

Electronic Supplementary Information

Recognition, Detection and Host-Guest Chemistry of Hydrogen Peroxide in a Fluorescent Biological Metal-Organic Framework with Chiral Helical Channels

Hong Cai,^{*a} Jie-Wen Wu,^a Xiao-Jun Cai,^a Zhou Lu,^b Ya-Liang Lai,^c Jing-Xuan Sun,^d Zhuo-Li Yuan,^a Yang-Ying Huang,^a Jing-Wen Cai,^a Wen Lu,^a Yi-Hong Lu,^a Hui-Ying Zhang^a and Dan Li^{*c}

^a School of Chemistry and Environmental Engineering, Hanshan Normal University, Chaozhou 521041, P. R. China. Email: tiddychen@163.com

^b Department of Chemistry, University of Rochester, Rochester, New York 14627, United States.

^c College of Chemistry and Materials Science, Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou 510632, P. R. China. Email: danli@jnu.edu.cn

^d College of Chemistry & Chemical Engineering, Shantou University, Shantou 515063, P. R. China.

Materials and Methods

All chemicals were purchased from commercial sources and used without further purification. The organic solutions were purchased from Xilong Science Co., Ltd. and Guangdong Guanghua Technology Co., Ltd. Single crystal X-ray diffraction (SCXRD) analysis was performed by a Rigaku XtaLAB PRO MM007-DW diffractometer system, RA-Micro7HF-MR-DW(Cu/Mo) X-ray generator and a Pilatus 3R-200K-A detector (Cu K α , $\lambda = 1.54178 \text{ \AA}$). PXRD patterns of the bulk samples were measured on a Rigaku MiniFlex600 X-ray diffractometer (Rigaku, Kyoto, Japan). ITC experiments were tested on Malvern MicroCal VP-ITC System (Malvern, Europe). Elemental analyses of C, H, and N were carried out on a PerkinElmer PE 2400II. pH was confirmed by PHS-3C pH meter. Thermogravimetric analyses (TGA) were performed using a Shimadzu synchronous differential thermal-thermogravimetric analyzer (DTG-60) in the temperature range of room temperature – 800 °C under nitrogen flow (40 mL · min⁻¹) at a typical heating rate of 10 °C/min. Infrared spectra (IR) were collected in KBr disks using a Shimadzu IRAffinity-1 in the range of 4000-400 cm⁻¹. Solid state and solution luminescence spectra were measured on a PF-5301PC. UV-Vis spectra and ultraviolet titrating experiments were recorded on an TU-1950 ultraviolet and visible spectrophotometer (Persee, Beijing, China). Circular dichroism (CD) spectra were measured on a Chirascan V100 (Applied Photophysics Ltd,UK) in the range of 200-500 nm (Equipped with PMT detector).

Synthesis of HSTC-1:

A mixture of Zn(CH₃COO)₂·2H₂O (0.12 mmol), purine (0.04 mmol), and acetonitrile (5 mL) was sealed in a Pyrex glass tube with the pH adjusted by 50 μ L 28% NH₃ aqueous solution, and heated in an oven at 120 °C for 72 h. After cooling to room temperature at rates of 5 °C/h, the colourless crystals were obtained by filtration and washed with acetonitrile 3 times. Selected suitable crystals were immediately mounted on single crystal X-ray diffractometer for structural determination. IR spectrum (see Fig. S4a). Elemental analysis (CHN), C₇H₆N₄O₂Zn(H₂O)_{1.2}, calculated (%): C, 31.7076; H,3.1931; N,21.1298. found (%): C,31.19; H,3.116; N,21.47.

Synthesis of HSTC-2:

A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.12 mmol), purine (0.04 mmol), and acetonitrile (5 ml) was sealed in a Pyrex glass tube with the pH adjusted by 400 μL 1M HNO_3 , and heated in an oven at 120 °C for 72 h. After cooling to room temperature at rates of 5°C/h, the yellowish crystals were obtained by filtration and washed with acetonitrile 3 times. Selected suitable crystals were immediately mounted on single crystal X-ray diffractometer for structural determination. IR spectrum (see Fig. S4b).

Determination of the Crystal Structures

The numerical absorption corrections were applied using the program of ABSCOR. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs. The unit cell volume included a large region of disordered solvent which could not be modelled as discrete atomic sites. Crystal data and structure refinement parameters are summarized in Tables S1.

Tables S1. Crystal data and structure refinement for all MOFs structures discussed in this work

Identification code	HSTC-1	H_2O_2 @HSTC-1	HSTC-2	Oxidized-HSTC-2	HSTC-1a
Empirical formula	$[\text{Zn}(\text{C}_5\text{H}_3\text{N}_4)(\text{CH}_3\text{COO})] \cdot \text{CH}_3\text{CN}$	$[\text{Zn}(\text{C}_5\text{H}_3\text{N}_4)(\text{CH}_3\text{COO})] \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$	$[\text{Zn}(\text{C}_5\text{H}_3\text{N}_4)(\text{CH}_3\text{COO})]$	$[\text{Zn}(\text{C}_5\text{H}_3\text{N}_4)(\text{CH}_3\text{COO})\text{OOH}]$	$[\text{ZnO}(\text{C}_5\text{H}_3\text{N}_4)]$
Formula weight	284.58	295.56	243.53	260.54	200.48
Temperature/K	299(2)	301.06(10)	150.15	99.98(12)	299.35(10)
Space group	$P2_12_12_1$		$I-4$		$P2_1/c$
a/Å	9.69687(15)	9.5293(3)	14.9679(2)	15.0686(4)	9.6930(4)
b/Å	9.74643(16)	9.9206(3)	14.9679(2)	15.0686(4)	10.4834(3)
c/Å	11.43337(20)	11.3847(5)	9.6787(2)	9.6371(3)	6.5421(2)
$\beta/^\circ$	-	-	-	-	105.143(4)
Volume/Å ³	1080.57(3)	1076.27(7)	2168.40(7)	2188.23(13)	641.70(4)
Z	4	4	8	8	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.749	1.824	1.492	1.582	2.075
μ/mm^{-1}	3.175	3.396	3.034	3.118	4.823
F(000)	576	600.0	976	1048.0	396.0
Wavelength/Å	Cu K_α ($\lambda = 1.54184$)				
2 θ range for data collection/ $^\circ$	11.932 to 145.314	11.832 to 157.83	8.354 to 133.014	10.898 to 154.498	9.452 to 146.586
Index ranges	-11 \leq h \leq 6, -11 \leq k \leq 11, -13 \leq l \leq 13	-8 \leq h \leq 11, -12 \leq k \leq 10, -13 \leq l \leq 14	-17 \leq h \leq 13, -17 \leq k \leq 17, -11 \leq l \leq 11	-16 \leq h \leq 19, -18 \leq k \leq 17, -11 \leq l \leq 4	-11 \leq h \leq 12, -12 \leq k \leq 12, -8 \leq l \leq 7

Reflections collected	3089	3730	5185	3159	2306
Independent reflections	1798 [R _{int} = 0.0172, R _{sigma} = 0.0256]	1977 [R _{int} = 0.0305, R _{sigma} = 0.0352]	1848 [R _{int} = 0.0223, R _{sigma} = 0.0244]	1874 [R _{int} = 0.0218, R _{sigma} = 0.0307]	2306 [R _{int} = ?, R _{sigma} = 0.0181]
Data/restraints/parameters	1798/0/157	1977/0/158	1848/121/167	1874/102/188	2306/0/101
Goodness-of-fit on F ²	1.104	1.052	1.055	1.088	1.149
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0249 wR ₂ = 0.0662	R ₁ = 0.0428, wR ₂ = 0.1184	R ₁ = 0.0482, wR ₂ = 0.1347	R ₁ = 0.0485, wR ₂ = 0.1378	R ₁ = 0.0299, wR ₂ = 0.0918
Final R indexes [all data]	R ₁ = 0.0257 wR ₂ = 0.0668	R ₁ = 0.0451, wR ₂ = 0.1204	R ₁ = 0.0485, wR ₂ = 0.1351	R ₁ = 0.0503, wR ₂ = 0.1395	R ₁ = 0.0324 wR ₂ = 0.0936
Largest diff. peak/hole / e Å ⁻³	0.39/-0.29	1.39/-0.57	0.65/-0.46	0.69/-0.47	0.77/-0.38

$$^a R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}^{1/2}$$

Topological analysis:

Systre files for the net

CRYSTAL

NAME HSTC-1-#1

GROUP I4132

CELL 2.82843 2.82843 2.82843 90.0000 90.0000 90.0000

NODE 1 3 0.37500 0.37500 0.37500

EDGE 0.37500 0.37500 0.37500 0.12500 0.37500 0.62500

EDGE_CENTER 0.25000 0.37500 0.50000

END

1: HSTC-1-#1/Systre

#####

Topology for C1

Atom C1 links by bridge ligands and has

Common vertex with					R(A-A)	
C	1	0.1250	0.3750	0.6250	(0 0 1)	1.000A 1
C	1	0.6250	0.1250	0.3750	(1 0 0)	1.000A 1
C	1	0.3750	0.6250	0.1250	(0 1 0)	1.000A 1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with C
Coordination sequences

C1: 1 2 3 4 5 6 7 8 9 10
Num 3 6 12 24 35 48 69 86 108 138
Cum 4 10 22 46 81 129 198 284 392 530

TD10=530

Vertex symbols for selected sublattice

C1 Point symbol:{10^3}
Extended point symbol:[10(5).10(5).10(5)]

Point symbol for net: {10^3}
3-c net; uninodal net

Topological type: srs; 3/10/c1 (topos&RCSR.ttd) {10^3} - VS [10(5).10(5).10(5)] (17888 types in 4 databases)

Elapsed time: 7.16 sec.

HSTC-2-#1/Systre

#####

Topology for C1

Atom C1 links by bridge ligands and has

Common vertex with					R(A-A)	
C 1	-0.1250	0.0000	0.0000	(0 0 0)	1.000A	1
C 1	0.2500	0.1250	-0.2500	(0 0 -1)	1.000A	1
C 1	0.2500	-0.1250	0.2500	(0 -1 0)	1.000A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with C

Coordination sequences

C1: 1 2 3 4 5 6 7 8 9 10

Num 3 6 12 22 35 50 69 92 116 142

Cum 4 10 22 44 79 129 198 290 406 548

TD10=548

Vertex symbols for selected sublattice

C1 Point symbol:{8².10}

Extended point symbol:[8.8.10(3)]

Point symbol for net: {8².10}

3-c net; uninodal net

Topological type: lig; 3/8/t1; sqc978 (topos&RCSR.ttd) {8².10} - VS [8.8.10(3)] (17888 types in 4 databases)

Elapsed time: 12.11 sec.

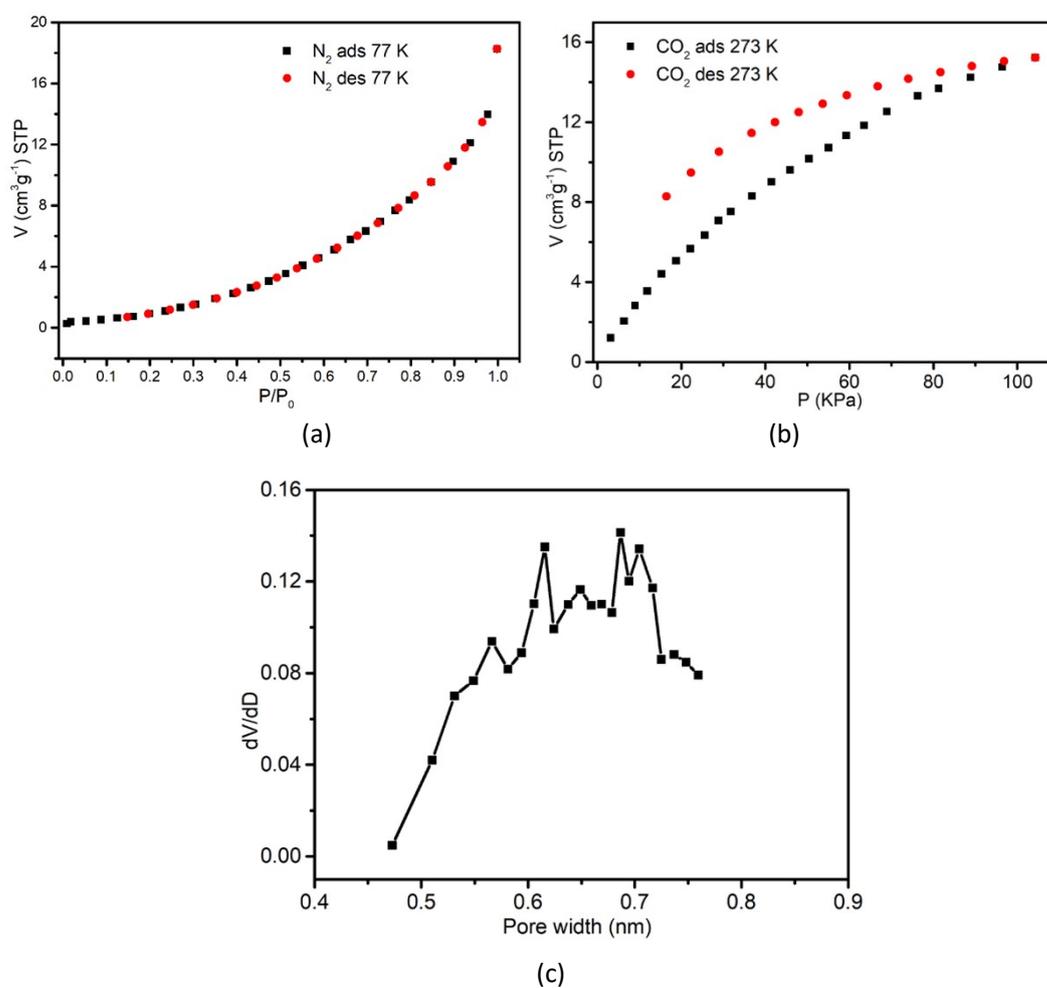


Fig. S1. (a) The N_2 adsorption isotherms at 77 K and (b) CO_2 adsorption isotherms at 273 K for HSTC-1. (c) HK porosity analysis of HSTC-1 by using the data of CO_2 adsorption at 273 K.

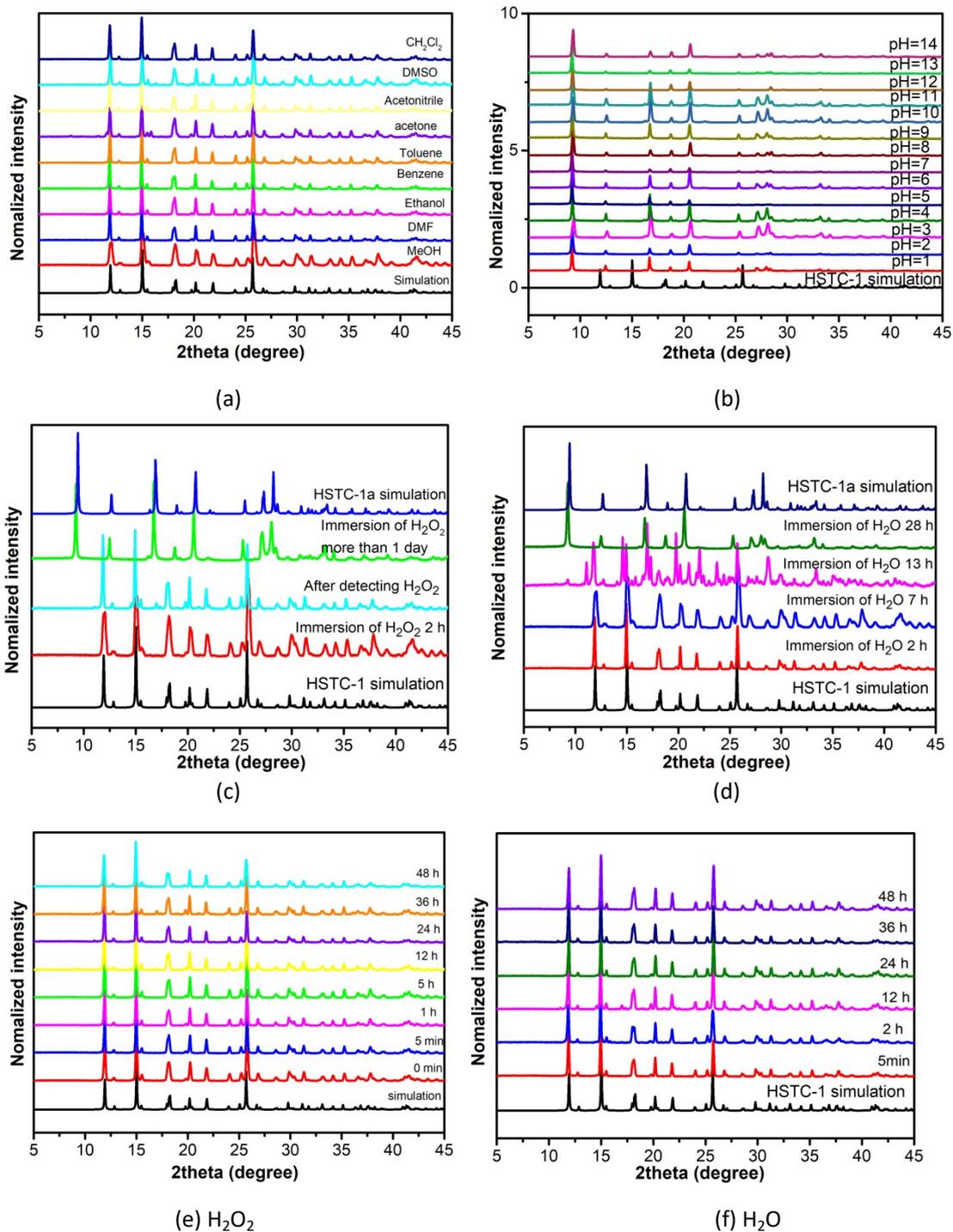
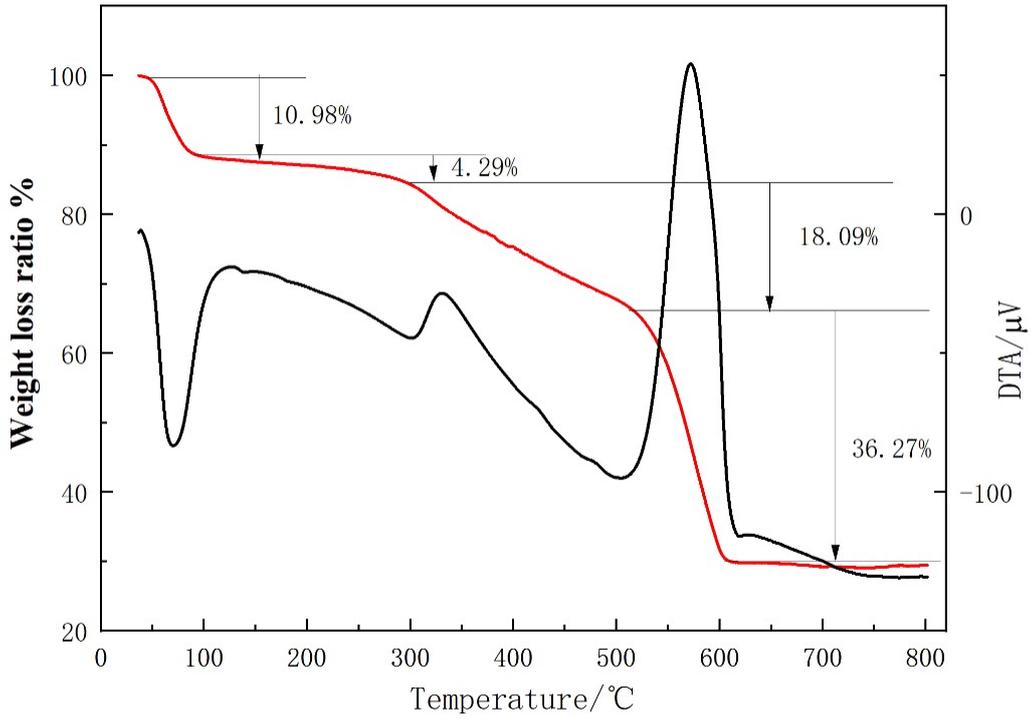
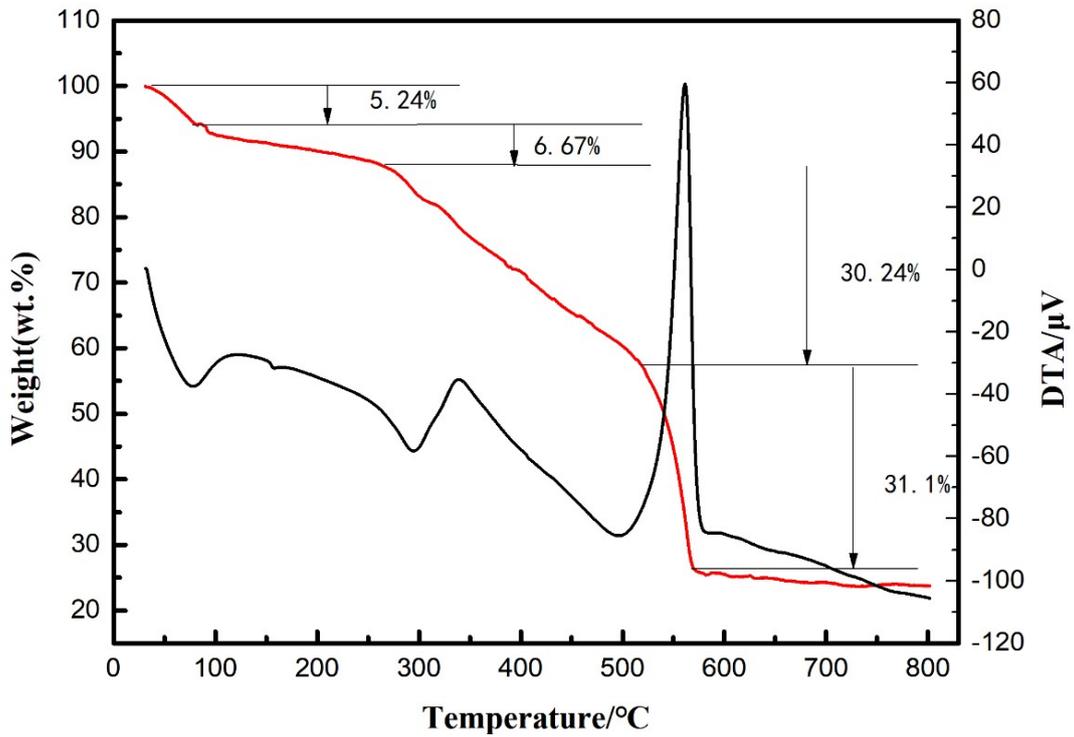


Fig. S2. (a) PXRD patterns of HSTC-1 soaked in different organic solvents. (b) PXRD patterns of HSTC-1 soaked in H_2O (pH=1-14) (c) Comparison of simulated PXRD patterns of HSTC-1, HSTC-1 being immersed in H_2O_2 for 2 h and the PXRD patterns of HSTC-1 sample after detecting hydrogen peroxide. (d) PXRD patterns of HSTC-1 immersed in H_2O at different times. (e) In situ PXRD pattern of H_2O_2 droplets on the HSTC-1 sample. (f) In situ PXRD pattern of H_2O droplets on the HSTC-1 sample.

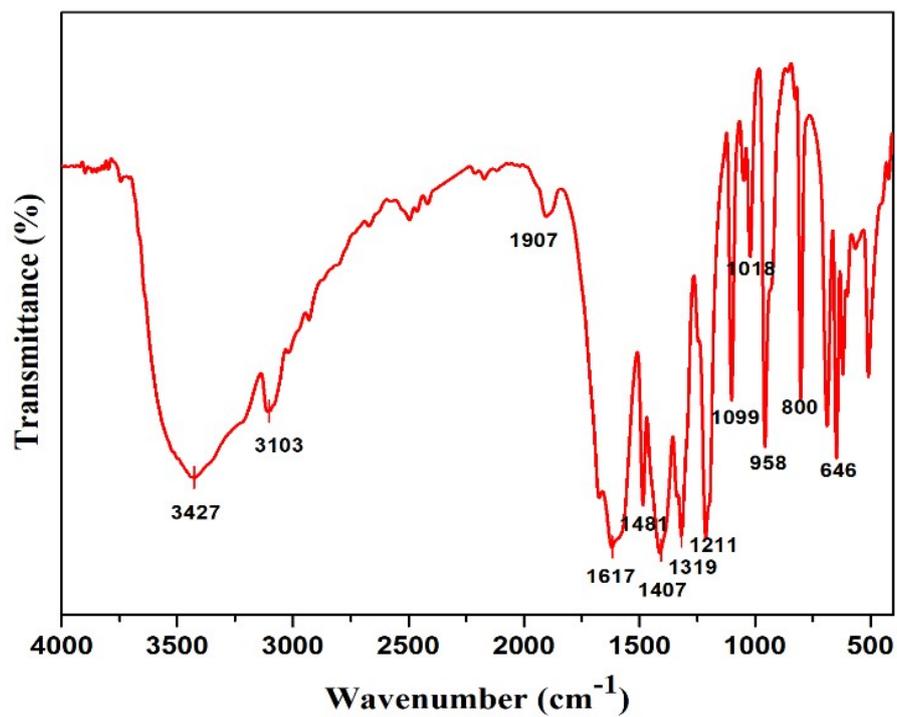


(a) HSTC-1

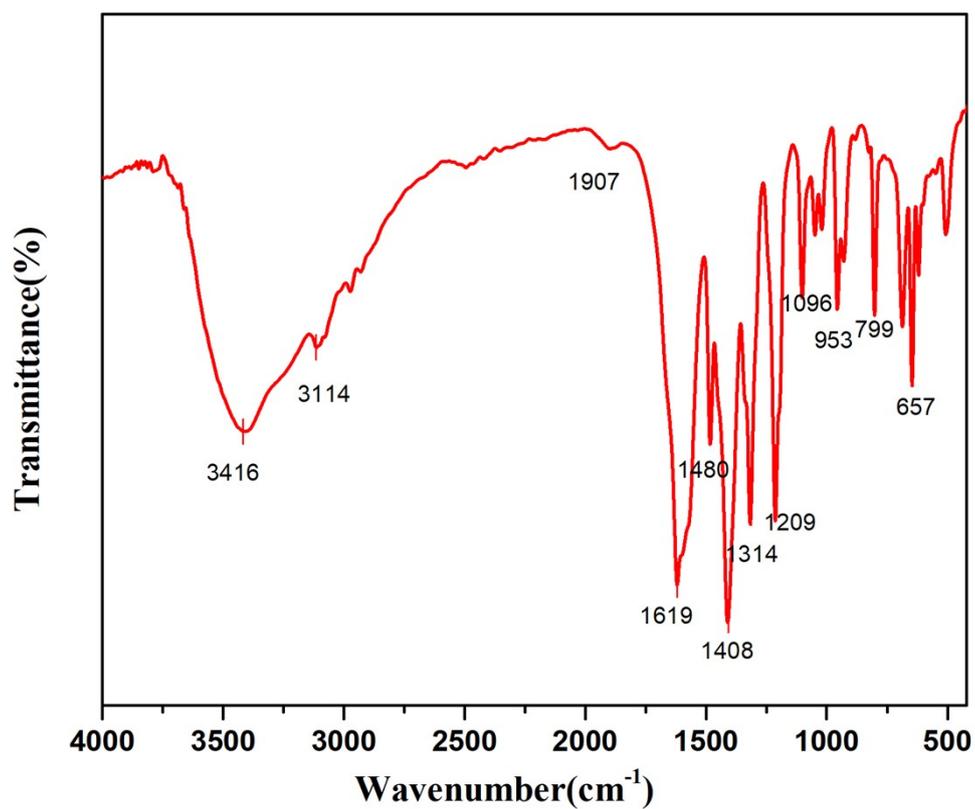


(b) HSTC-2

Fig. S3. Thermogravimetric analysis of (a) HSTC-1 and (b) HSTC-2.



(a) HSTC-1



(b) HSTC-2

Fig. S4. The FTIR spectra of (a) HSTC-1 and (b) HSTC-2.

Luminescence Properties Measurements

HSTC-1 acetonitrile suspension (3 mL) was placed in four-way cuvettes with the gradual addition of different concentrations H_2O_2 , respectively. After dispersing evenly, the fluorescent intensity was recorded at 15 minutes intervals. It is noteworthy that each sample has 3 replicates.

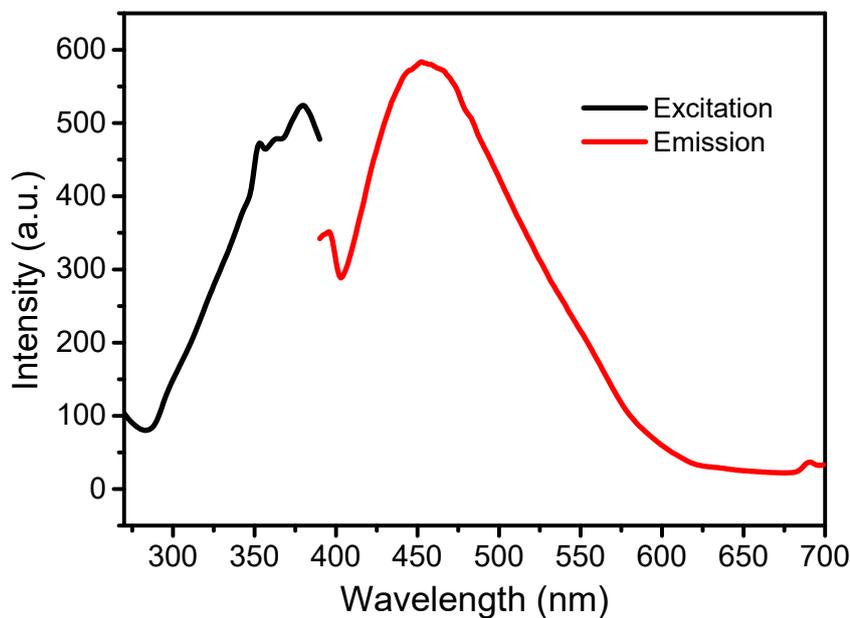


Fig. S5. The excitation and emission spectra of solid HSTC-1.

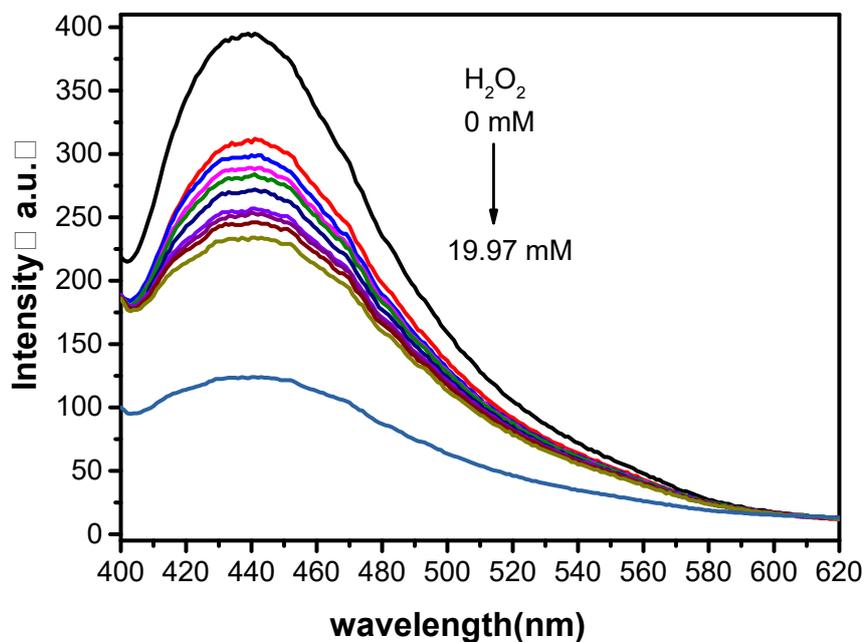


Fig. S6. Emission spectra of HSTC-1 acetonitrile suspension excited at 380 nm upon the incremental addition of H_2O_2 in the range of 0 – 20 mM. The bottom dark blue line is the addition of H_2O_2 to a cumulative concentration of 100 mM.

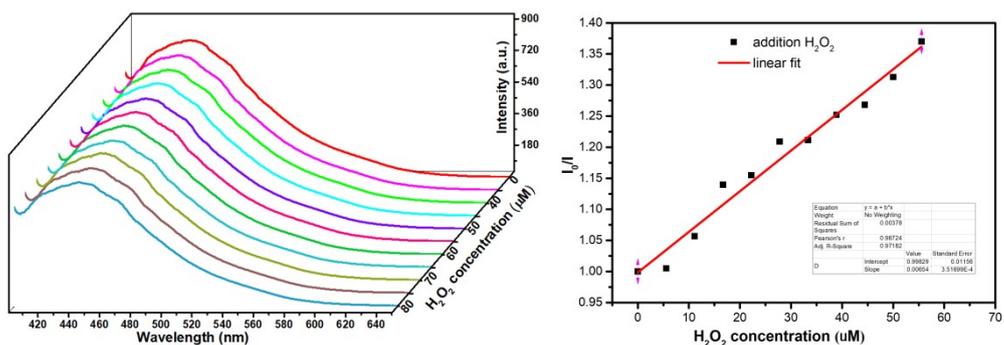


Fig. S7. Emission spectra of HSTC-1 acetonitrile suspension excited at 380 nm upon the incremental addition of H₂O₂ with a Stern-Volmer equation of $I_0/I=0.9983-0.00654x$ ($R^2=0.9718$) in the range of 0-80 μM (I_0 = luminescence intensity of pristine HSTC-1, I = luminescence intensity of HSTC-1 after addition of H₂O₂).

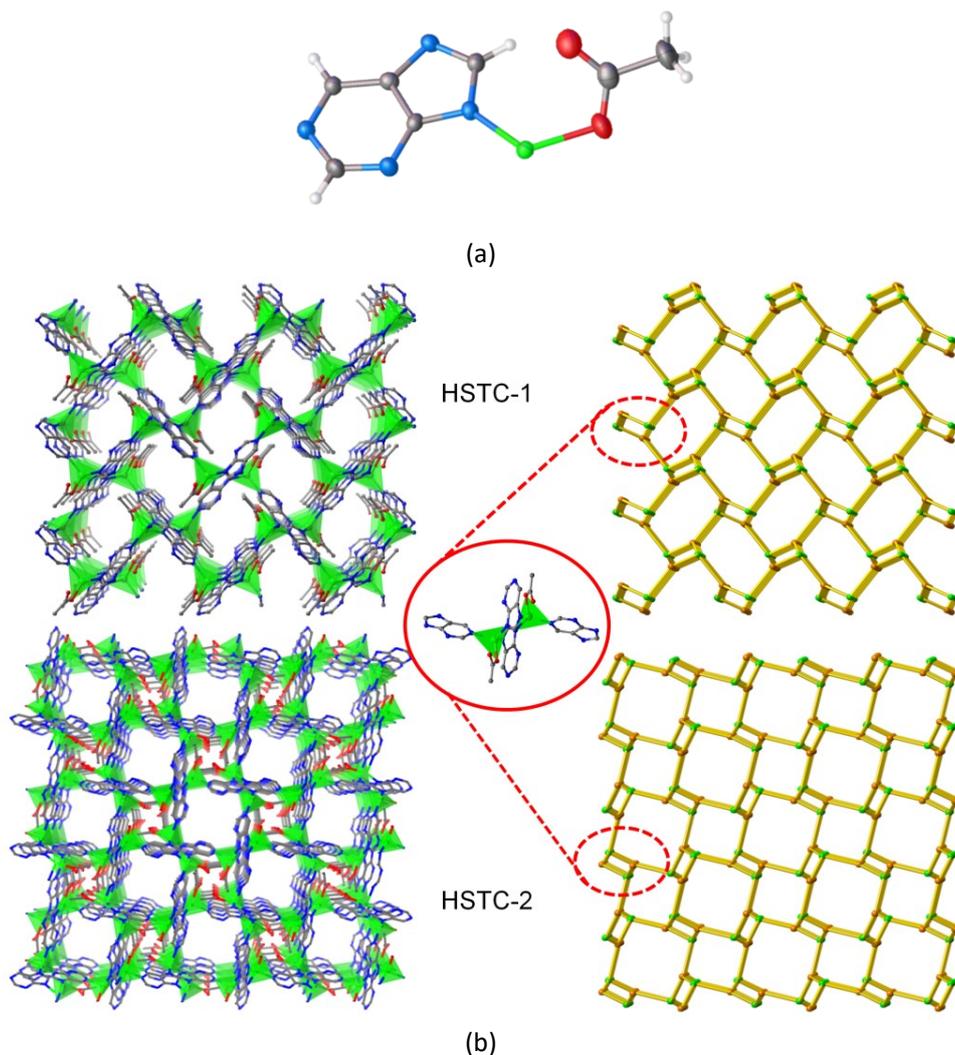


Fig. S8. (a) Asymmetric unit of HSTC-2. (b) The 3D structure framework and topological type of HSTC-1 and HSTC-2.

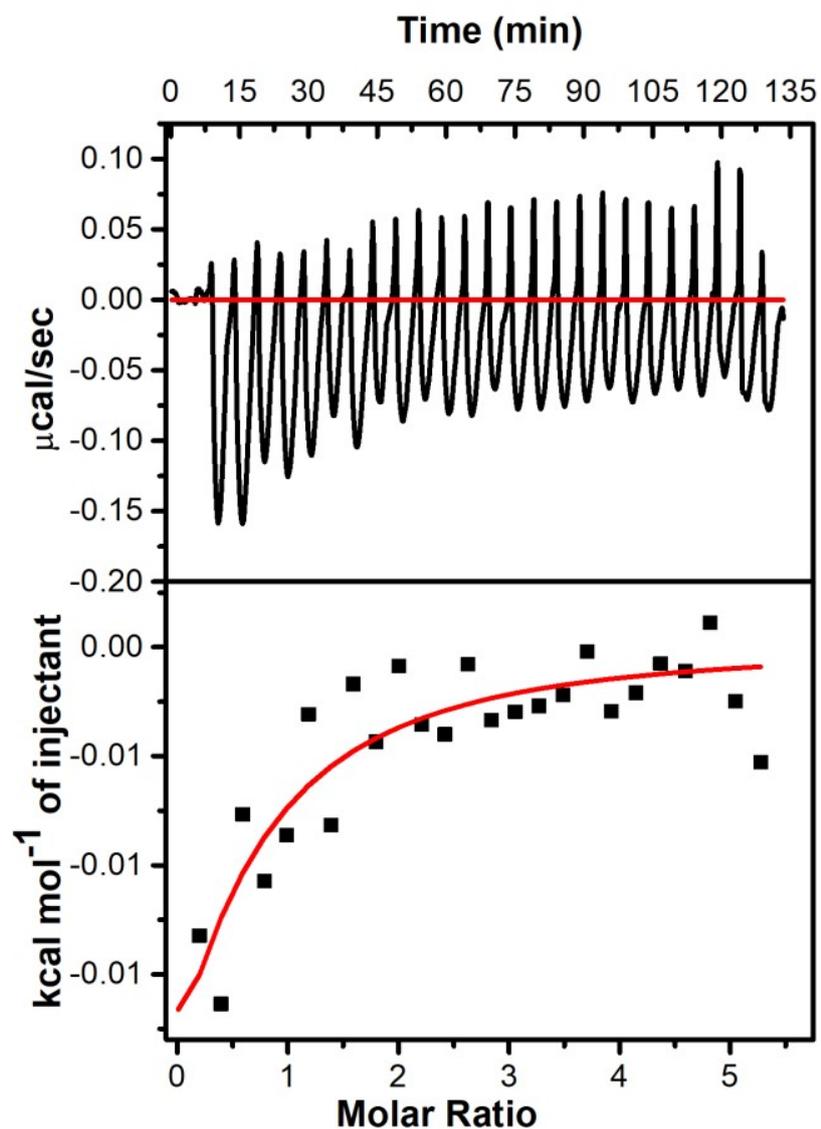
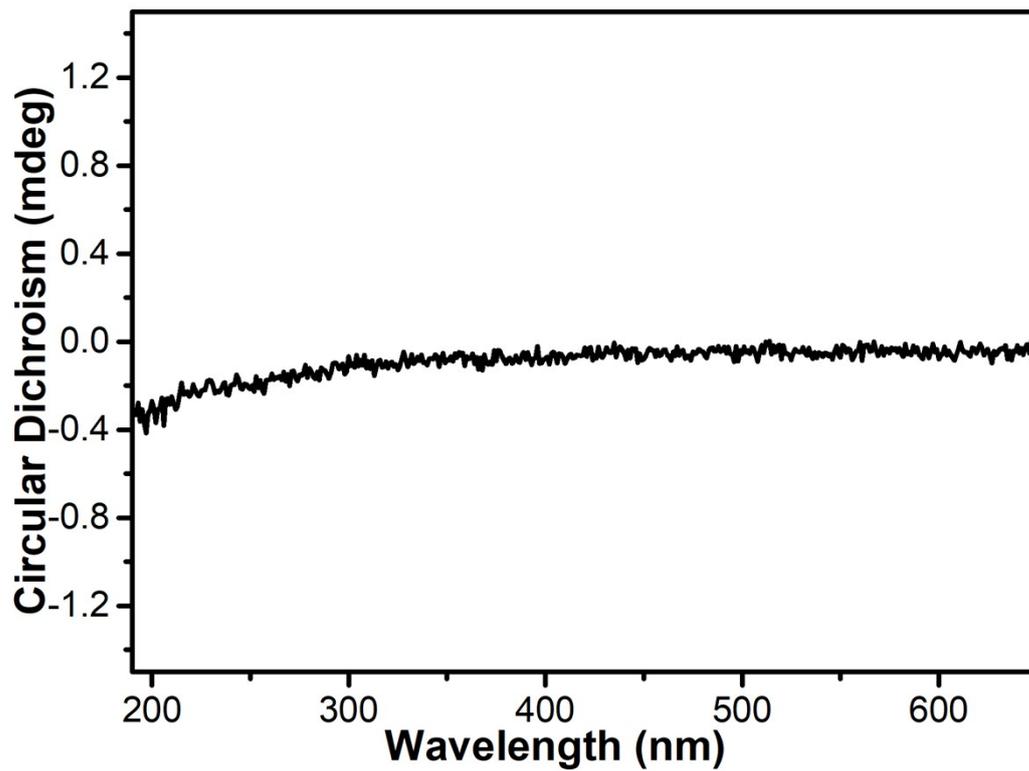
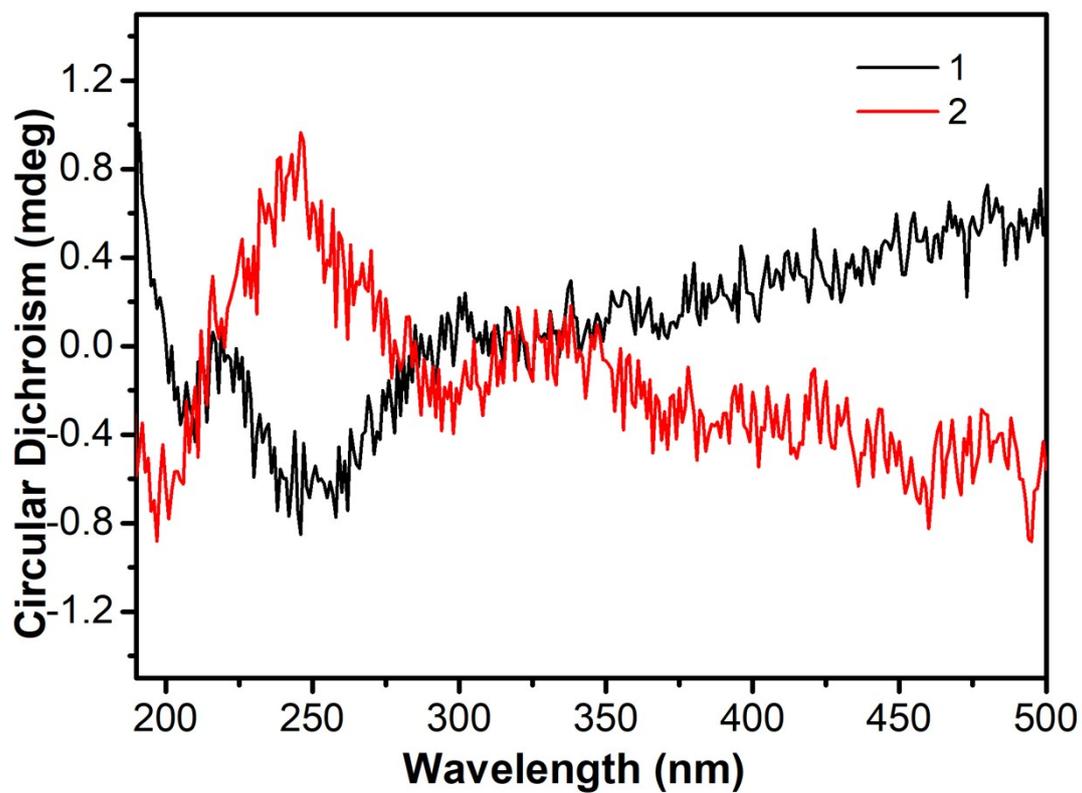


Fig. S9. ITC thermogram from titration of a HSTC-1 suspension (4 mM, 1.8 mL) with H₂O (15 μL each injection) and the low fitting with a single site model. No significant thermal changes were observed in the thermogram and thermodynamic parameters could not be obtained.

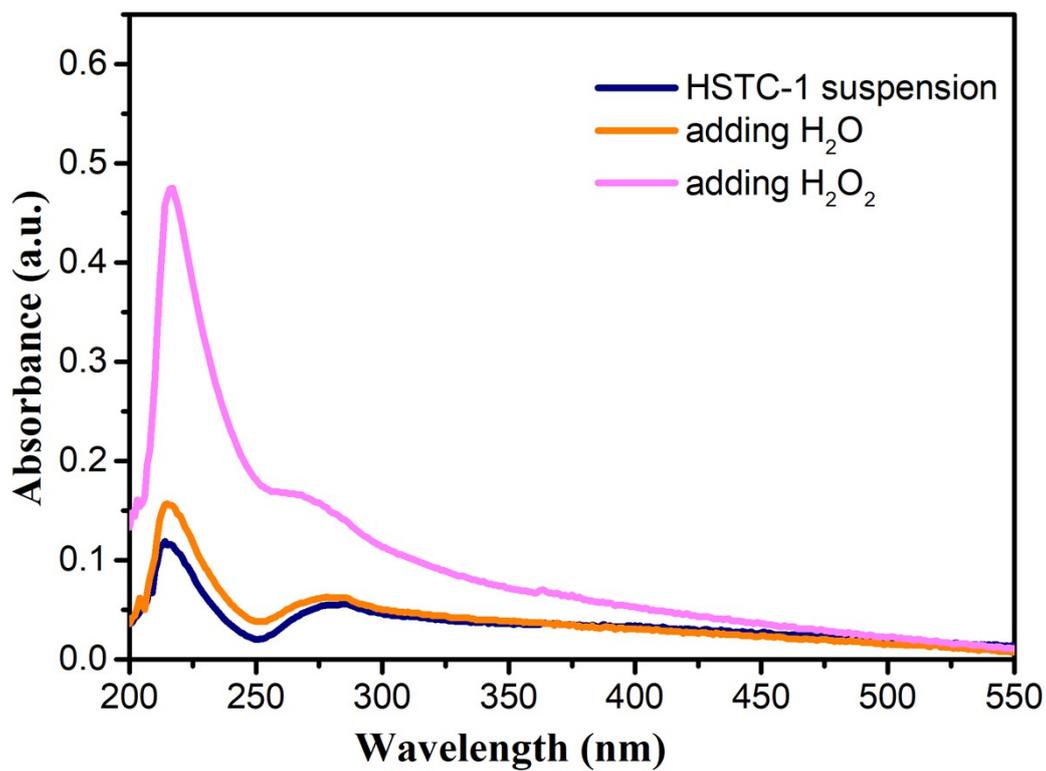


(a)

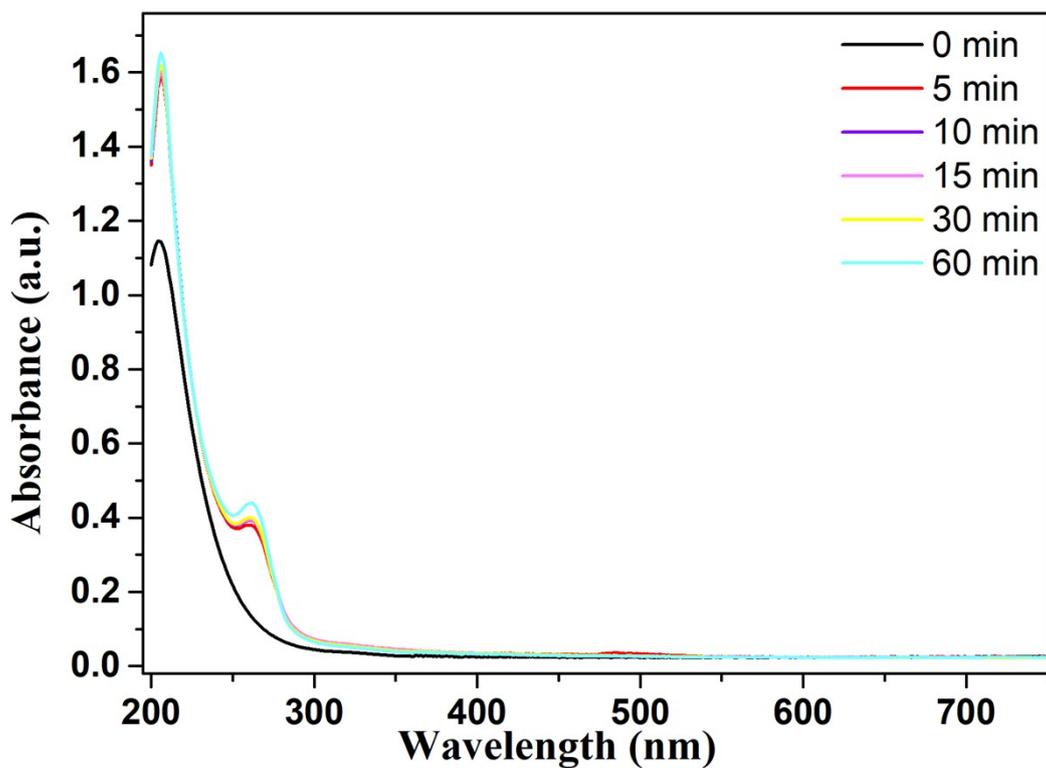


(b)

Fig. S10. Solid-state CD spectra of HSTC-1 measured using (a) bulk sample and (b) two different chiral single crystals, tableted, and diluted by KCl.



(a)



(b)

Fig. S11. (a) UV-Vis absorption spectra of the addition of H₂O and H₂O₂ in HSTC-1 acetonitrile suspension. (b) Time-dependent monitoring of the UV-Vis absorption spectra of H₂O₂ solution added to HSTC-1 crystals.

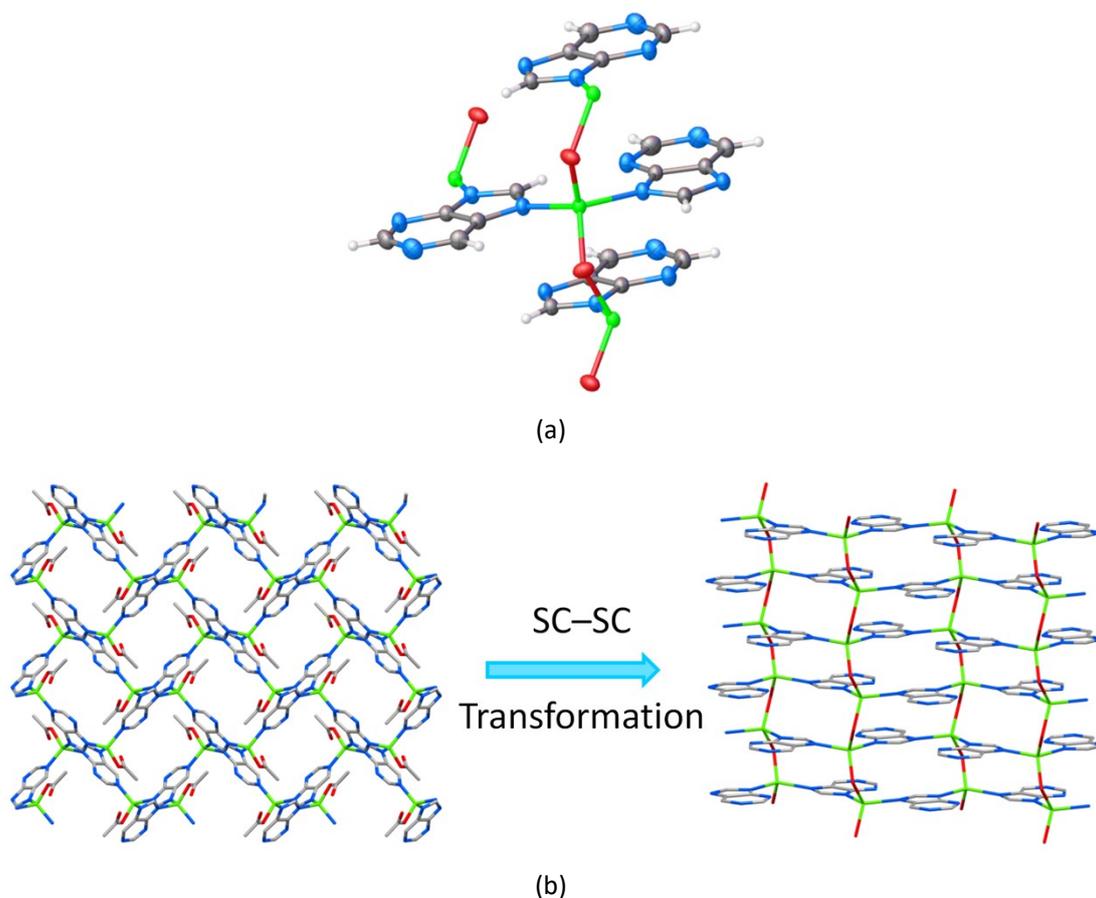


Fig. S12. (a) The coordination environment of HSTC-1 after soaking in H_2O_2 for more than 1 day. (b) Crystallization transformation of HSTC-1 from three-dimensional framework to two-dimensional framework.

Table S2. Binding energies (unit: kcal/mol) for host-guest interactions between H_2O_2 molecules and HSTC-1 or HSTC-2.

No. of H_2O_2 molecules	Binding energies of different equilibrium structures					Average binding energy
HSTC-1						
1	-8.86	-6.13	-8.55	-3.25	-	-6.70 ± 2.61
2	-20.24	-14.00	-17.78	-17.17	-17.38	-17.31 ± 2.22
3	-23.26	-22.69	-17.21	-19.58	-22.52	-21.05 ± 2.58
4	-29.25	-21.75	-21.46	-27.55	-22.76	-24.55 ± 3.59
5	-48.11	-42.55	-39.71	-34.04	-19.21	-36.72 ± 11.03
6	-28.53	-33.83	-49.63	-40.64	-30.72	-36.67 ± 8.57
HSTC-2						
1	-6.91	-9.43	-8.71	-8.01	-6.76	-7.96 ± 1.15
2	-16.36	-13.60	-16.07	-17.54	-18.20	-16.35 ± 1.77
3	-16.41	-6.82	-19.87	-10.83	-18.45	-14.48 ± 5.49
4	-30.36	-20.14	-20.03	-19.83	-27.46	-23.56 ± 4.99
5	-29.14	-30.70	-31.73	-29.16	-27.80	-29.71 ± 1.53
6	-33.41	-33.95	-35.69	-22.79	-26.06	-30.38 ± 5.62

Tables S3. Binding energies (unit: kcal/mol) for guest-guest' interactions between H₂O₂ molecules in HSTC-1 or HSTC-2.

No. of H ₂ O ₂ molecules	Binding energies of different equilibrium structures					Average binding energy
HSTC-1						
2	-1.32	-0.03	-1.44	-1.81	0.00	-0.92 ± 0.85
3	-3.38	-1.68	-5.87	-2.40	-2.26	-3.12 ± 1.66
4	-7.98	-7.02	-6.45	-3.86	-7.93	-6.65 ± 1.69
5	-12.26	-12.22	-15.07	-11.36	-9.12	-12.01 ± 2.14
6	-13.03	-13.55	-8.54	-11.84	-13.56	-12.10 ± 2.11
HSTC-2						
2	0.00	0.00	0.00	0.00	0.00	0.00 ± 0.00
3	0.65	-2.86	-2.29	-2.41	-1.34	-1.65 ± 1.40
4	-5.22	-5.92	-3.44	-5.45	-5.07	-5.02 ± 0.94
5	-5.92	-5.48	-5.06	-4.27	-3.96	-4.94 ± 0.82
6	-13.41	-7.47	-5.48	-4.03	-1.93	-6.46 ± 4.38