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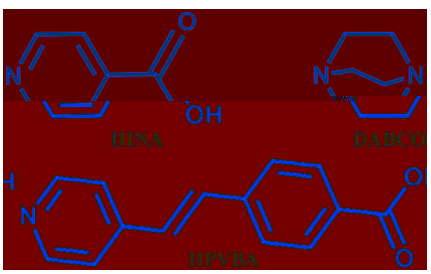
.[27–31] F s , F-8 s s s *via* s , s [27] [3(D -)2( )2]·2.5D F *n* (= 4-(-4-) 4) ss ss s s s - s s, s *via* π- s s s.[28] -1 s s s s s s *via* s s -1 s .[29] L s s s s C - s Fs s , s s .[32–35] s s s, s s C - s Fs s s . , s (1), C - s Fs [C 2(2)2(C 4-)(A)4]·s (**1**) (A = s), [C 2(2)2(C 4-)(A)4(DABC)2]·2D A (**2**) (DABC = 1,4-4 [2.2.2] , D A = *N*,*N*′-) [(C 2)2(BA)8(C 4-)]·D F (**3**) (BA = 4-(2-(4-)-4) , D F = *N*,*N*′-) ; s Fs s 3- s (3D) s s s - C 2(C 2)4 C 4- s s. s , **1** s - 3D s 1D s s 2.4 × 2.7 2; **2** s 2- s s s. F , **3** s s s C 2(C 2)4 BA⁻ s, s C 4- s. A s , **2** s / s s s . A , s s **2** s s .

Experimental

Materials and measurements

A s s s s s s s . 4-(2-(4-)) (BA) s s s s.[36] - (D) D A 2500 C - α (λ = 1.54178 A)



Scheme 1 Schematic structural illustration of ligands HINA, DABCO and HPVBA in this work.

2θ 5–50° . s s (A) A/ D A 851 s 10 °C 800 °C . E s s (EA) C, C . - s s s s E L 35 s . ( ) s s 50 .

Gas adsorption analysis

s s s 2 s A A s 2020 (A A -2020) s s 77 . C 2 s s s s 273 298 . s s s s s 99.999% . B s s, s s **2** s s 5 s - - s s. s s **2** ss s s 333 8 .

Synthesis of $Cu_2(H_2O)(Cu_4I_4)(INA)_4$·solvent (1)

20 L , C C 2·2 (0.23 , 40), C (0.63 , 120), A (0.32 , 40) 4,4′- (0.10 , 26) D A (2 L) *N*,*N*′- (DEF, 2 L) s 1 . , s s 100 °C 4 s. A , s s **1** s s s - s s s , s D A . : *ca.* 14% (s C). (B , *ν*/ $^{-1}$): 3358( ), 2940( ), 1598( ), 1557( ), 1501(s), 1381( ), 1265(s), 1179(s), 1052( ), 1013( ), 846(s), 770( ), 684( ), 588( ).

Synthesis of $Cu_2(H_2O)_2(Cu_4I_4)_2(INA)_4(DABCO)_2$·2DMA (2)

20 L , C C 2·2 (0.23 , 40), C (0.42 , 80), A (0.32 , 40), DABC (0.18 , 20) 5 L D A s 1 . , s s 100 °C 4 s. A , s s s **2** s s s - s s s , s D A . : *ca.* 52% (s C): C, s s (%) **2**: C 20.53, 2.42, 5.44; : C 20.74, 2.16, 5.49. (B , *ν*/ $^{-1}$): 3414( ), 2940( ), 2885(s), 1608( ), 1547(s), 1497( ), 1391( ), 1265( ), 1179( ), 1052(s), 1013( ), 861(s), 796(s), 765( ), 680( ), 583( ).

Synthesis of $[(Cu_2)_2(PVBA)_8(Cu_4I_4)]$·DMF (3)

20 L , C (0.26 , 50), BA (0.14 , 30) 4 L D F s

1 . , s s 100 °C 4 s. A , s s s **3** s s s - s s , s D F . : *ca.* 18% (s C). C, s s (%) **3**: C 47.91, 3.04, 4.37; : C 47.07, 2.86, 4.29. (B , ν/ $^{-1}$): 2920( ), 2082( ), 1663( ), 1593( ), 1537( ), 1492( ), 1370( ), 1245(s), 1209(s), 1088( ), 1013( ), 942( ), 831( ), 800( ), 760( ), 669( ), 538( ).

Single crystal structure analyses

s - (C D) B A CCD 175 s C α (λ = 1.54178 A) **1** **3** 175 s / α (λ = 0.71073 A) **2**. s s s s s **1–3**. s s **1–3** - s -s s s s F^2 EL -2014 .[37] A s s s . A s s s . s s s **1–3** EE E[38] IA . C s s s **1–3** s 1. s s s s CCDC s s 1910020 (**1**), 1910018 (**2**) 1910019 (**3**).

Results and discussion

Structural description of 1

C D s s **1** s *R3c* s . s s s s C $^{+}$ s (C 1, C 2), C $^{2+}$ (C 3) , s, A^{-} s (F . 1†). As s F . 1 , C $^{2+}$ s s - s C $^{-}$ A^{-} s - s . , - C $^{2+}$ s ss - C $_2$(C $_2$)$_4$ s *via* A^{-} . F , A^{-} - C $_{4-x}$ s (F . 1). C – C – C – s s 2.63–2.79, 1.92–2.10, 1.95–2.03 A, s s [39] , C $_2$(C $_2$)$_4$ s s s B , C $_{4-x}$ s s B . s 4- B s s 3D s (F . 1). s s s s s ss ss s - 1D s s 2.4 × 2.7 ^{2} *c* s (F . 1). s s s s

Table 1 Crystal data and structure refinement for **1–3**

	1	**2**	**3**
E	C$_{24}$ $_{20}$C $_{6-x}$ $_4$ $_{10}$	C$_{36}$ $_{44}$C $_{10-x}$ $_8$ $_{10}$	C$_{112}$ $_{80}$ C $_{8-x}$ $_8$ $_{16}$
F	1413.34	2399.39	2809.84
C s s s			
	R3c	*Cmca*	*C2/c*
a (A)	49.26 (9)	29.00 (3)	63.59 (2)
b (A)	49.26 (9)	17.61 (15)	19.66 (7)
c (A)	35.34 (14)	16.93 (15)	41.56 (14)
V (A^3)	74 301 (4)	8654.1 (13)	39 490 (2)
Z	18	4	8
F(000)	11 842	5140	11 038
θ /°	2.706 50.513	1.810 25.041	1.829 66.895
L s	−49 ≦ *h* ≦ 46	−28 ≦ *h* ≦ 34	−72 ≦ *h* ≦ 75
	−49 ≦ *k* ≦ 48	−16 ≦ *k* ≦ 20	−22 ≦ *k* ≦ 21
	−33 ≦ *l* ≦ 33	−14 ≦ *l* ≦ 20	−49 ≦ *l* ≦ 38
ρ ($^{-3}$)	0.569	2.110	0.945
( )	175(2)	175(2)	175(2)
μ ($^{-1}$)	6.820	5.295	6.137
.	48 890	14 839	92 426
.	8589	3879	32 917
s	217	166	1333
R	0.0977	0.0239	0.0473
F F^2	1.003	1.050	1.065
F *R* s (I = 2σ(I))	R_1 = 0.0684, R_2 = 0.1879	R_1 = 0.0315, R_2 = 0.0896	R_1 = 0.0894, R_2 = 0.3184
R s ( )	R_1 = 0.1111, R_2 = 0.2071	R_1 = 0.0384, R_2 = 0.0926	R_1 = 0.0973, R_2 = 0.3334

$R_1 = \sum||F| - |F||/\sum|F|$. $R_2 = \left[\sum (F^2 - F^2)^2/\sum (F^2)^2\right]^{1/2}$; $= 1/\sigma^2(F^2) + (xP)^2 + yP]$, $P = (F^2 + 2F^2)/3$, x = 0.116100, y = 0 **1**; x = 0.054600, y = 57.403599 **2**; x = 0.280000, y = 0 **3**.

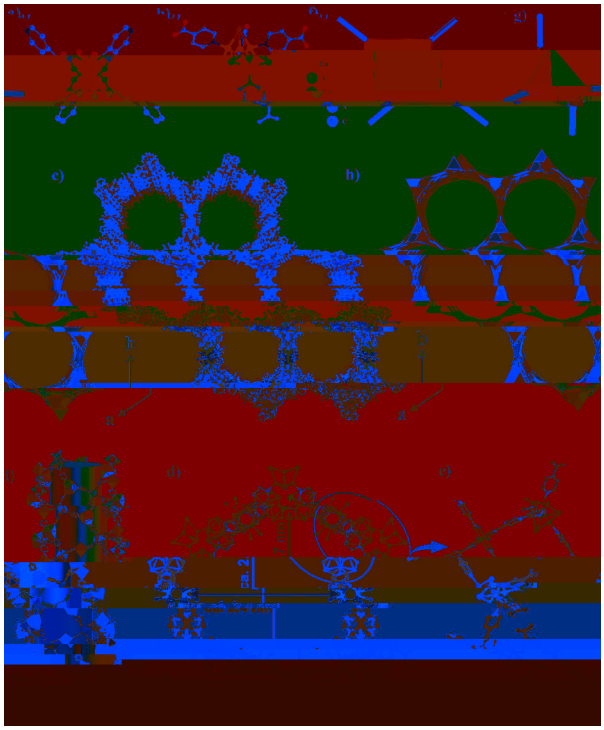


Fig. 1 Crystal structure of **1**: a and b) the paddle-wheel $Cu_2(CO_2)_4$ and cubane-like Cu_4I_4 clusters. c) View of the 3D honeycomb-like framework structure. d) View of the 1D hexagonal channel with the size of 2.4 × 2.7 nm^2. e) The connection mode between $Cu_2(CO_2)_4$ and Cu_4I_4 clusters. f and g) The topological representation of $Cu_2(CO_2)_4$ and Cu_4I_4 clusters. h) The topological representation of 3D honeycomb-like framework. i) View of 1D hexagonal channels viewed along the *b* axis.

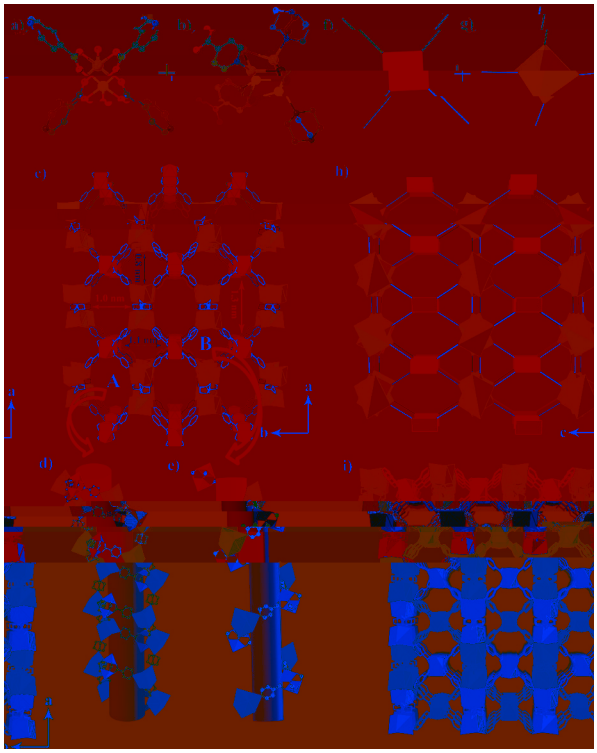


Fig. 2 Crystal structure of **2**: a and b) the paddle-wheel $Cu_2(CO_2)_4$ and cubane-like Cu_4I_4 clusters. c) View of the 3D framework along the *c* axis. d and e) View of tubular channels. f and g) The topological representation of $Cu_2(CO_2)_4$ and Cu_4I_4 clusters. h) The topology of the 3D framework. i) View of the 2-fold interpenetrated framework structure in **2**.

C 2(C 2)4 s s, C 4-4 s s
- A− s (F . 1).
, s 3D - s s
.[40] , s s
s B s . As s , **1**
s s - s
s s - s. F
, C 2(C 2)4 C 4-4 s s
s s 4-
4- , s (F . 1).
s s 4,4-
s $4^2{\cdot}6^2{\cdot}8^2$ $4^2{\cdot}6^4$ (F . 1). IA
s s - ss
s 61 758.7 A^3, s
83.1% s (74 301.0 A^3).

Structural description of 2

C D s s **2** s
Cmca s . As s F . 2,† s
s s s C + s (C 1, C 2),
C 2+ (C 3) , − s, A− ,
DABC
. s s B s **2** s s

s **1** (F . 2). , s
s s **1.** s s
s DABC s
C 4-4 B s. As s F . 2 , C 4-4 B s
s A− DABC s, s
1. s , **2**
s s (
A s B) *c* s (-
F . 2 –); s s
1.3 × 1.0 2 1.1 × 0.8 2,
s . B s s s *c* s,
s s s - s
b s s 1.0 × 1.1 2 (F . 3†).
, s s
4,4- s 6^4
$\cdot 8^2$ 6^6 2 ss C 2(C 2)4 C 4-4 s s s
s 4- s (F . 2 –). s
s 2-
s - s
s (F . 2). IA s
2 s 3342.5 A^3,
s 38.6% (8654 A^3).
, **2** s s
1, s 2-
2.

Structural description of 3

C D s **3** s *C*2/*c* s . As s F . 4,† s s C $^{+}$ s (C 1, C 2, C 3, C 4), C $^{2+}$ s (C 5, C 6, C 7, C 8), $^{-}$ s BA^{-} s. s B s **3** s s **1** **2**. s C $_2$(C $_2$)$_4$ s s **3**. , s s **1** **2**. **3**, s C $_2$(C $_2$)$_4$ s s s s BA^{-} s s s **1** **2** (F . 3). As s , C $_2$(C $_2$)$_4$ s 6- C $_2$(C $_2$)$_4$ s s C $_4$I$_4$ s s. C $_4$I$_4$ s s s s s **1** **2** (F . 3). s s s **3** s C $_2$(C $_2$)$_4$ s s s - ss BA^{-} s (F . 5 †). ss ss s *b* s s 1.5 × 1.8 ^{2} (F . 3). F , BA^{-} s s s s C $_4$I$_4$ s s s (F . 5 †). , s - ss BA^{-} s/ s s s s BA s . [36,41] ,

C $_4$I$_4$ s s s, **3** s - s . , C $_2$(C $_2$)$_4$ s s s 6- s C $_4$I$_4$ s s s 4- s. C s , **3** s 4,6- s $4^2{\cdot}6^4$ $4^6{\cdot}6^7{\cdot}8^2$ $_2$ (F . 6†). IA s 56.2% **3** s - ss .

Syntheses

D , s s s s s s **1–3**. F s , s A BA ss **1–3**. C $_2$(C $_2$)$_4$ s s - B C $_4$I$_4$ s s - B , A^{-} BA^{-} s s s s s B s s -s – s . , **1–3** s s s s s. - s s (D A DEF **1**, D A **2**, D F **3**) - s s s s C C C $_2$C $_2$, C C , E , . , s - s s s

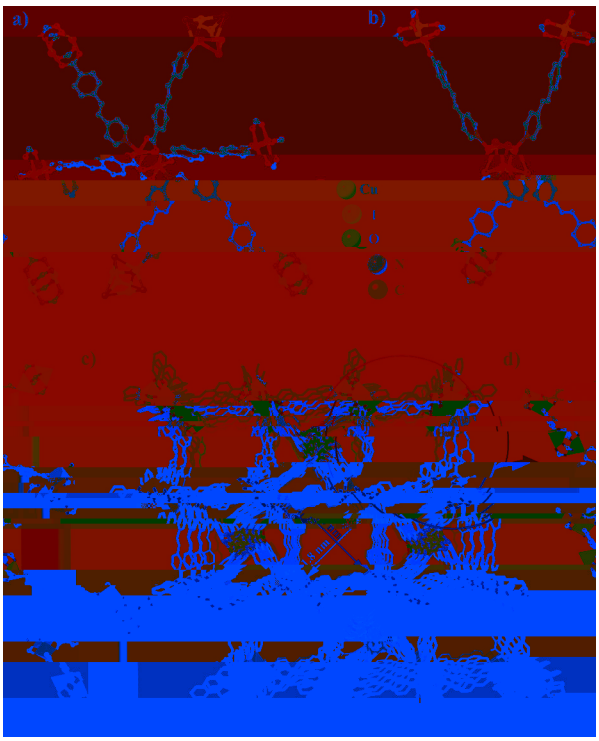


Fig. 3 Crystal structure of **3**: a) view of the coordination environment of the $Cu_2(CO_2)_4$ cluster. b) View of the coordination environment of the Cu_4I_4 cluster. c) View of the 3D framework of **3** along the *b* axis. d) View of the rhombic channels.

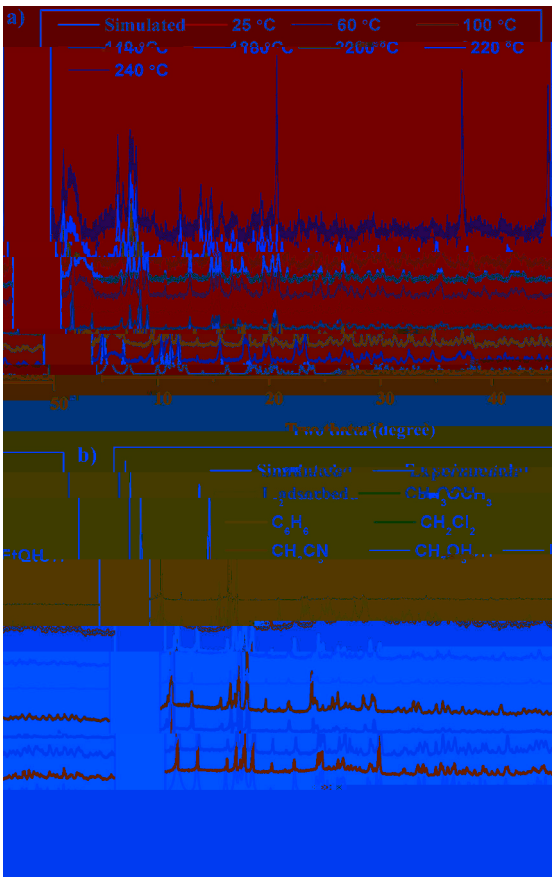


Fig. 4 The PXRD patterns of **2** under a) thermal conditions and b) immersion in a variety of common organic solvents.

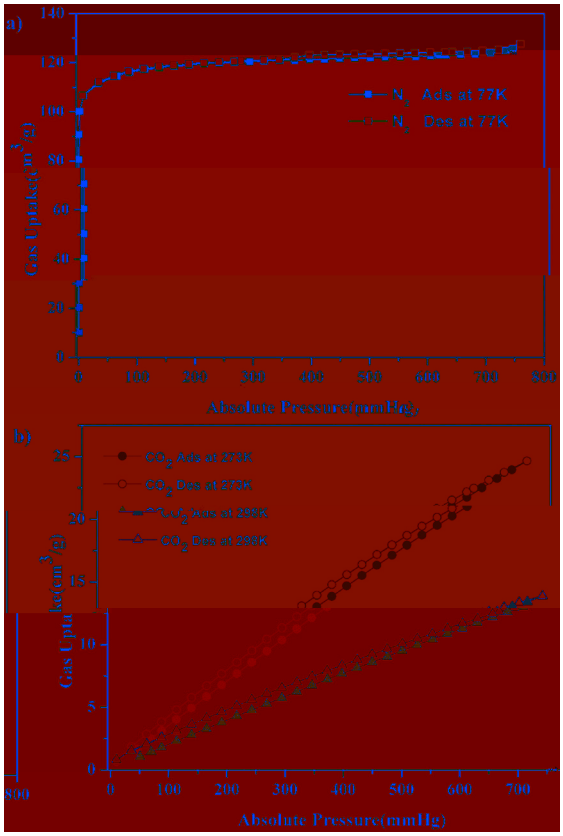


Fig. 5 a) The N_2 and b) CO_2 adsorption isotherms of **2**.

s . F , 4,4′-
s s s **1**

s s s . 4,4′-B
s s
1.

Gas adsorption property

s **1–3** s
s . , **1** **3**
s s ,
s . s, s
s **2** s s . -
D s s s s s
2 s s 240 °C
s -
s s (, C C 2, C C , C E
s (F . 4). As s F . 5 , 2
s **2** 77 s s s **I** s
s .
s **L** /B –
E – (BE) s s 127.56 3 −1
530.71/347.23 2 −1, s s
Fs s s **CPM-24** (**L** /BE s
s 296/186 2 −1).[42] s
s s s s
8.0 A (F . 10†). A , C 2 s
273 298 760 24.64 13.87
3 −1, s (F . 5).

Iodine sorption/release study

/s s
s- s s s

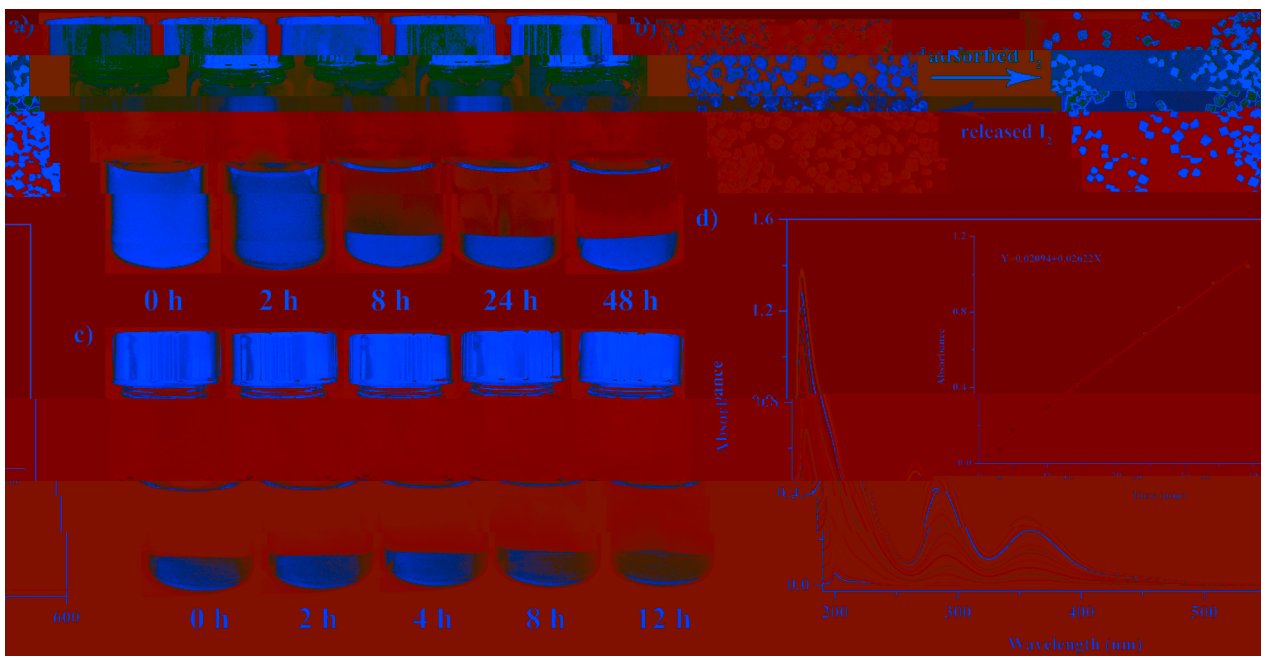


Fig. 6 a) and c) Pictures of different time intervals for the I_2 adsorption/release process in 10 mL of cyclohexane and CH_3OH, respectively. b) Photographs showing the color change of **2** before and after I_2 adsorption. d) I_2 release from **I_2@2** in CH_3OH at different time intervals. Inset: the release rate of **I_2@2** in the first 40 min.

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