Electronic supporting information (ESI)

A rare (3,4,5)-connected metal-organic framework featuring an unprecedented 1D + 2D → 3D self-interpenetrated array and O-atom lined pore surface: structure and drug controlled release

Di-Chang Zhong,* Lie-Qiang Liao, Ji-Hua Deng, Qing Chen,* Ping Lian, and Xu-Zhong Luo*

Experimental Section

General Remarks. All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser. The IR spectra were recorded in the 4000 to 400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) was carried out on Netzsch TG-209 Thermogravimetry Analyzer in air atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The single crystal data were collected on a Bruker Smart 1000 CCD diffractometer.

Preparation. $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.148 g), 5,5'-(1,3,6,8-tetraoxobenzo[lmn][3,8]phenanthroline-2,7(1H,3H,6H,8H)-diyl)diisophthalic acid (0.5 mmol, 0.071 g) and DMF (5 mL) were mixed and stirred for ten minutes. The resulted solution was transferred to Teflon-lined autoclave and heated at 110°C for 72 h. Then the autoclave was cooled over a period of 16 h with a rate of 5 $°C \cdot h^{-1}$. Block-shaped brown crystals

of **1** generated. The crystals were collected by filtration and dried in air. Yield: 55%. Anal. Calcd for $C_{71}H_{90}N_{12}O_{31}Zn_2$: C, 49.06; H, 5.22; N, 9.67. Found: C, 48.94; H, 5.15; N, 9.73. IR (KBr, cm^{-1}): 3431(s), 1713(s), 1676(vs), 1623(s), 1579(s), 1449(m), 1348(s), 1253(s), 1120(w), 1117(w), 985(w), 769(m), 744(w), 725(w), 652(m), 571(w), 421(w).

X-ray Crystallography. Single-crystal data for **1** was collected on a Bruker Smart 1000 CCD diffractometer, with Mo-Kα radiation (λ = 0.71073 Å). All empirical absorption corrections were applied using the SADABS program.[1] The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. The disordered electron density of some DMF and H_2O molecules in **1** were treated as a diffuse contribution using the program SQUEEZE.[2] The hydrogen atoms attached to the atoms of the ligand and $[NH_2(CH_3)]^+$ were placed in calculated position, with fixed isotropic thermal parameters and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs.[3]

Ibuprofen loading and releasing. 100 mg of guest-exchanged sample of **1** was immersed in 25 mL hexane containing 100 mg of ibuprofen for three days. The precipitate was isolated by centrifugation and dried in vacuum oven at 60 ^oC. The ibuprofen-containing **1** was compacted by uniaxial and isostatic pressure (＜3 MPa) to obtain disks used for elemental analysis, thermogravimetric analysis, as well as the releasing experiment. The ibuprofen releasing experiment was conducted in 50 mL

methanol solution at room temperature and monitored by UV-Vis spectra.

Elemental analysis. To determine the guest molecules in the pore of **1**, freshly prepared **1** was dried in air over night and then used for elemental analysis. The result is presented in the preparation part. To determine the amount of ibuprofen loaded in **1**, we compared the results of the elemental analyses for desolvated **1**, ibuprofen, and ibuprofen-loaded **1**, from which the amount of ibuprofen loaded in 100 mg of **1** can be calculated. These samples were dried in a vacuum oven at 60 ^{o}C over night. The results are presented in Table S1. Each sample was measured for three times and the content of each element shown in the table are the average value.

According to the result of C elemental analysis, the ibuprofen loaded in **1** ($m_{\text{Ibuprofen}}$) can be calculated as following:

$$(100 \times 53.13\% + m_{\text{Ibuprofen}} \times 75.52\%)/(100 + m_{\text{Ibuprofen}}) = 60.67\%$$

$$m_{\text{Ibuprofen}} = 50.77 \text{ mg}$$

According to the result of H elemental analysis, $m_{\text{Ibuprofen}}$ can be calculated as following:

$$(100 \times 2.31\% + m_{\text{Ibuprofen}} \times 8.83\%)/(100 + m_{\text{Ibuprofen}}) = 4.51\%$$

$$m_{\text{Ibuprofen}} = 51.03 \text{ mg}$$

According to the result of N elemental analysis, $m_{\text{Ibuprofen}}$ can be calculated as following:

$$(100 \times 5.18\%)/(100 + m_{\text{Ibuprofen}}) = 3.44\%$$

$$m_{\text{Ibuprofen}} = 50.46 \text{ mg}$$

Therefore, the average amount of ibuprofen loaded in 100 mg of **1** is 50.75 mg,

corresponding to one gram of **1** can accommodate 0.5075 g of ibuprofen.

Thermogravimetric analysis. To further determine the amount of ibuprofen loaded into **1**, we have measured the TG measurements for **1** and **1** loaded with ibuprofen (after dried in a vacuum oven at 60 ^{o}C over night), respectively. As shown in Fig. S5, the TG curve of **1** loaded with ibuprofen can be divided into three processes. The first weight loss (27.9%), from 25 to 260 °C, corresponds to the removal of the ibuprofen molecules. The second weight loss (8.6%), from 261 to 320 °C, is corresponding to the removal of residual ibuprofen that has not fully departed in the first stage and the decomposition of part of framework of **1**. The last weight loss, from 321 to 610°C, corresponds to the fully decomposition of the framework of **1**.

From the result of the first weight loss, we can calculate the amount of ibuprofen loaded into **1**:

$$m_{\text{Ibuprofen}}/(100 + m_{\text{Ibuprofen}}) = 27.9\%$$

$$m_{\text{Ibuprofen}} = 38.70 \text{ mg}$$

Topological Analysis by TOPOS 4.0.

####################

1: $C_{53}H_{38}N_6O_{20}Zn_2$

####################

Atom coordinates (Sc1 = 3-conntected [HL^{3-}] anion, V1 = 4-conntected [L^{4-}] anion, Ti1 = 5-connected binuclear Zn2 unit

Topology for Sc1

The links to Atom Sc1

Ti1	0.2213	0.9359	0.3376	(0 0 0)	8.386 Å
Ti1	0.2787	0.4359	0.1624	(0 -1 0)	8.700 Å
Ti1	-0.2213	1.0641	-0.3376	(0 2 0)	14.294 Å

Topology for V1

The links to Atom V1

Ti1	0.2213	-0.0641	0.3376	(0 -1 0)	10.069 Å
Ti1	-0.2213	0.0641	0.6624	(0 1 1)	10.069 Å
Ti1	-0.2787	0.4359	0.3376	(-1 -1 0)	12.596 Å
Ti1	0.2787	-0.4359	0.6624	(0 0 1)	12.596 Å

Topology for Ti1

The links to Atom Ti1

Sc1	0.0954	0.7591	0.0282	(0 0 0)	8.386 Å
Sc1	0.4046	1.2591	0.4718	(0 0 0)	8.700 Å
V1	0.0000	1.0000	0.5000	(0 1 0)	10.069 Å
V1	0.5000	0.5000	0.5000	(0 0 1)	12.596 Å
Sc1	-0.0954	1.2409	-0.0282	(0 2 0)	14.294 Å

Coordination sequences

Sc1	1	2	3	4	5	6	7	8	9	10
Num	3	11	23	69	94	214	218	427	372	679
Cum	4	15	38	107	201	415	633	1060	1432	2111

V1	1	2	3	4	5	6	7	8	9	10
Num	4	14	24	72	102	232	230	444	382	700
Cum	5	19	43	115	217	449	679	1123	1505	2205

Ti1	1	2	3	4	5	6	7	8	9	10
Num	5	10	35	55	145	163	333	300	563	465
Cum	6	16	51	106	251	414	747	1047	1610	2075

Vertex symbols for selected sublattice

Sc1 Point (Schlafli) symbol:{4.8^2}

Extended point symbol:[4.8(3).8(6)]

Ti1 Point (Schlafli) symbol:{$4^2.8^8$}

Extended point symbol:[4.4.8(2).8(2).8(2).8(2).8(3).8(3).8(4).8(6)]

V1 Point (Schlafli) symbol:{$4^2.8^3.10$}

Extended point symbol:[4.4.8(2).10(28).8(7).8(7)]

Point (Schlafli) symbol for net: $\{4.8^2\}_2\{4^2.8^3.10\}\{4^2.8^8\}_2$

3,4,5-*c* net with stoichiometry (3-*c*)$_2$(4-*c*)(5-*c*)$_2$; 3-nodal net

New topology, please, contact the authors (67358 types in 9 databases)

Elapsed time: 8.41 sec.

References

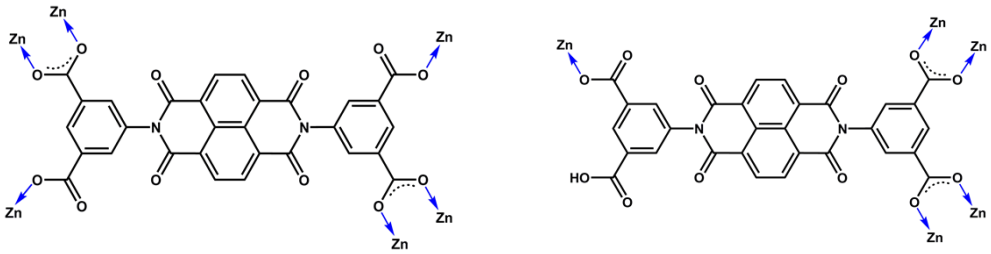
[1] G. M. Sheldrick, *SADABS, Program for empirical absorption correction of area detector data*; University of Göttingen: Göttingen, 1996.

[2] P. van der Sluis and A. L. Spek, Acta Cryst., 1990, **A46**, 194.

[3] G. M. Sheldrick, *SHELXS 97*, *Program for crystal structure refinement*; University of Göttingen, Göttingen, 1997.

Table S1 The results of C, H, N elemental analyses for desolvated **1**, ibuprofen, and ibuprofen-loaded **1**.

	C	H	N
Desolvated **1**	53.13%	2.31%	5.18%
Ibuprofen	75.52%	8.83%	Not measured
Ibuprofen-loaded **1**	60.67%	4.51%	3.44%



Mode I **Mode II**

Scheme S1 The symmetrical (Mode I) and asymmetrical (Mode II) coordination modes of H_4L in **1.**

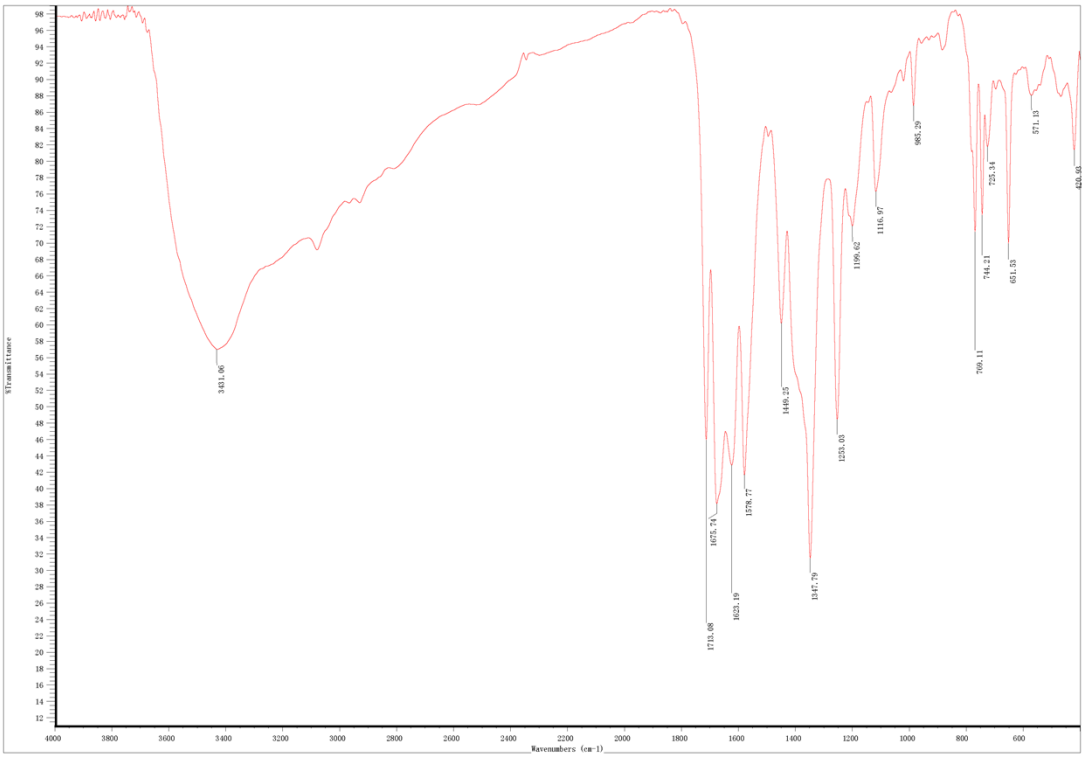


Fig. S1 IR spectra of **1**

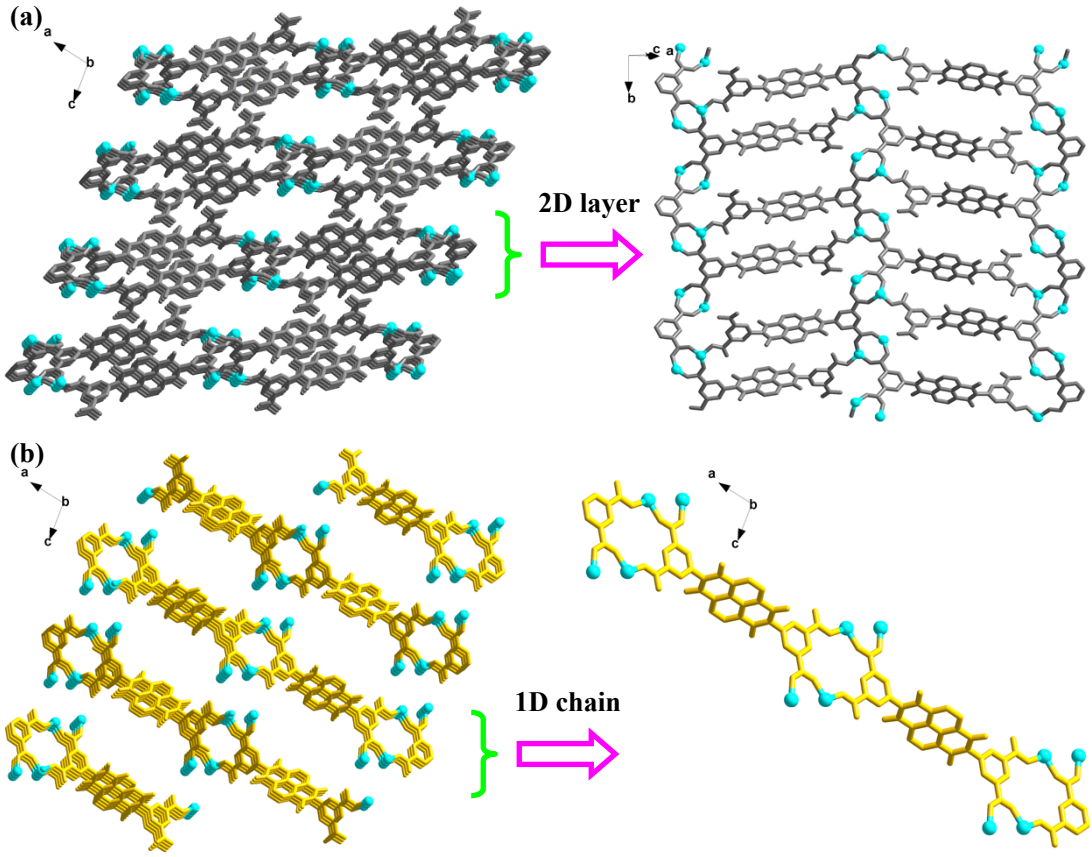


Fig. S2 (a) HL^{3-} anion ligands connect Zn1 and Zn2 together, forming a 2D layer with 38-membered rhombuses. (b) L^{4-} anion ligands connect Zn1 and Zn2 together, generating a 1D chain.

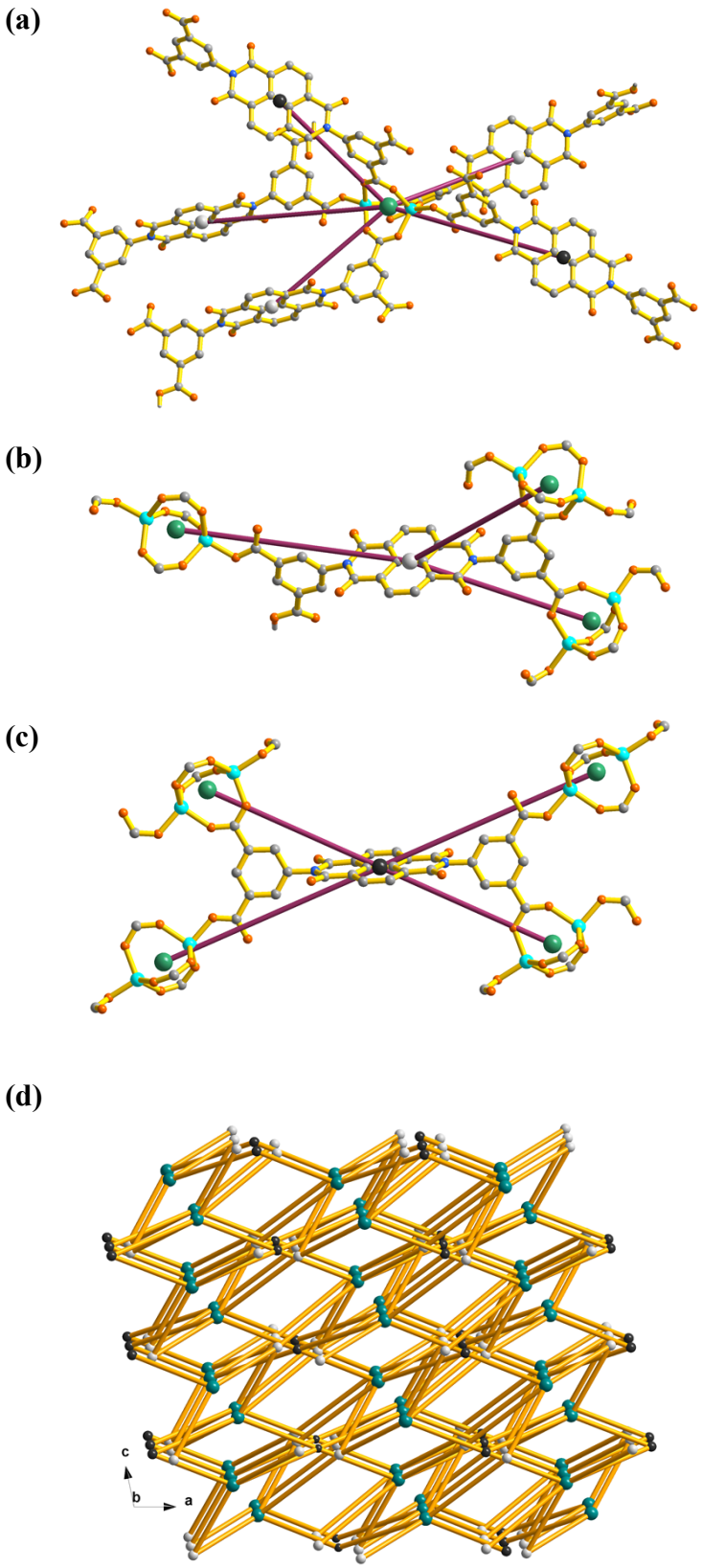


Fig. S3 Schematic representation for the nodes of binuclear Zn(II) construction unit (a), HL^{3-} anion (b) and L^{4-} anion (c). (d) The (3, 4, 5)-*c* self-interpenetrated topological net in **1**.

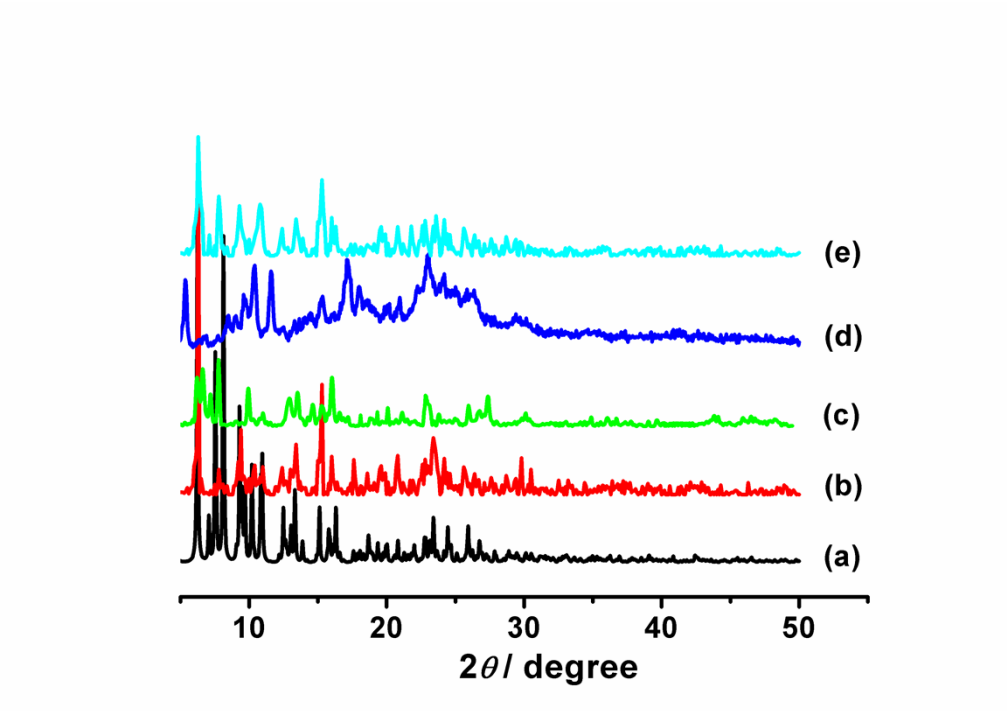


Fig. S4 Powder X-ray diffraction patterns of **1** (a) simulated from single crystal diffraction data, (b) as synthesized, (c) after exchanged with methanol, (d) after removal of solvent guests. (e) after loaded with ibuprofen.

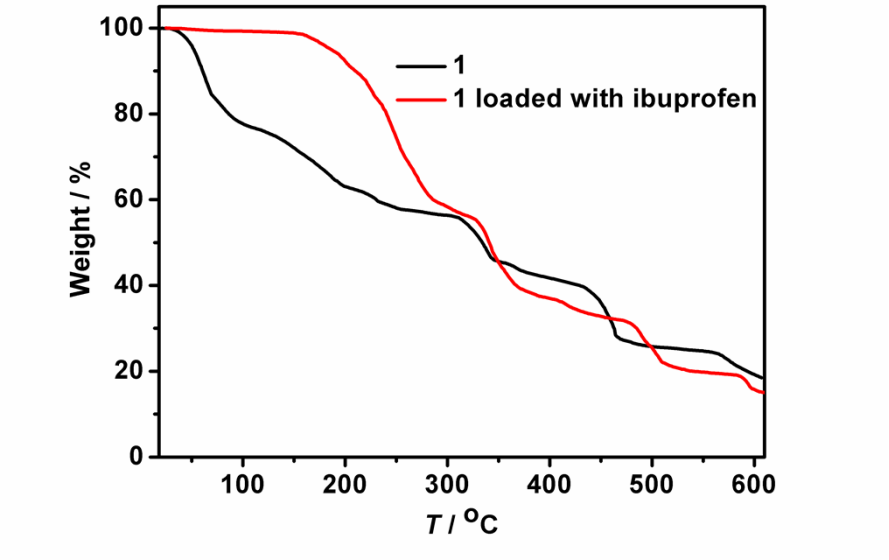


Fig. S5 TG curves for **1** and **1** loaded with ibuprofen.

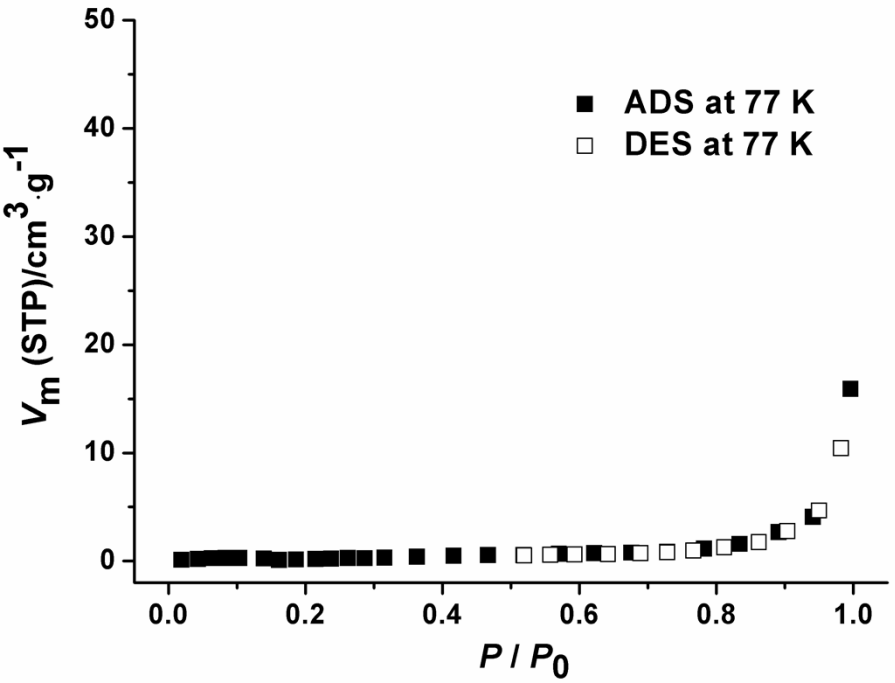


Fig. S6 N_2 sorption isotherms of desolvated **1**.

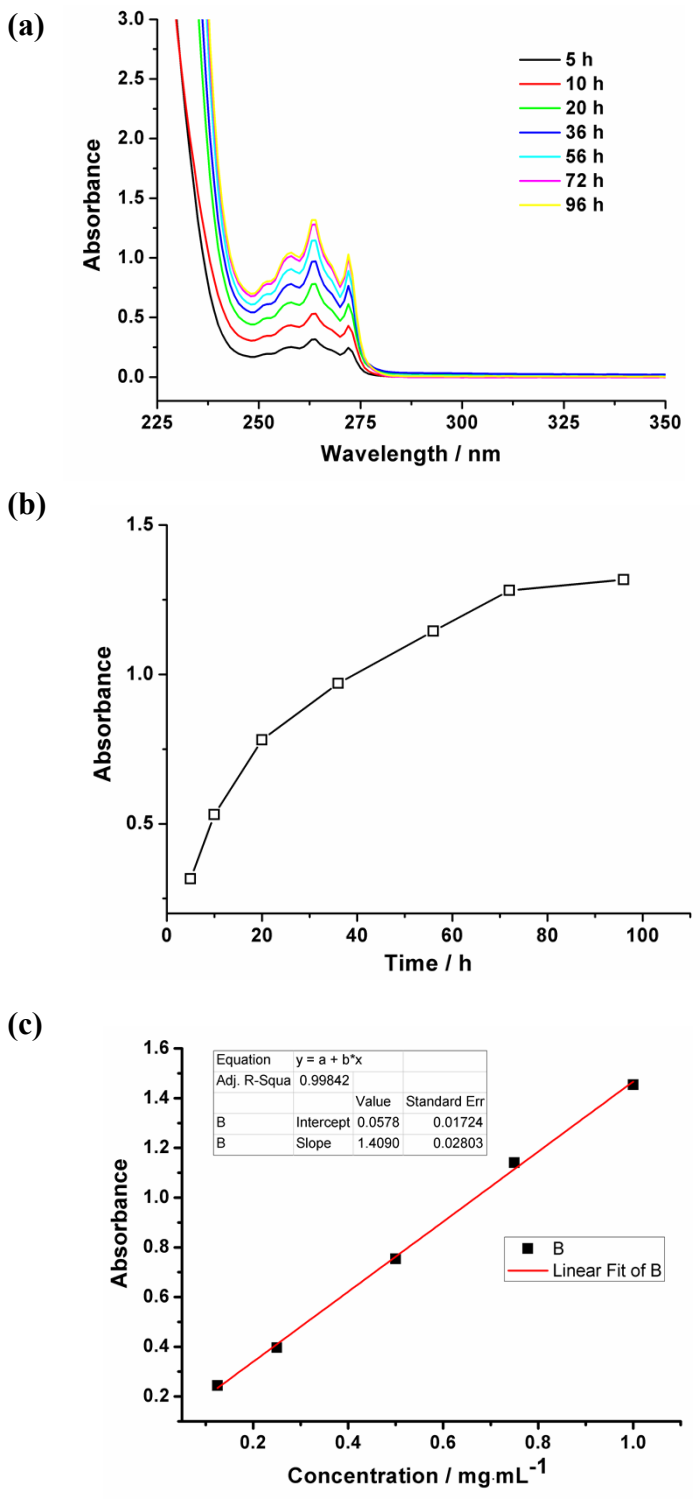


Fig. S7 (a) Time-dependent UV-Vis absorption spectra of methanol solution (50 mL) where ibuprofen-loaded **1** was soaked. (b) Time course plots for hyperchromicity of methanol solutions (50 mL) where ibuprofen-loaded **1** was soaked. (c) Stardard curve of ibuprofen in methanol solution.