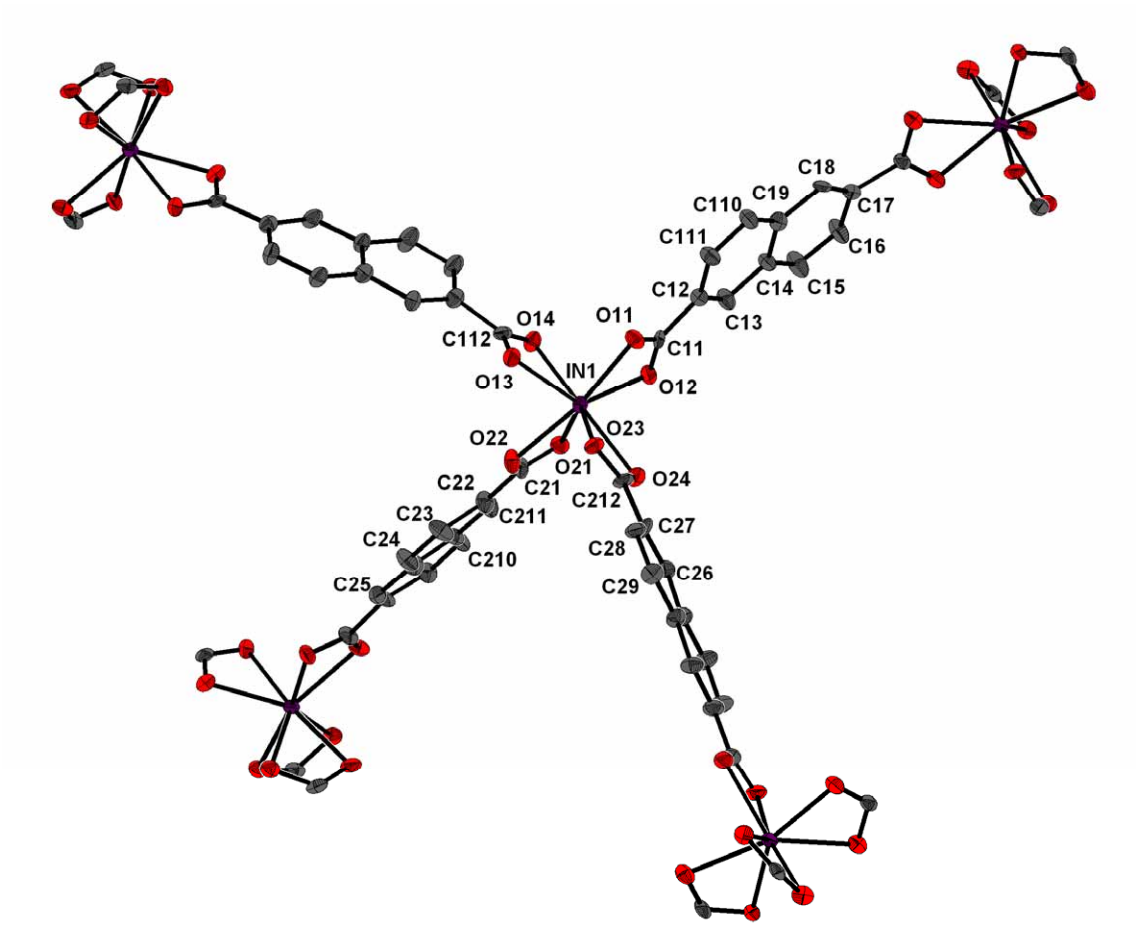

Figure S2. Connolly surface of **1** with a probe radius of 1.4 Å (a) and pore dimensions for the three 1D channels in Å (b).

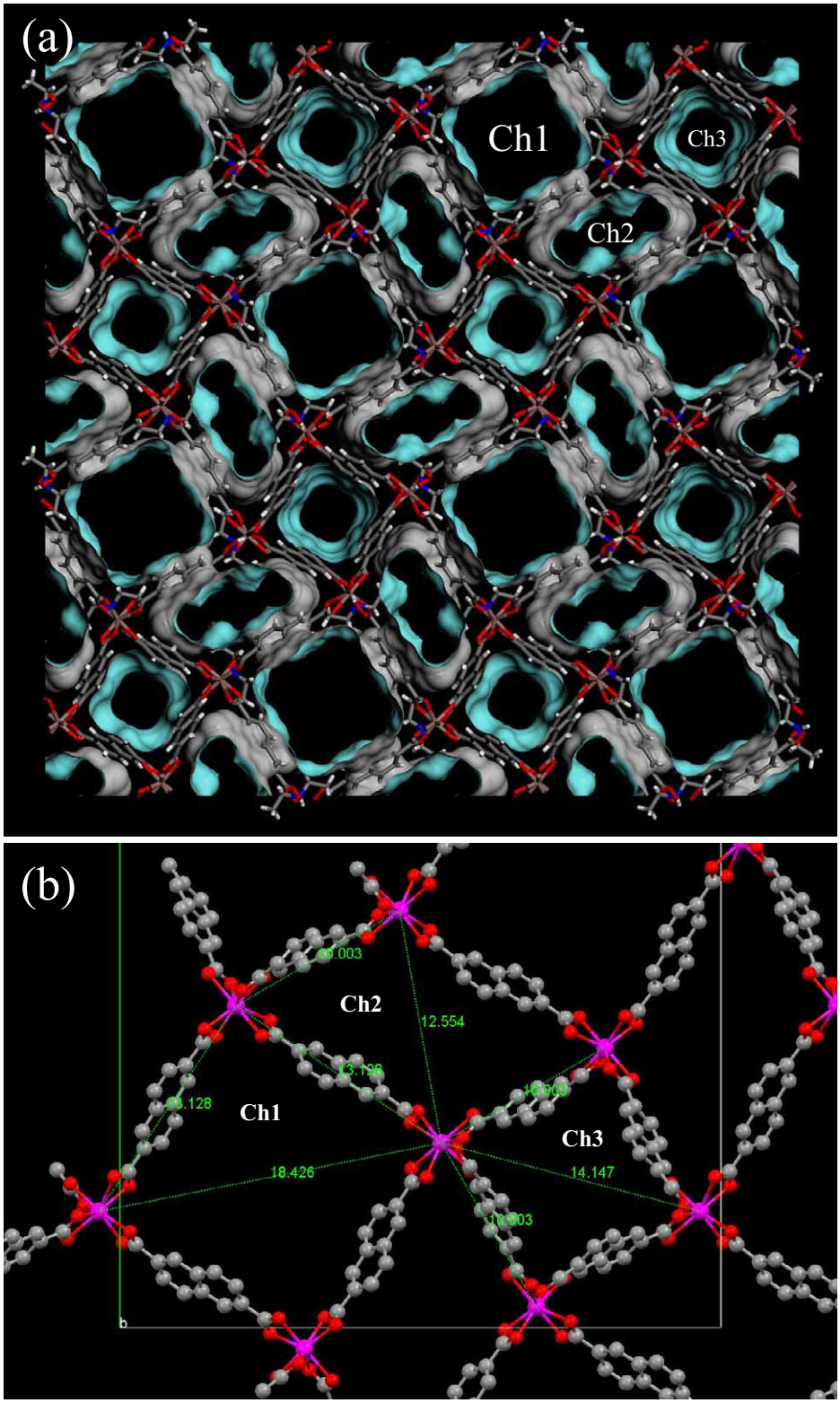

Figure S3. The detailed structure of the Ch1 with two water solvates (oxygen atoms as red spheres), a DEF, and an $Et_2NH_2^+$ ion: a view along *c*-axis (a) and a view along *a*-axis (b).

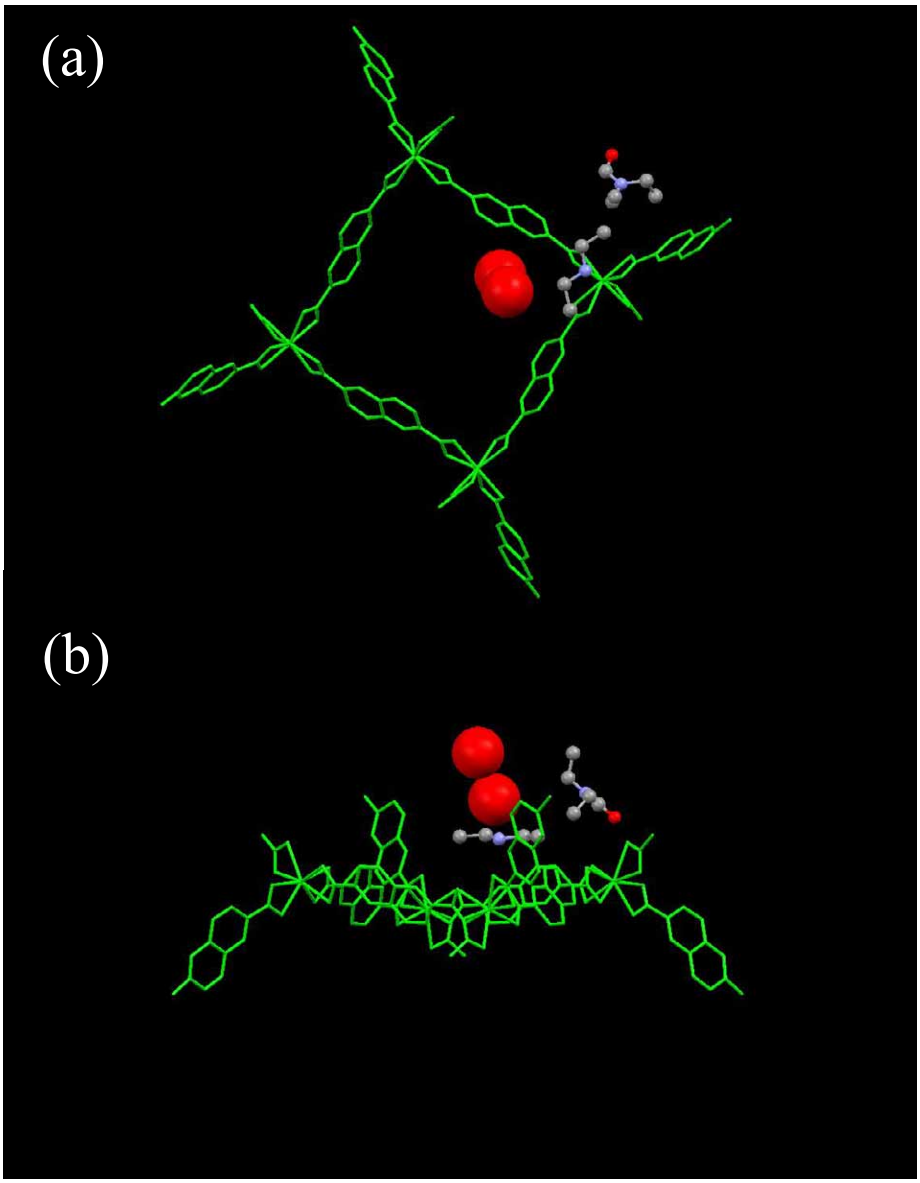

Figure S4. The 4-fold interpenetrated $4^3 \cdot 6^2 \cdot 8$-**gis** network of **1**: a view along *c*-axis (a) and its tilted view (b). Solvates, $Et_2NH_2^+$ ions, and hydrogen atoms are omitted for clarity.

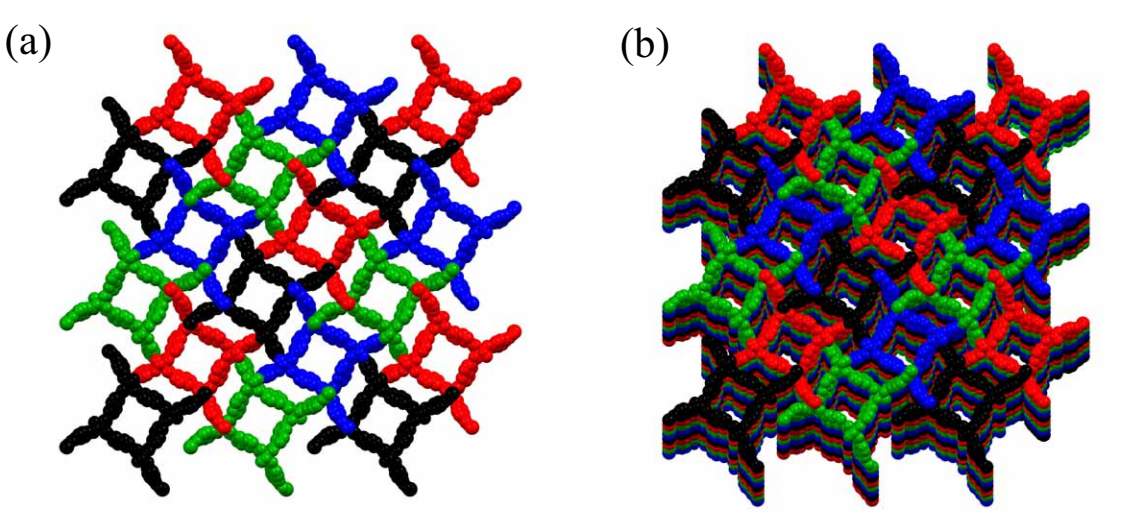

Figure S5. Pore size distribution curves obtained by the MP method. Both samples were activated at 120°C under high vacuum for 2 h.

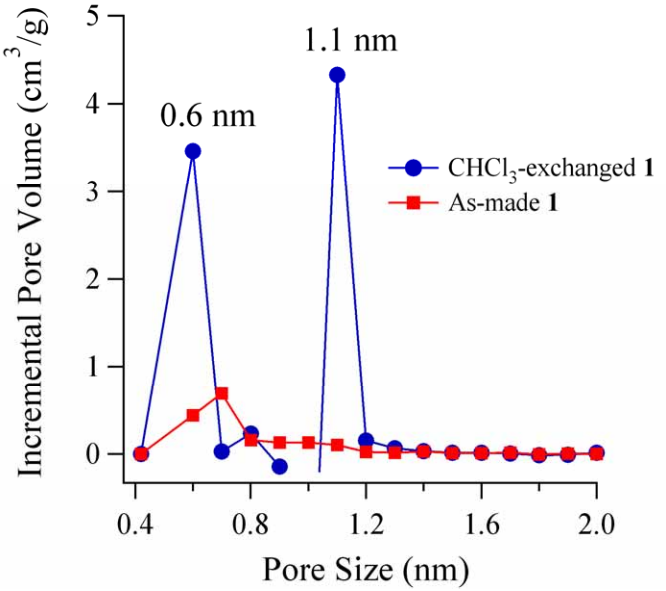

Figure S6. The PXRD patterns of **1** activated at various conditions with the relevant simulated patterns.

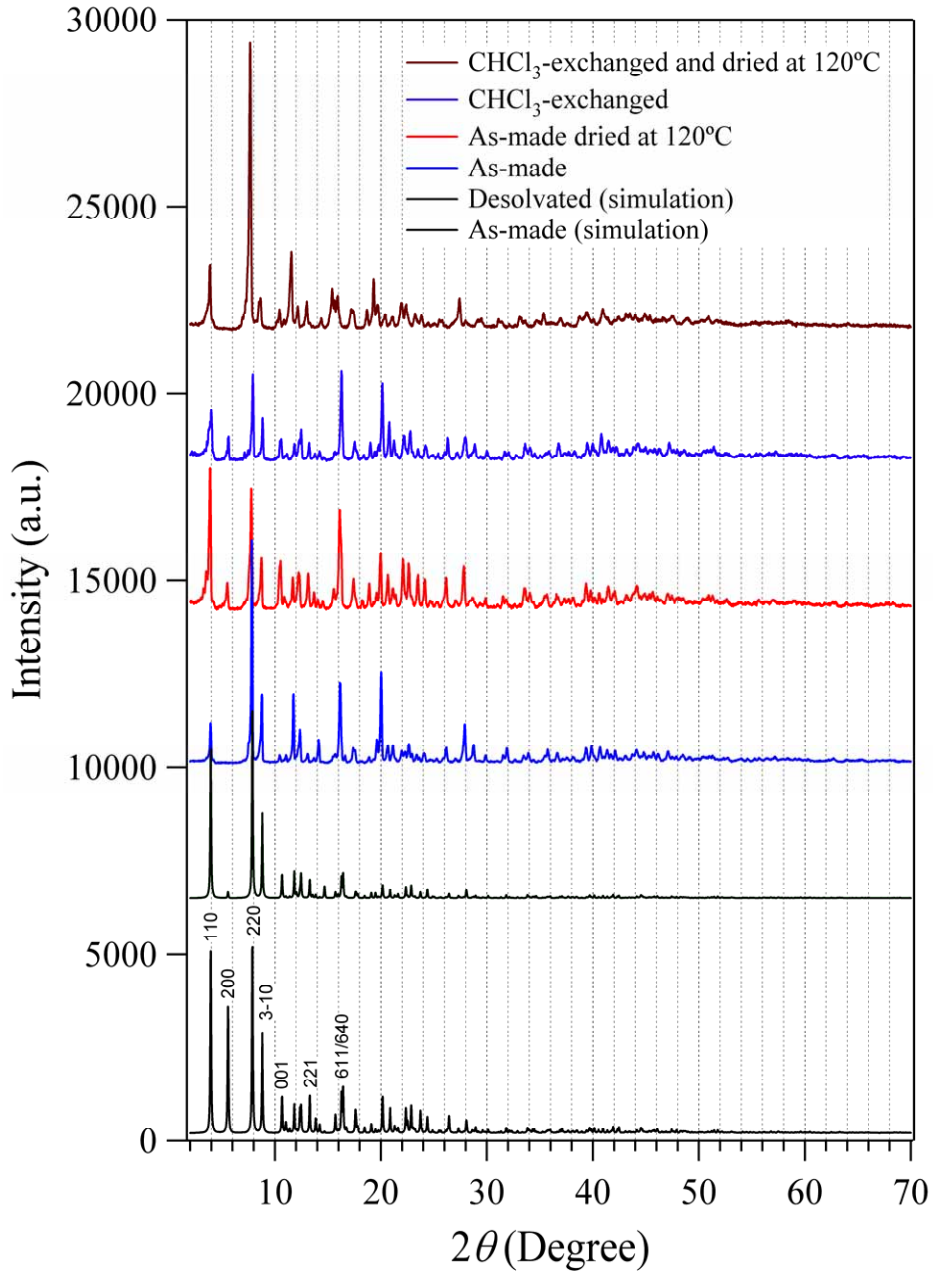

Figure S7. The optimized geometry with H_2 on site C calculated with the LDA.