Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2020

*Supplementary Material for*

# Construction of a Helicate Metal-Organic Nanotubes and Enantioselective Recognition

Yan-Wu Zhao, Xian-Ming Zhang*

Key Laboratory of Magnetic Molecules & Magnetic Information Materials Ministry of Education, School of Chemistry & Material Science, Shanxi Normal University, Linfen, 041004, Shanxi, P. R. China.

* Corresponding authors

E-mail addresses: zhangxm@dns.sxnu.edu.cn.

# Table of contents

**Molecule configuration and coordination mode of RR-CHCAIP**

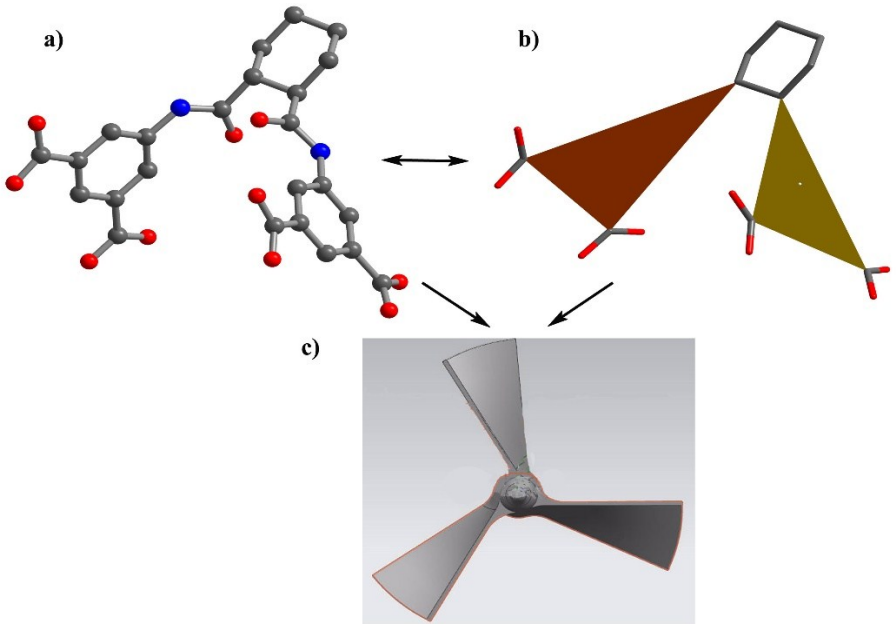



**Fig. S1** a) and b) molecular configuration of organic ligand **RR-CHCAIP**; c) photo of propeller, configuration of organic ligand **RR-CHCAIP** is similar to twin blades (the part encompassed by red line) of propeller

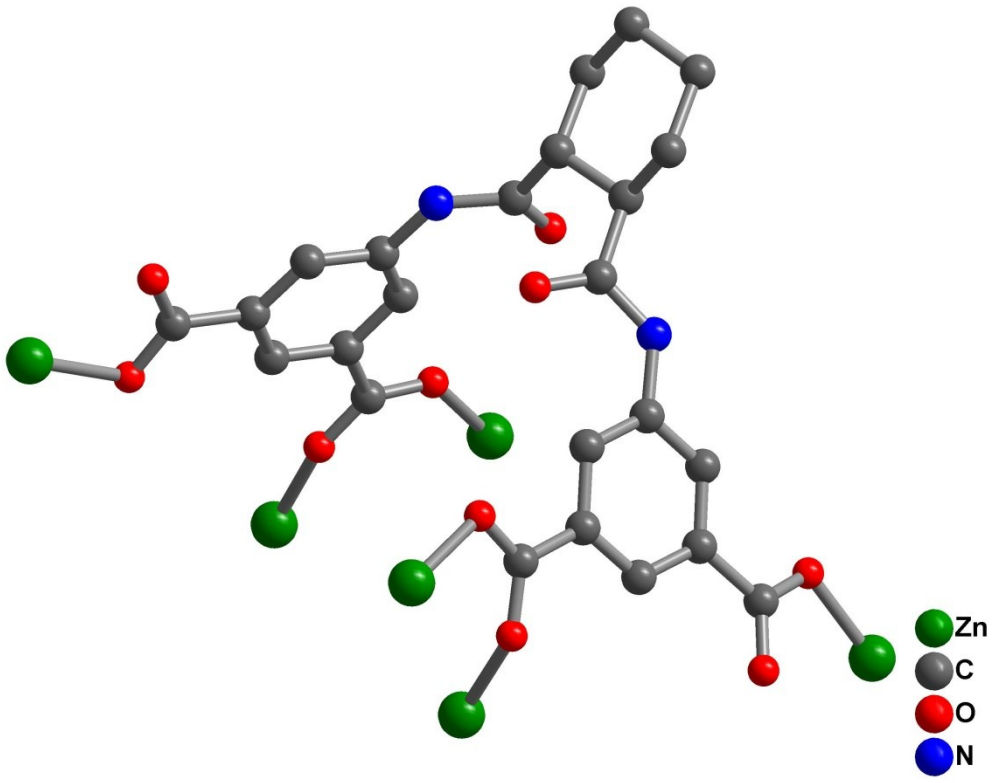



**Fig. S2** coordination mode of organic ligand **RR-CHCAIP**

## Experiment section

### 1. Materials and chemicals

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) were purchased from National drug group chemical reagents Co. Ltd.. Pyridine, trithylamine, 5-aminoisophthalic acid, oxlayl chloride, α-hydroxyl carboxylic acids and amino acids were purchased from Aladdin reagents Co. Ltd.. The (1R,2R)-cyclohexane-1,2-dicarboxylic acid were obtained from Gansu boshi biochemical technology Co. Ltd.. DMF, DMA, $CH_2Cl_2$ and $CHCl_3$ were purchased from Sailboat Chemical Reagent Technology Co. Ltd., respectively. All of the other chemicals used were of analytical reagent grade and used without further purification.

### 2. Measurements

The FT-IR spectra were recorded from KBr pellets in range 400-4000 $cm^{-1}$ on a Perkin-Elmer Spectrum BX FT-IR spectrometer. UV absorption spectra were recorded in $H_2O$ solution and solid with aU-3310 spectrophotometer. Elemental analysis was performed on a Vario EL-II elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded in a Bruker D8 ADVANCE powder X-ray diffractometer. The thermogravimetric analyses (TGA) were carried out in an air atmosphere using SETARAMLABSYS equipment at a heat in grate of 10°C/min. Luminescence spectra for solid and liquid samples were recorded, and lifetime measurements were measured by a single-photon counting spectrometer using an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 xenon lamp, a mF900 μs flash lamp, a red-sensitive Peltier-cooled Hamamatsu R928P

photomultiplier tube (PMT), and a closed Janis CCS-350 optical refrigerator system. The corrections of excitation and emission for the detector response were performed from 200 to 900 nm. Lifetime data were fitted with two-exponential-decay functions. Scanning electron microscopic (SEM) images were obtained with a JSM-7500F operated at beam energy of 25.0 kV. Transmission electron microscopy (TEM) was performed on a JEM-3010 electron microscope. The specific rotation was determined with an WXG-4 Polarimeter (china) using a standard 6 mL-cell (path length = 10 cm) at the wavelength of sodium-D ($\lambda$ = 589 nm) line at 25$^{o}$ C. The CD spectra were recorded on a JASCO J-815 CD spectrometer (with an accuracy of 0.1-0.3 nm) flushed with dry nitrogen at 25$^{o}$ C, using a 10 mm quartz cell cuvette with a scanning rate at 100 nm min$^{-1}$. The baseline correction was performed with the spectrum of corresponding solvents. All spectra were recorded for the wavelength range of 200-400 nm. The solid-state CD spectra were measured on the resulting complexes as crystals (ca. 0.56 mg) in 100 mg of oven-dried KBr. The baseline correction was performed with the spectrum of a pure KBr disk.

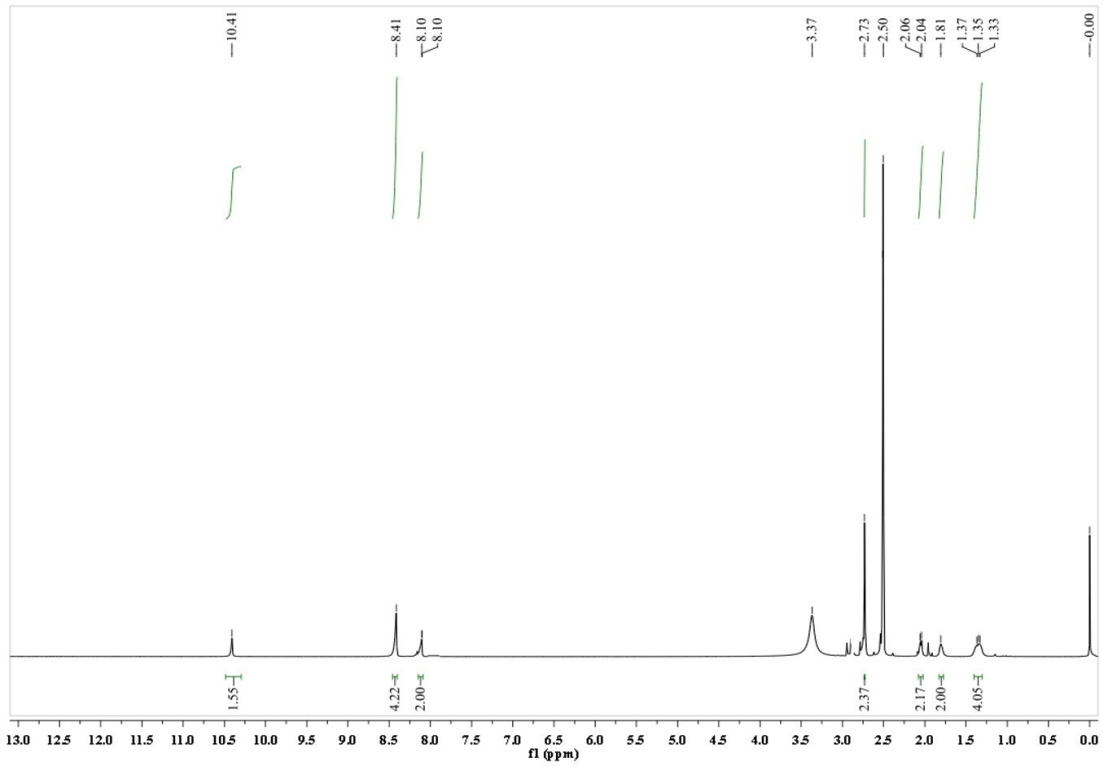
3. Synthesis of (1R, 2R)-cyclohexane-1,2-dicarbonyl dichloride **(2)**

To a solution of compound **1** (1.72 g, 10mmol) in dry $CH_2Cl_2$ (15 mL) was added dropwise into oxlayl chloride (4.44 g, 35 mmol) and stirred violently in 0 ºC ice-water bath. The resulting mixture was then dropped to 2 drops DMF and stirred at room temperature for 1h. After the mixture was concentrated in vacuum, the residue was dissolved in dry $CHCl_3$ repeatedly, and the solution was repeatedly concentrated in vacuum to offer the crude chloride **2**. The crude product was not purified further and

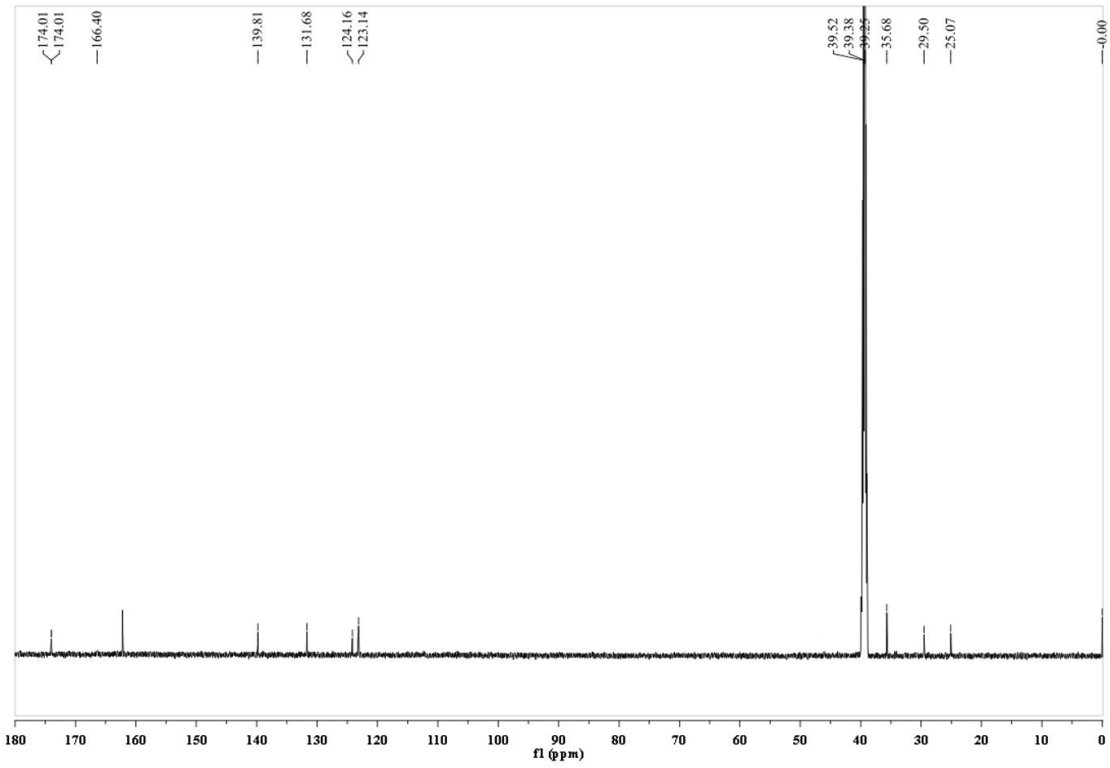
directly used in next step.

4. Synthesis of 5,5′-((1R,2R)-cyclohexanedicarbonyl bis(azanediyl))disophthalic acid (R, R-CHCAIP ) (**3**)

5-Aminoisophthalic acid (3.8 g, 20mmol) dissolved in dry DMA (30 ml) was well stirred and then compound **2** in 4 mL dry DMA was slowly added. The mixture was stirred for 3 h at room temperature and then TEA (2.2g, 20mmol) was added dropwise. The mixture was heated to 60 ºC and stirred for 30 min., again heated to 120 ºC and stirred for 20 min. The resulting mixture was poured into water. The precipitate was collected by filtration and washed thoroughly with $H_2O$ and dried in vacuum. The pure 5,5′-((1R,2R)-cyclohexanedicarbonylbis(azanediyl))disophthalic acid **3** was obtained in 90% yield (4.49 g). [$\alpha$]25 D = -147.5 (50 mg in 10 mL DMF). $^1$H NMR (600 MHz, DMSO-$d_6$): δ1.35 (m, 4H), 1.85 (s, 2H), 2.08 (d, 2H), 2.74 (d, 2H), 8.10 (s, 2H), 8.41 (s, 4H), 10.41 (s, 2H), 13.25 (s, 4H) ppm. Anal.Calcd for $C_{24}H_{22}N_2O_{10}$ (%): C, 57.83; H, 4.45; N, 5.62. Found: C, 57.85; H, 4.47; N, 5.59. ESI-MS: m/z 499.4 (Calcd m/z 499.44 for $[M+H]^+$).




**(a)**




**(b)**

**Fig. S3** $^{1}$H NMR (a) and $^{13}$C NMR (b) of solid compound **3**.

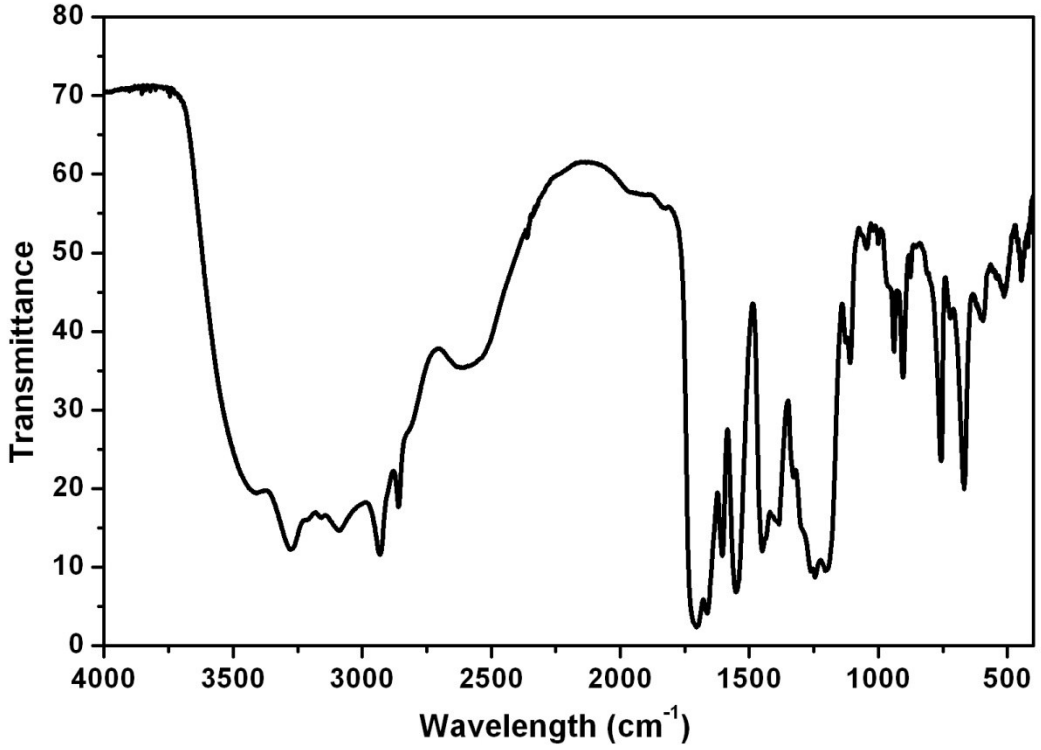



**Fig. S4** IR spectra of solid compound **3.**

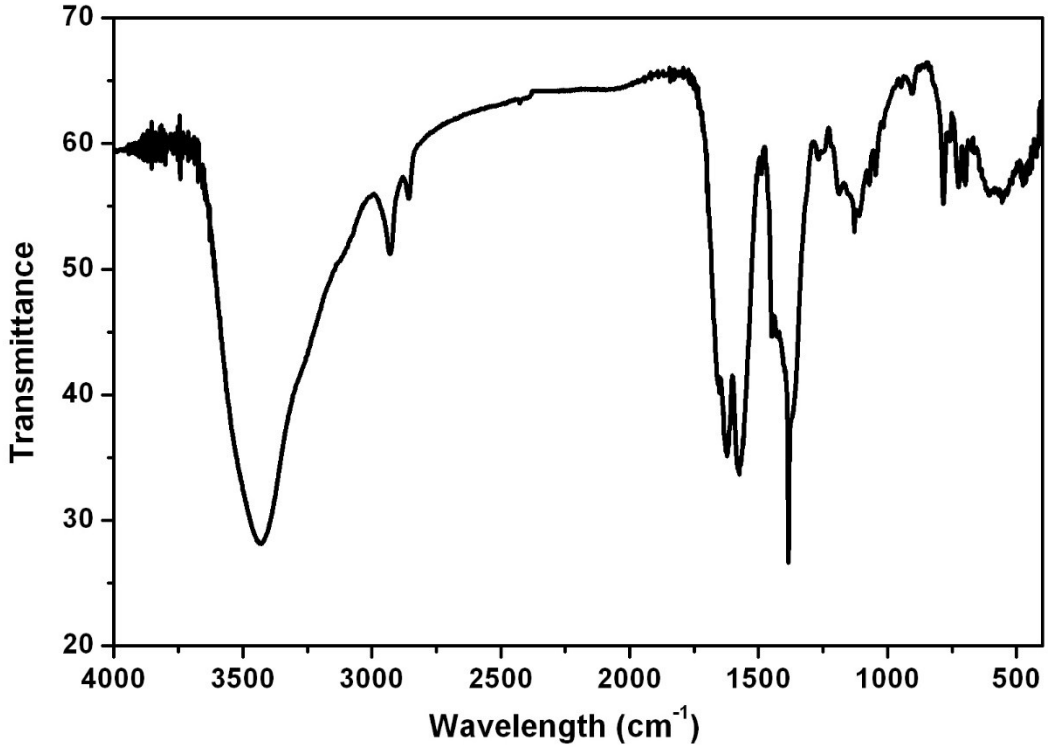



**Fig. S5** IR spectra of HMOF-**2**.

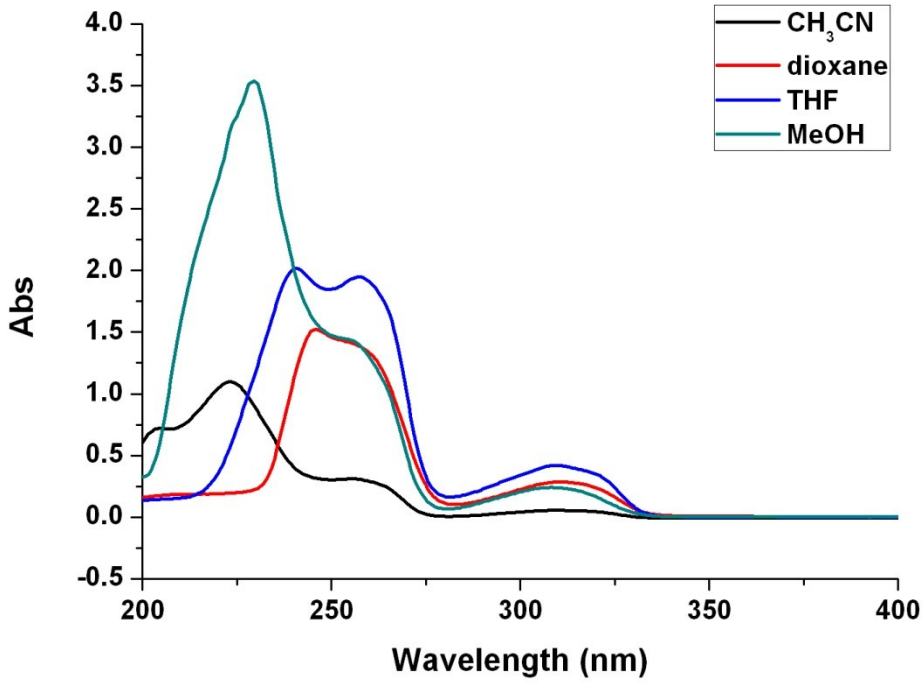



**Fig. S6** UV absorption spectra of compound **3** in $CH_3CN$ (black line), dioxane (red line), THF (blue line), MeOH (green line), respectively.

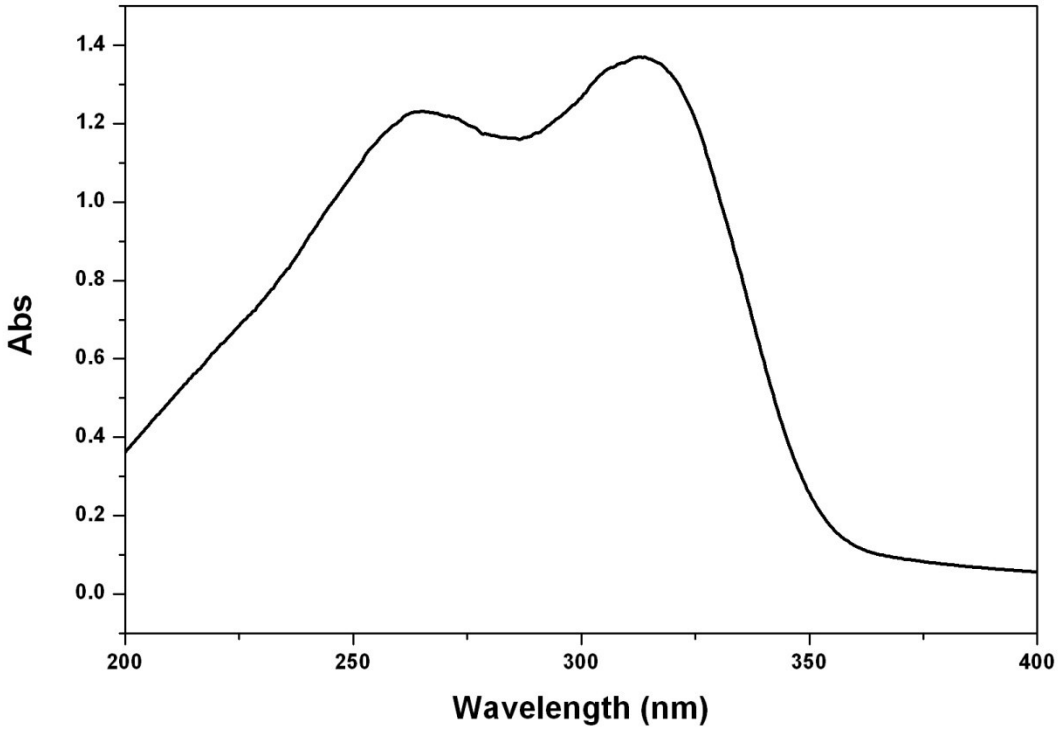



**Fig. S7** UV absorption spectra of solid compound **3.**

**Description of SBU and 1D nanotube**

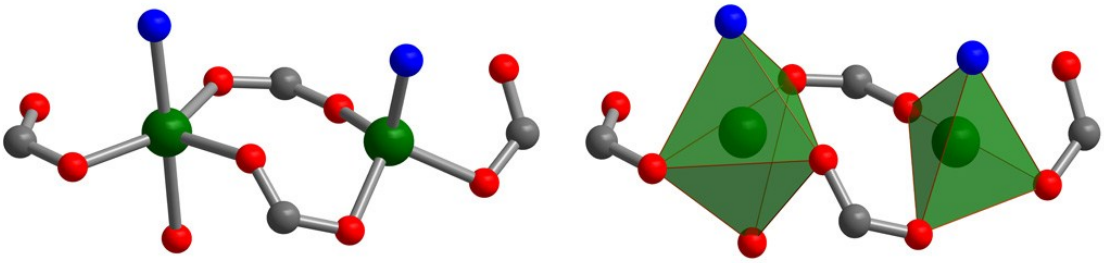
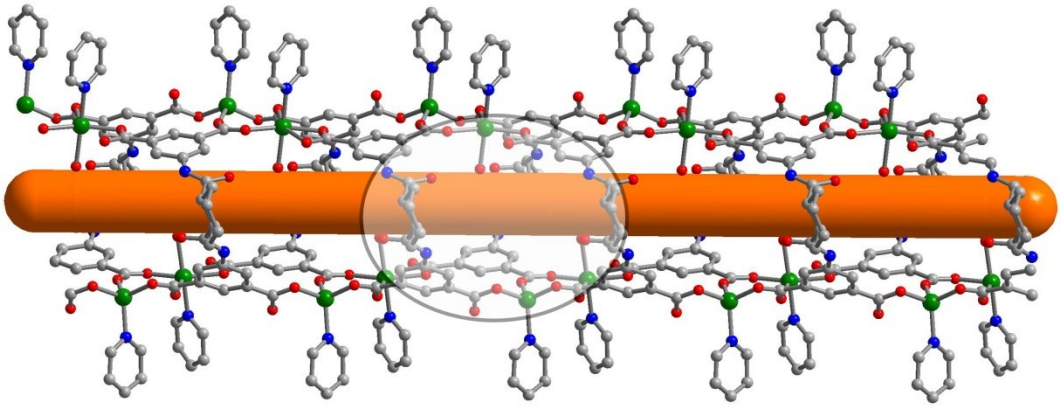
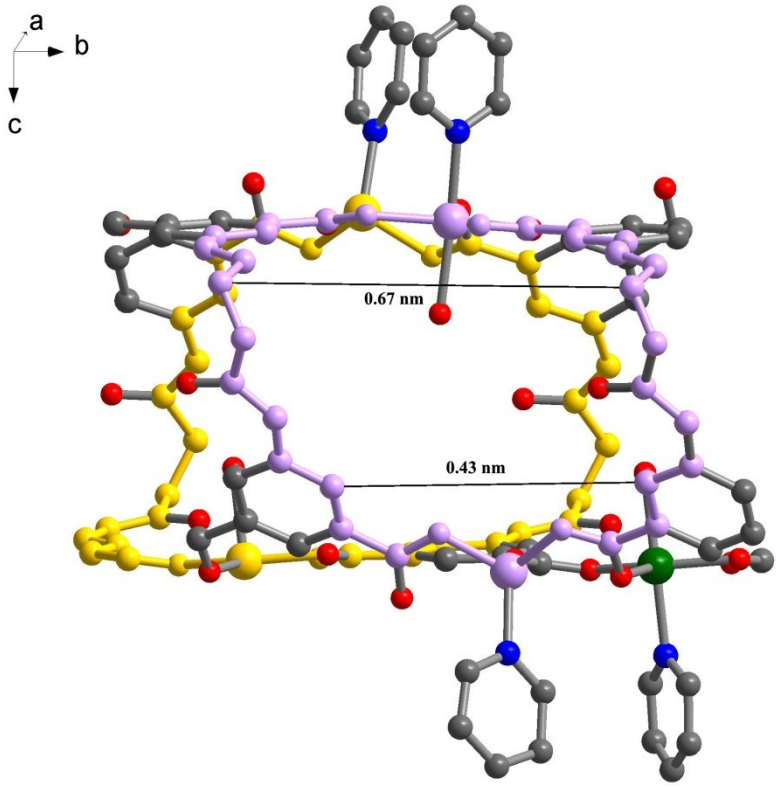


**Fig. S8** SBU composed by Zn cluster in **HMOF-2**



**(a)**




**(b)**

**Fig. S9** **a)** View of 1D helical nanotube in **HMOF-2** along the b axis; **b)** representative and amplified windows of helical nanotube in **(a)**. In the windows, the maximum width reaches 6.7 Å, and the minimum width reaches 4.3 Å (subtracted the Vander Waals radii of carbon atoms).

**Table S1 Crystal data and refinement parameters for HMOF-2.**

| Parameters | HMOF-2 |
|---|---|
| Empirical formula | $C_{34}H_{30}N_4O_{11}Zn_2$ |
| Formula weight | 801.36 |
| Temperature/K | 293(2) |
| Crystal system | monoclinic |
| Space group | *C*2 |
| a (Å) | 30.339(2) |
| b (Å) | 10.0939(4) |
| c (Å) | 16.2638(11) |
| α (°) | 90 |
| β (°) | 112.167(6) |
| γ (°) | 90 |
| Volume ($Å^3$) | 4612.5(5) |
| Z | 4 |
| Calculated density ($g/cm^3$) | 1.154 |
| Absorption coefficient ($mm^{-1}$) | 1.090 |
| F(000) | 1640 |
| Crystal size/$mm^3$ | 0.41 × 0.18 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection (°) | 6.836 to 52.744 |
| Index ranges | -37≤h≤37, -12≤k≤12, -20≤l≤20 |
| Reflections collected | 33233 |
| Independent reflections | 9406 [$R_{int}$ = 0.0355, $R_{sigma}$ = 0.0411] |
| Data/restraints/parameters | 9406/2/461 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0380, $wR_2$ = 0.0908 |
| Final R indexes [all data] | $R_1$ = 0.0485, $wR_2$ = 0.0955 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.61/-0.31 |
| Flack parameter | -0.006 (5) |

**Table S2 Bond lengths [Å] and angles [º] for HMOF-2.**

| | |
|---|---|
| Zn(1)-O(3a) | 2.050(5) |
| Zn(1)-O(5) | 2.029(6) |
| Zn(1)-O(10b) | 2.051(5) |
| Zn(1)-O(11) | 2.222(8) |
| Zn(2)-O(4b) | 1.965(6) |
| Zn(2)-O(7a) | 1.952(6) |
| Zn(2)-O(9) | 2.000(6) |
| Zn(1)-N(3) | 2.150(6) |
| Zn(2)-N(4) | 2.026(7) |
| | |
| O(5)-Zn(1)-O(10b) | 102.9(2) |
| O(5)-Zn(1)-O(11) | 91.9(3) |
| O(5)-Zn(1)-N(3) | 89.3(2) |
| O(10b)-Zn(1)-N(3) | 90.3(2) |
| O(10b)-Zn(1)-O(11) | 93.7(3) |
| N(3)-Zn(1)-O(11) | 175.5(3) |
| O(4)-Zn(2c) | 1.956(6) |
| O(7)-Zn(2d) | 1.952(6) |
| O(4b)-Zn(2)-O(9) | 119.0(2) |
| O(4b)-Zn(2)-N(4) | 114.7(3) |
| O(7a)-Zn(2)-O(9) | 98.23(2) |
| O(7a)-Zn(2)-O(4b) | 104.4(3) |
| O(7a)-Zn(2)-N(4) | 110.7(3) |
| O(9)-Zn(2)-N(4) | 108.3(3) |

Symmetry transformations used to generate equivalent atoms:

a) x,-1+y,+z; b)1/2-x,-1/2+y, 1-z; c) 1/2-x,1/2+y, 1-z; d) x,1+y, z

**SEM and TEM of HMOF-2**

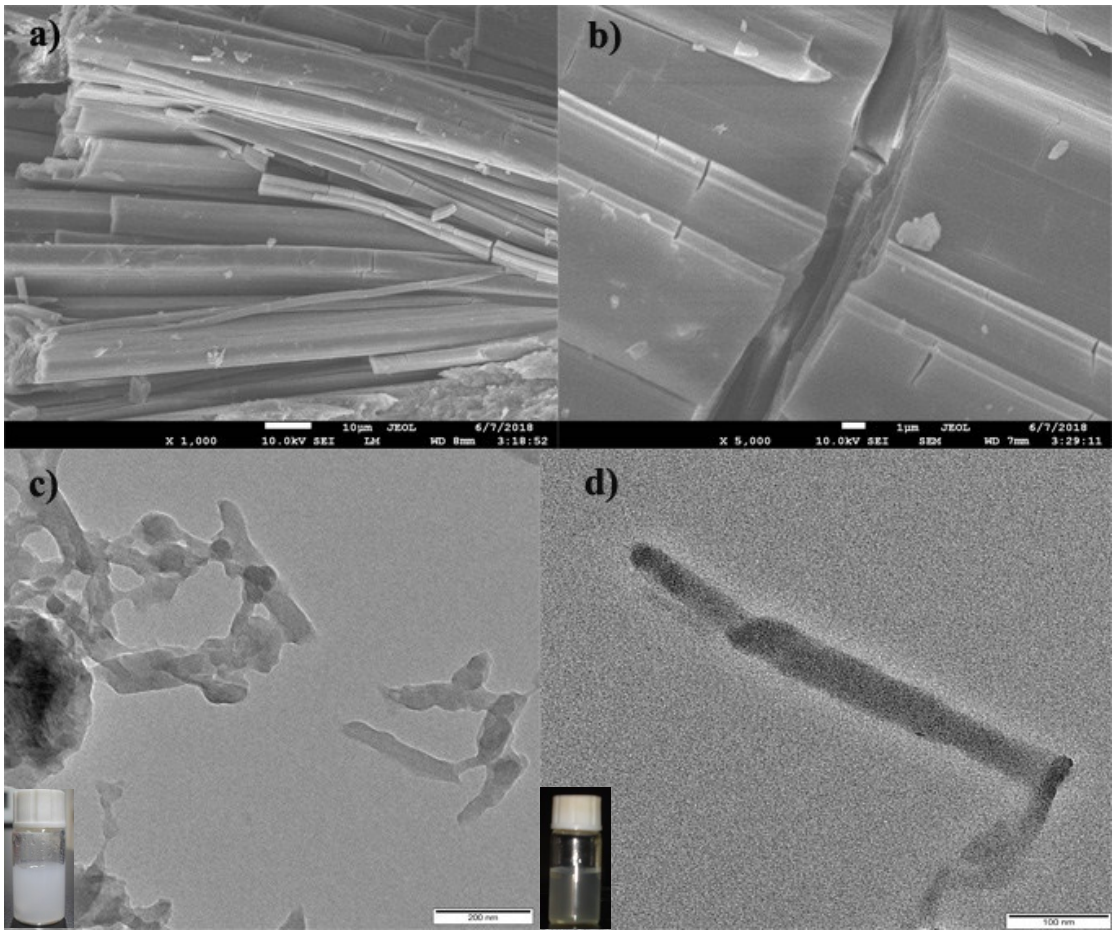



**Fig. S10** a) and b) Representative SEM image of HMOF-2. c) TEM image of HMOF-2 micelles; d) amplified image of (c). The inset in (c) presents the emulsified solution of 5 mg of HMOF-2 in 3 mL of $CH_3CN$, and the inset in (d) does diluted HMOF-2 stock solution.

**Thermogravimetric analysis**

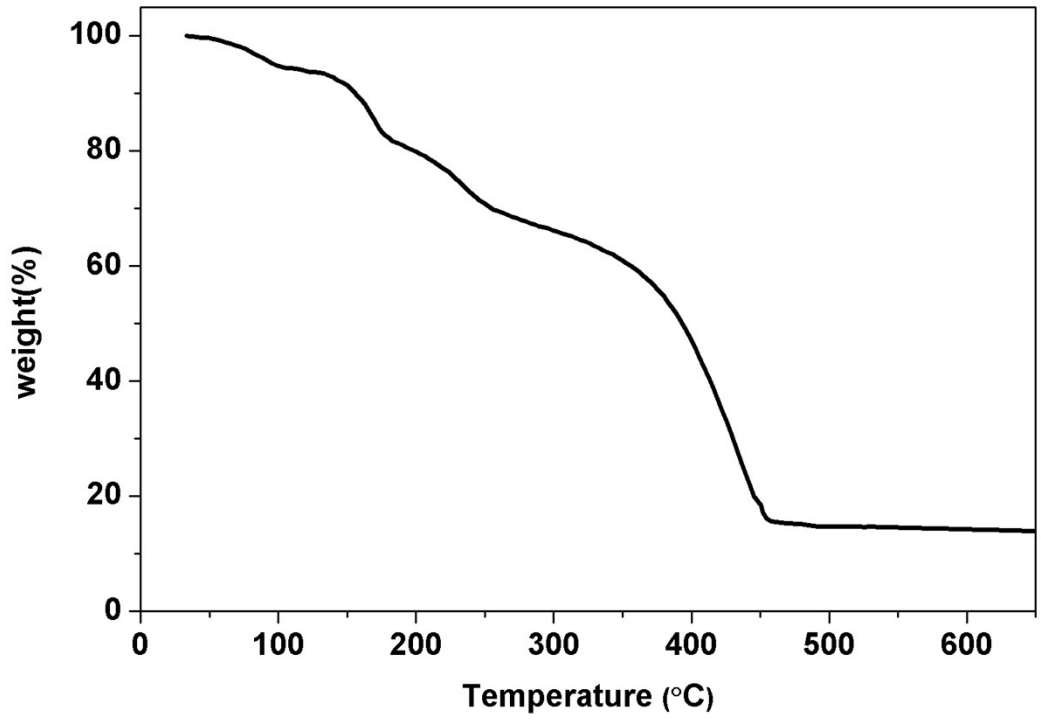



**Fig. S11** Thermogravimetric analysis of the as-synthesized HMOF-2.

**PXRD of HMOF-2**

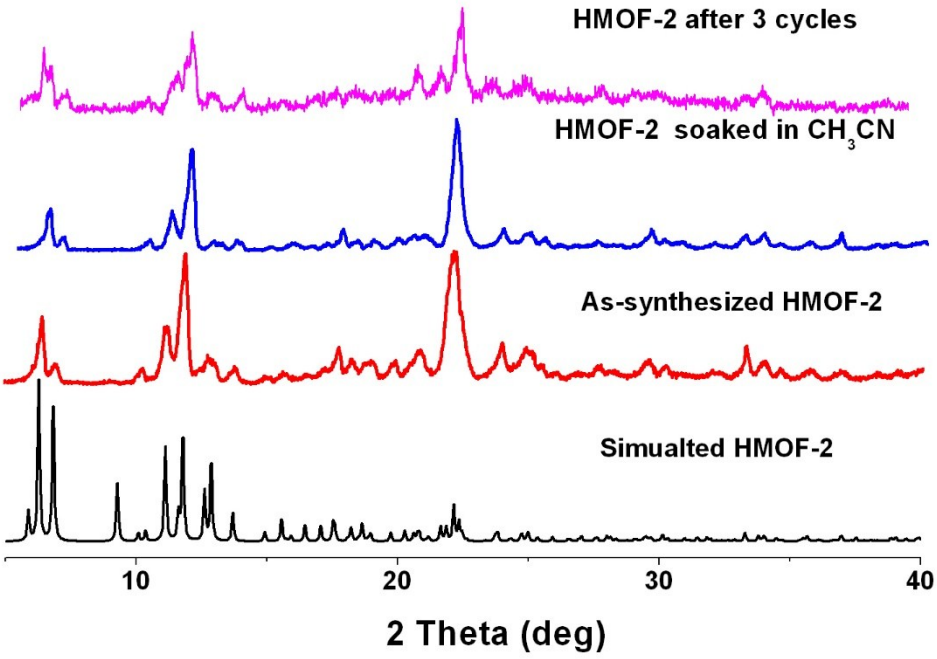
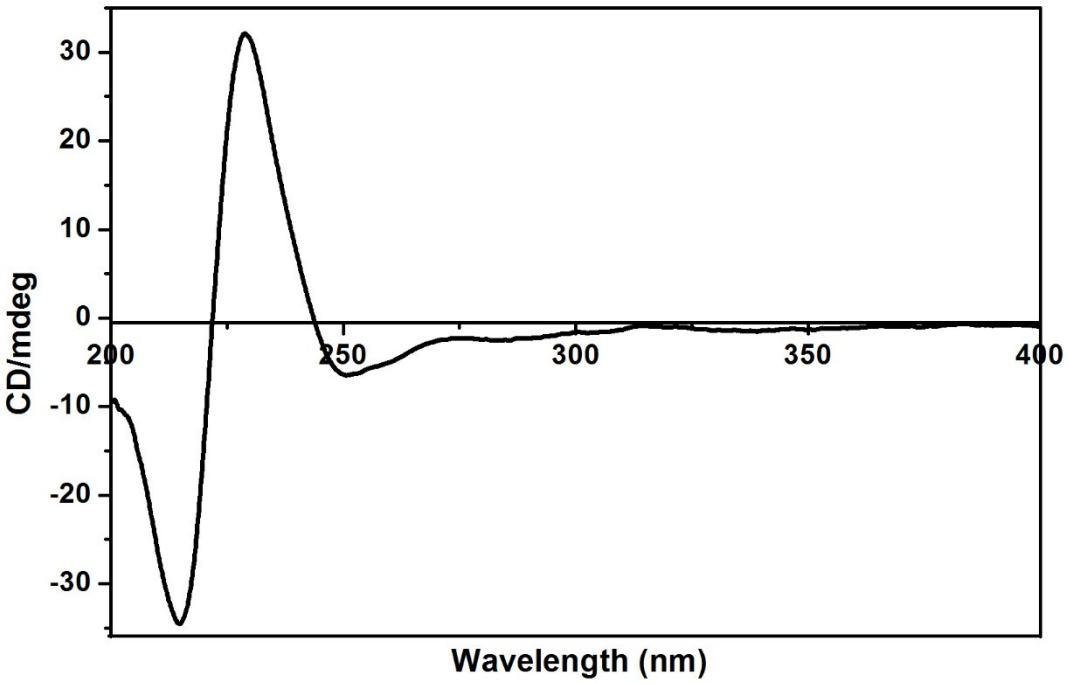
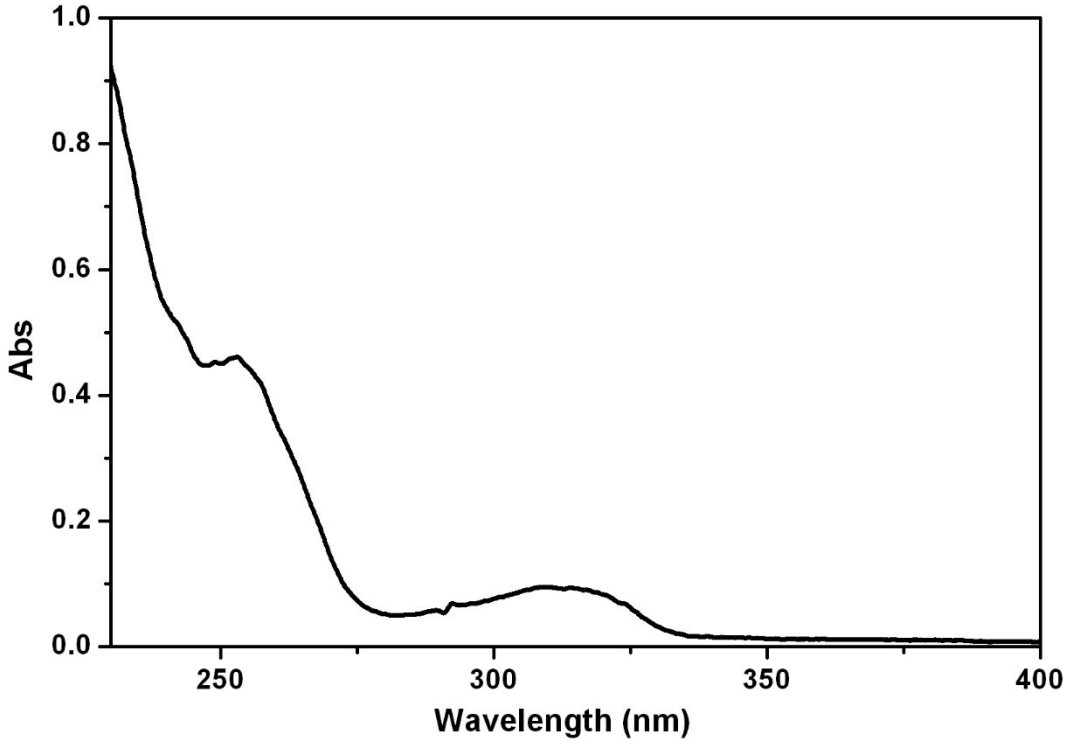



**Fig. S12** Powder X-ray diffraction patterns of HMOF-2, including simulated HMOF-2 (black), as-synthesized HMOF-2 (red), HMOF-2 soaked in $CH_3CN$ (blue) and HMOF-2 after 3 cycles (pink).

**Circular dichroism (CD) spectra of ligand and HMOF-2**

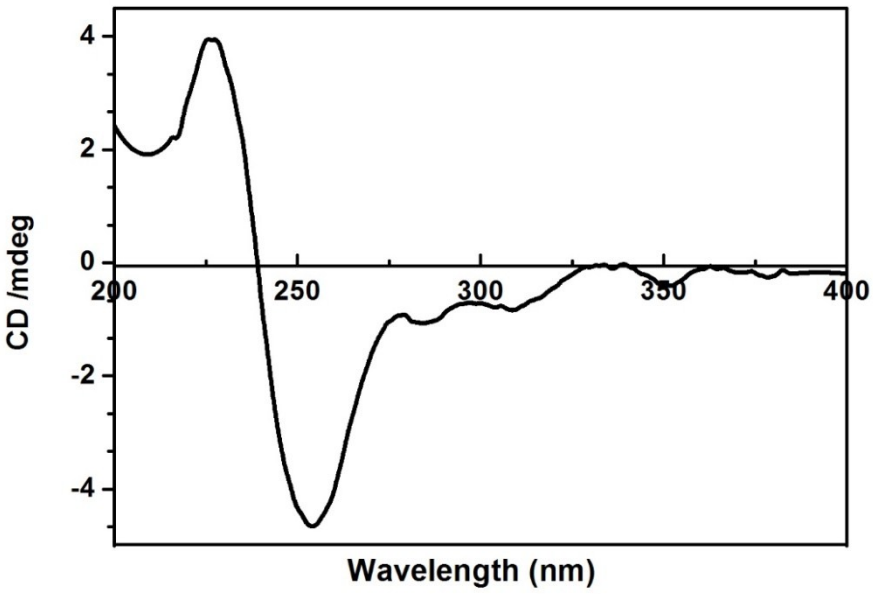



**(a)**

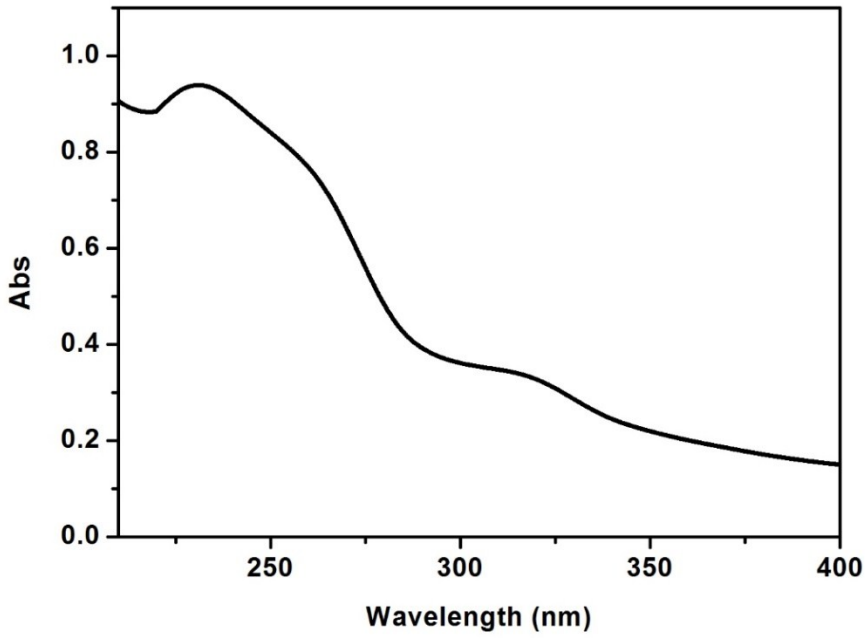



**(b)**

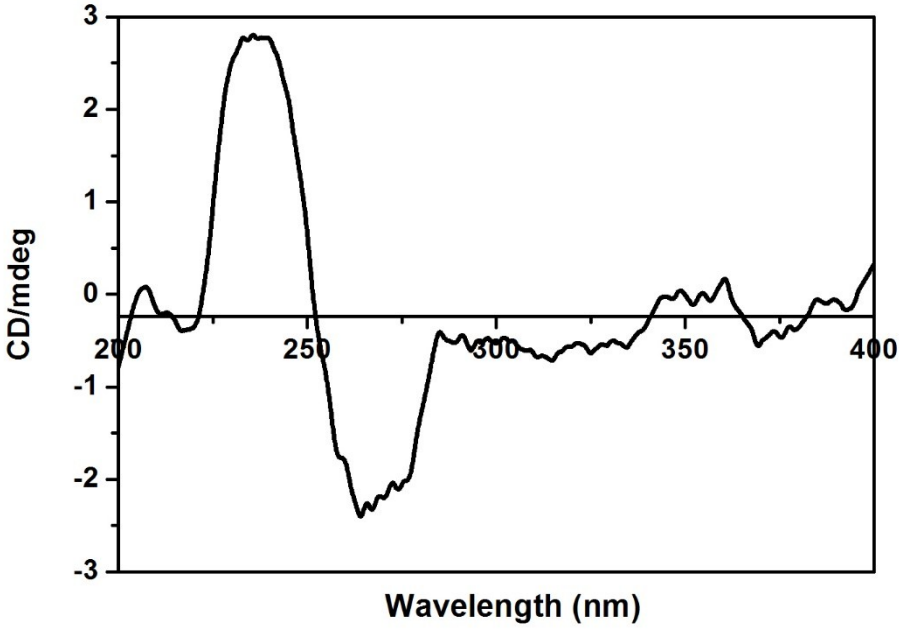
**Fig. S13** CD spectra (a) and the corresponding UV absorption spectra (b) of ligand **RR-CHCAIP** in $CH_3CN$.




**(a)**




**(b)**




**(c)**

**Fig. S14** CD spectra (a) and the corresponding UV absorption spectra (b) of HMOF-2 in $CH_3CN$ solution. Owing to weak dissolution of HMOF-2 in $CH_3CN$, CD signal of HMOF-2 is weaker than ligand **RR-CHCAIP** in $CH_3CN$; (c) CD spectra of solid HMOF-2.

**Preparation of HMOF-2 stock solutions and Description of fluorescence properties**

Preparation of HMOF-2 stock solutions: 5 mg of HMOF-2 crystals were placed in a vial with 3 mL $CH_3CN$, which was mechanically crushed by vigorous stirring overnight. The resulting white emulsion was then diluted with $CH_3CN$ to 50 mL for fluorescence measurements of α-hydroxy carboxylic acids. Exactly 3 mL of newly prepared HMOF-2 stock solution was added to a quartz cuvette for each fluorescence experiment.

Preparation of free ligand stock solutions: 3.1 mg of free organic ligand (RR-CHCAIP) was dissolved in 50 mL $CH_3CN$ (identical concentration with HMOF-2 emulsion in $CH_3CN$). Exactly 3 mL of newly prepared stock solution was added to a quartz cuvette for each fluorescence experiment.

Measurement of fluorescence spectroscopy: Before measurements on fluorescence spectra of HMOF-2 and probe α-hydroxy carboxylic acids, stock solution of HMOF-2 and quencher α-hydroxyl carboxylic acids in $CH_3CN$ was prepared. The mixed HMOF-2 and α-hydroxy carboxylic acids stock solution was ultrasounded for 10 min before fluorescence measurements to give sufficient time for the diffusion of quencher through the MONTs channel. An intensity reading was performed before the addition of α-hydroxyl carboxylic acids solutions and again after each addition of the quencher. Every measuring experiment was repeated for three times.

The measurement of fluorescence spectroscopy of free organic ligand and different concentration of α-hydroxyl carboxylic acids in $CH_3CN$ is similar to above

methods.

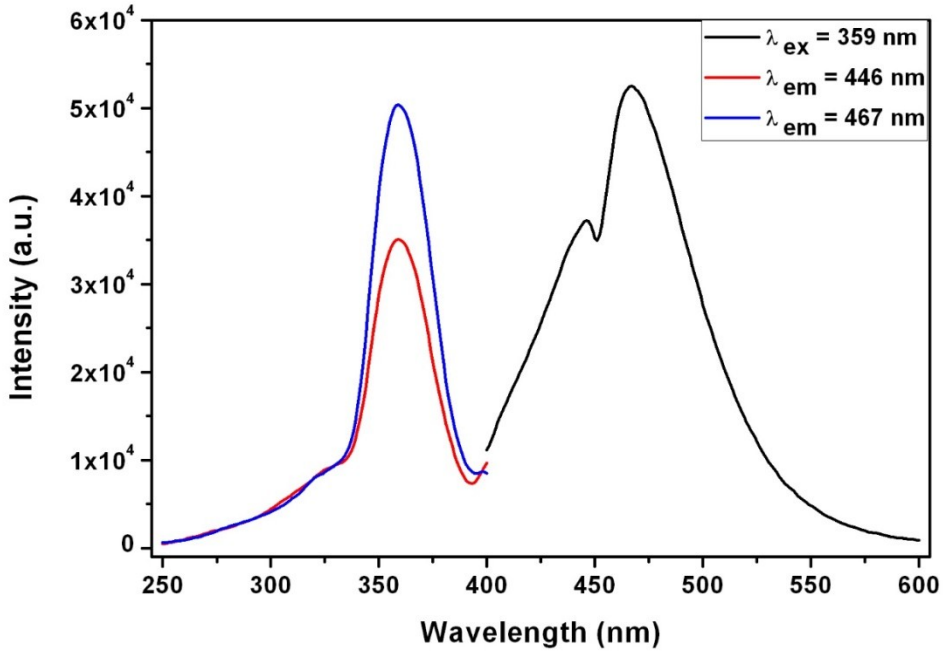



**Fig. S15** Excitation and emission spectra of solid **HMOF-2.** The maximum excitation wavelength of **RR-CHCAIP** is 359 nm, and it show maximum fluorescence emission peaks of 467 nm and small shoulder peak of 446 nm under excitation of 359 nm.

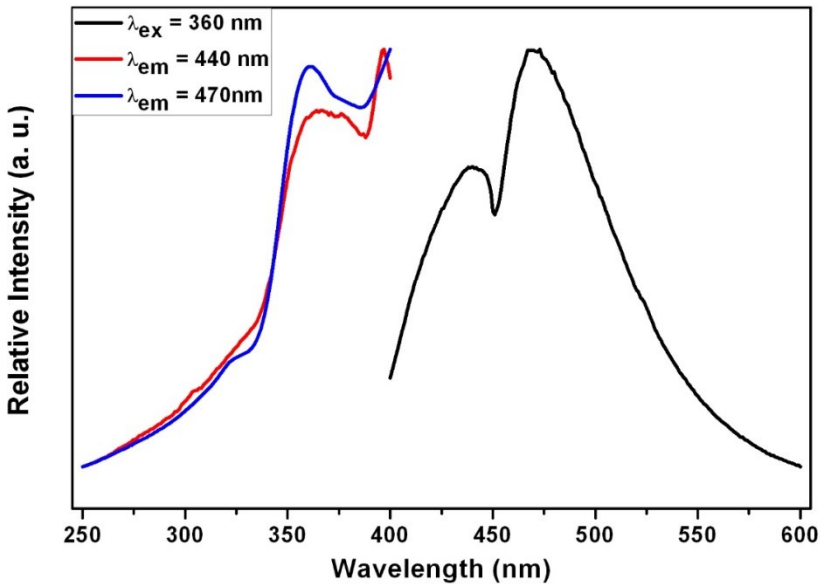
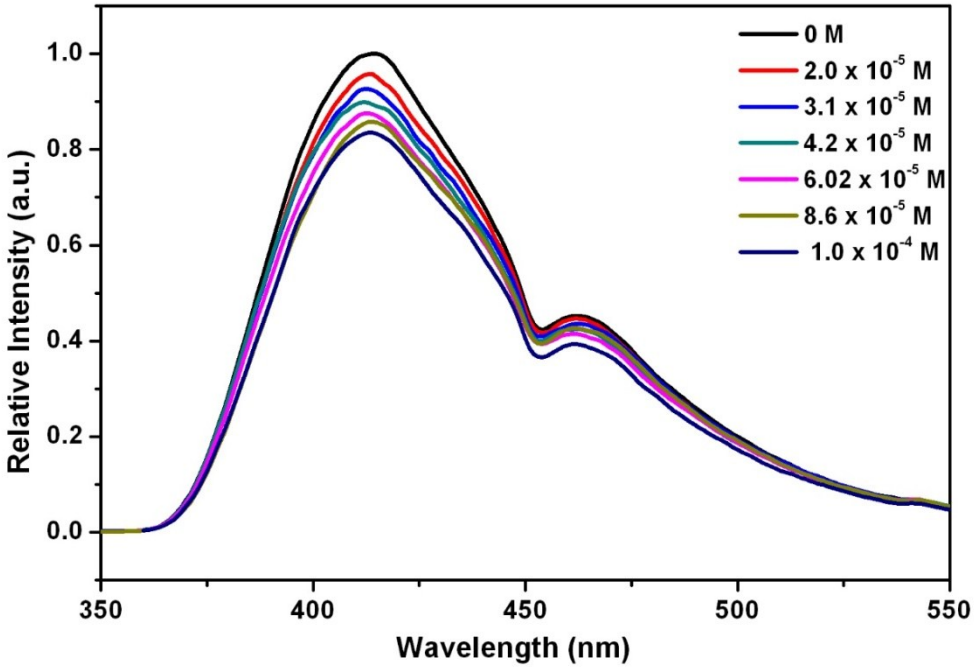
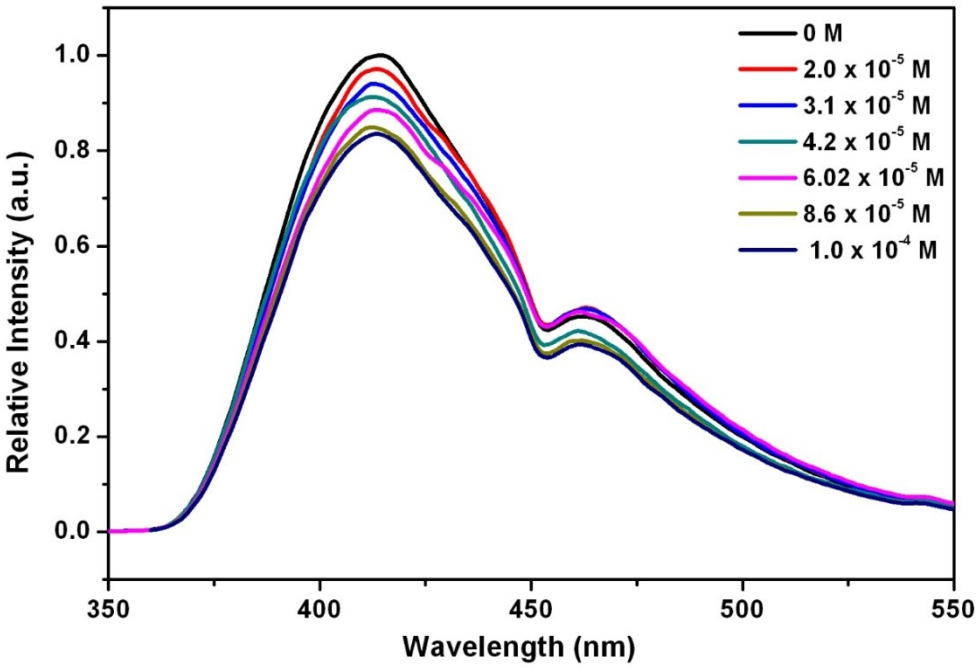



**Fig. S16** Excitation and emission spectra of solid organic ligand **RR-CHCAIP.** The

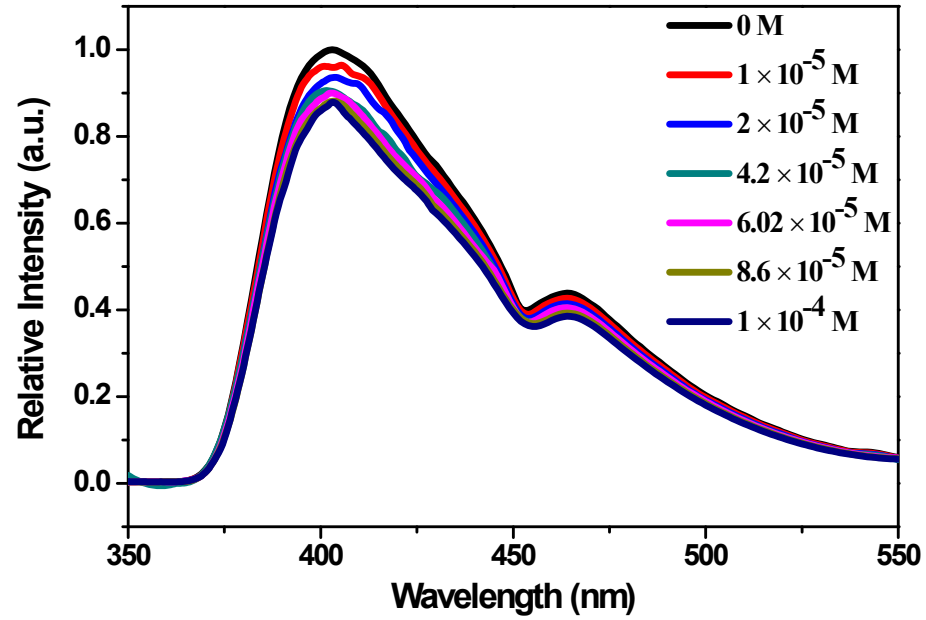
maximum excitation wavelength of **RR-CHCAIP** is 360 nm, and it show fluorescence emission of 440 and 470 nm under excitation of 360 nm.



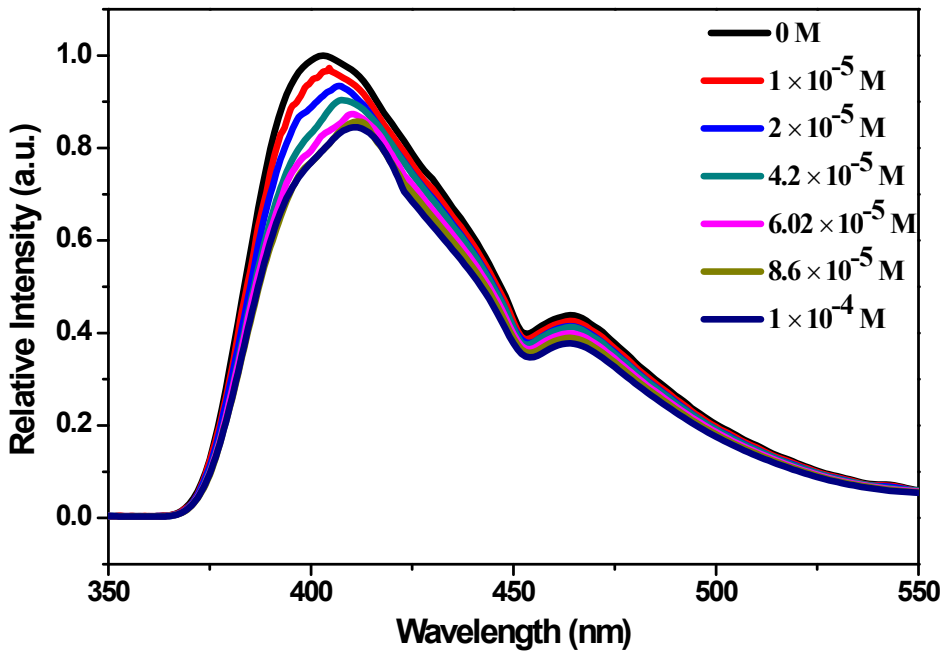

**(a)**




**(b)**




(c)




(d)

**Fig. S17** Fluorescence spectra of HMOF-2 emulsion in $CH_3CN$ upon titration with different concentration of (a) D-mandelic acid and (b) L-mandelic acid acetonitrile solution, c) D-tyrosine and f) L-tyrosine acetonitrile/deionized water (trace water), respectively.

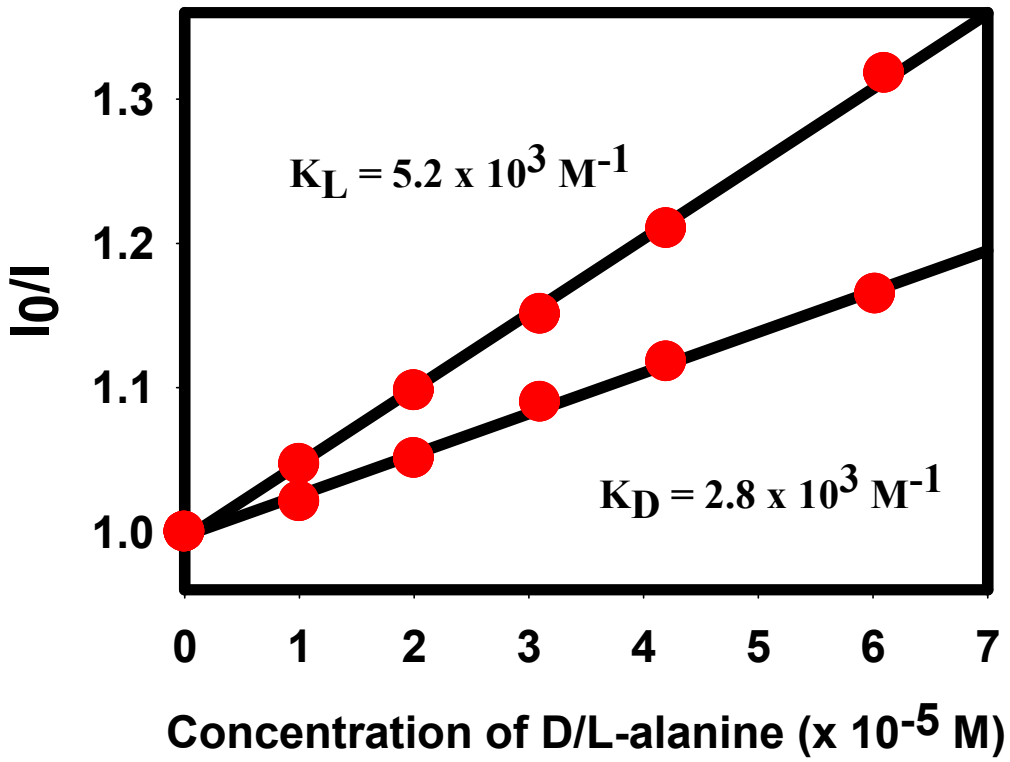



**Fig. S18** The Stern-Volmer quenching plots for D/L-alanine. Under the concentration (0-0.06 mM), the Stern–Volmer (SV) equation is found to be $I_0/I$ = 0.028 $C$ ($10^{-5}$ M) + 1 (for D-alnine), $I_0/I$ = 0.052 $C$ ($10^{-5}$ M) + 1 (for L-alanine) with the correlation coefficient ($r^2$) of 0.9963, 0.9986, respectively, and the resulting $K_L/K_D$ is 1.9:1.

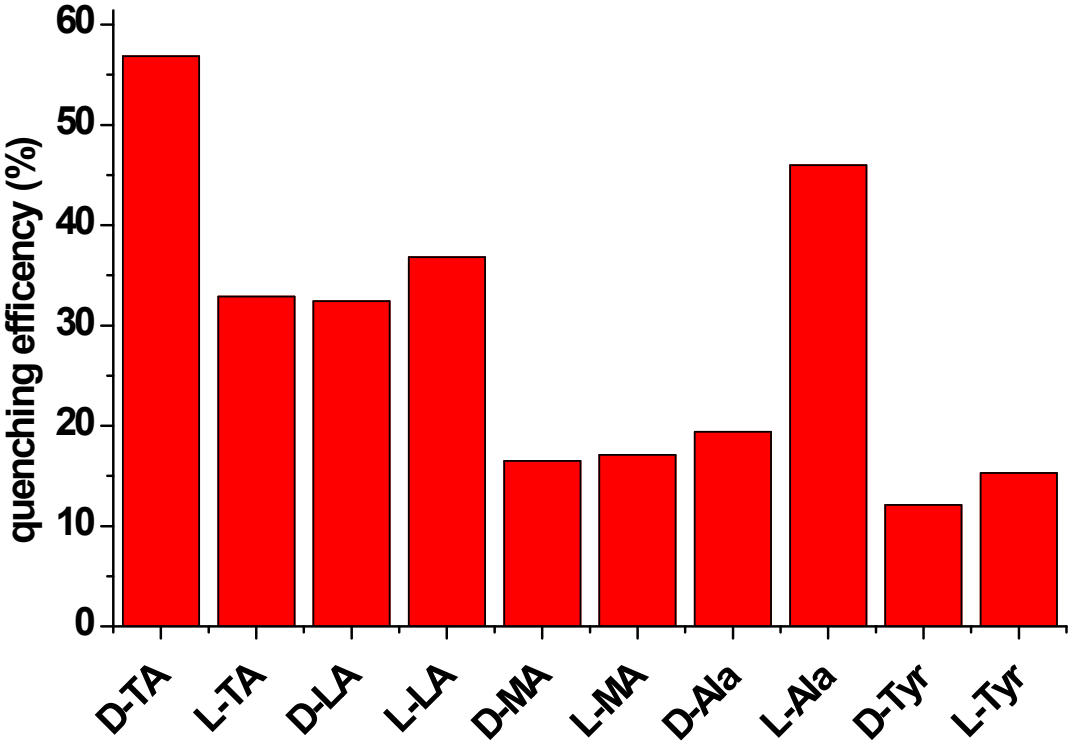



**Fig. S19** The fluorescence quenching efficiency of an acetonitrile emulsion of HMOF-2 unpon addition to D/L-TA (tartaric acid), D/L-LA (lactic acid), D/L-MA (mandelic acid), D/L-Ala (alanine), D/L-Tyr (tyrosine), respectively.

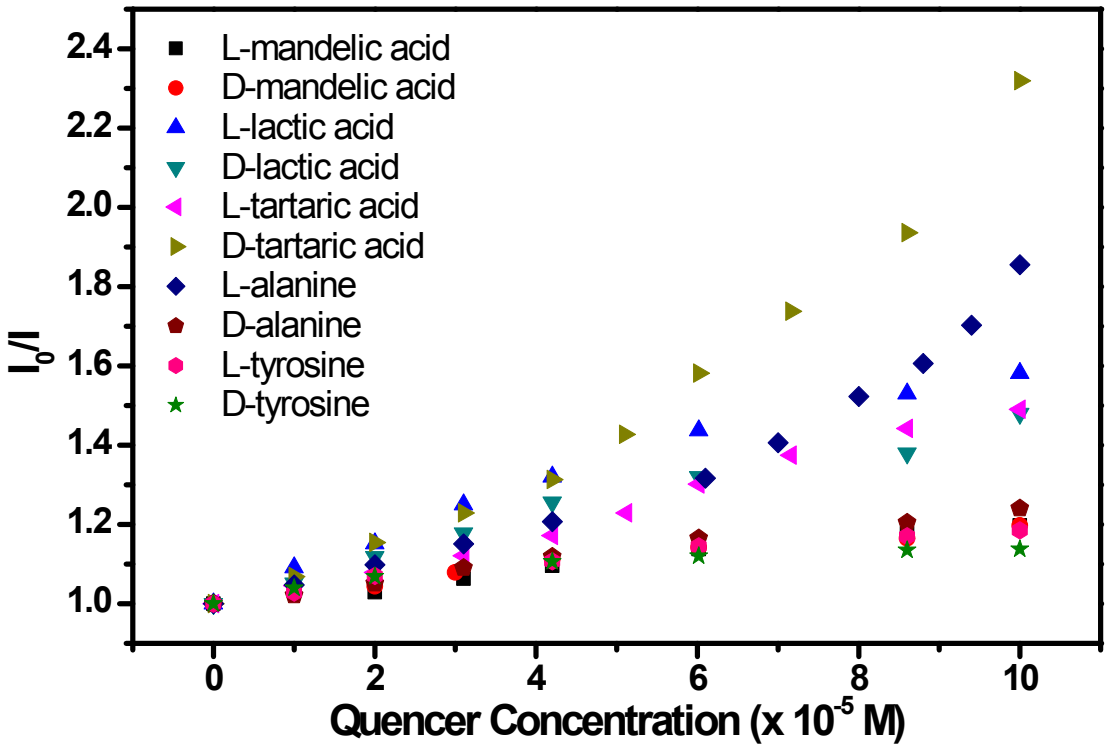


**Fig. S20** Stern-Völmer plot for HMOF-2 emulsion in acetonitrile with quencher, D/L-lactic acid, D/L-tartaric acid, D/L-mandelic acid, D/L-alanine and D/L-tyrosine.

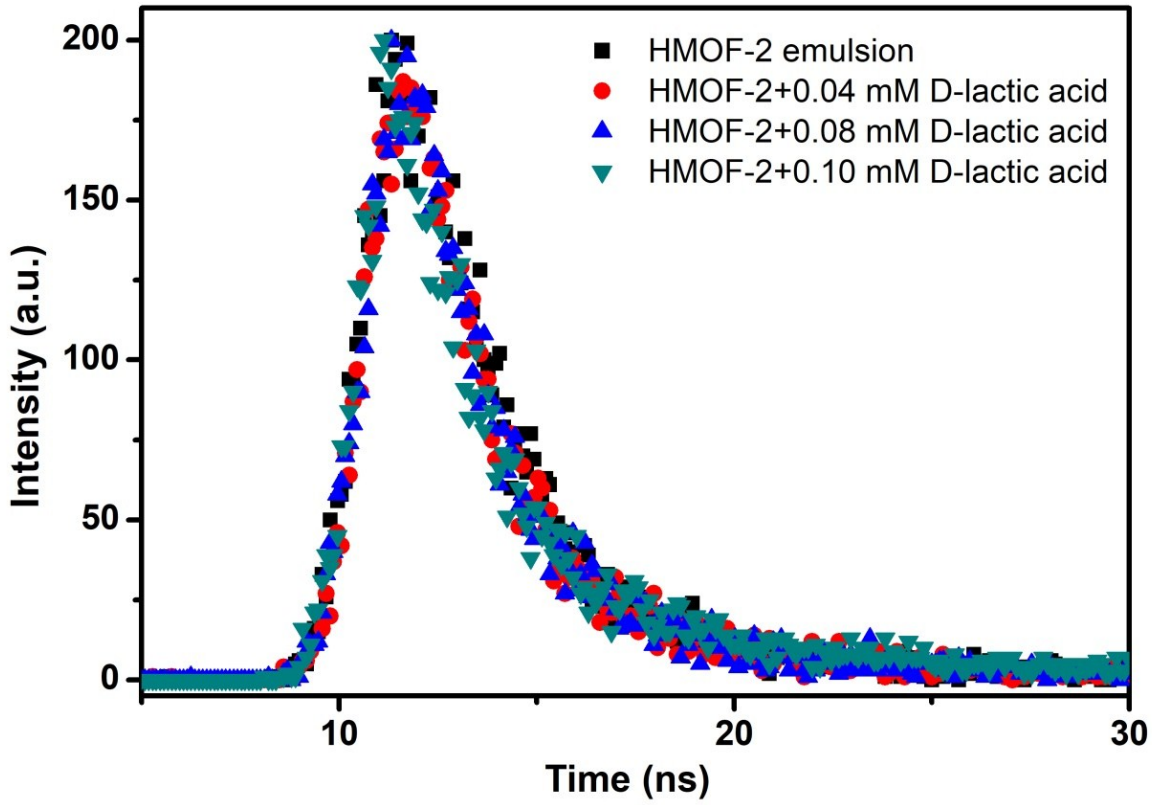



**Fig. S21** Fluorescence decay profile of HMOF-2 in the presence and absence of D-lactic acid with different concentration in $CH_3CN$.

**Table S3**. Lifetime of HMOF-2 in different concentration of D-lactic acid

| **HMOF-2** and different concentration of **D-lactic acid** | **Fluorescence lifetime (ns)** |
|---|---|
| **HMOF-2** emulsion | 2.99 ns |
| **HMOF-2** + 0.04 mM D-lactic acid | 2.89 ns |
| **HMOF-2** + 0.08 mM D-lactic acid | 2.76 ns |
| **HMOF-2** + 0.10 mM D-lactic acid | 2.68 ns |

Quantum yield of HMOF-2

The measurement and calculation for quantum yield for HMOF-2 acetonitrile emulsion refer to our previous research (ACS Appl. Mater. Interfaces 2016, 8, 24123−24130). The quantum yields (QY) are calculated with the software supplied by the manufacturer based on the equation 1.

$$\eta = \frac{\int L_{Sample}}{\int E_{Solvent} - \int E_{Sample}}$$ (η is the QY of the emission from 350 to 550 nm)

**Table S4**. The raw data for the calculation of HMOF-2 acetonitrile emulsion sample

| sample | $\int E_{solvent}$ | $\int E_{Sample}$ | $\int L_{Sample}$ | η (%) |
|---|---|---|---|---|
| HMOF-2 | $1.92 \times 10^6$ | $1.23 \times 10^5$ | $7.14 \times 10^4$ | 3.97±0.02 |

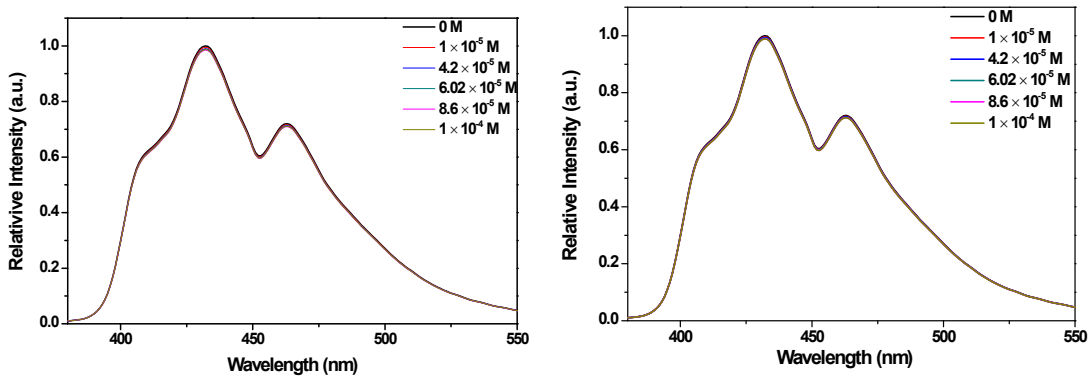
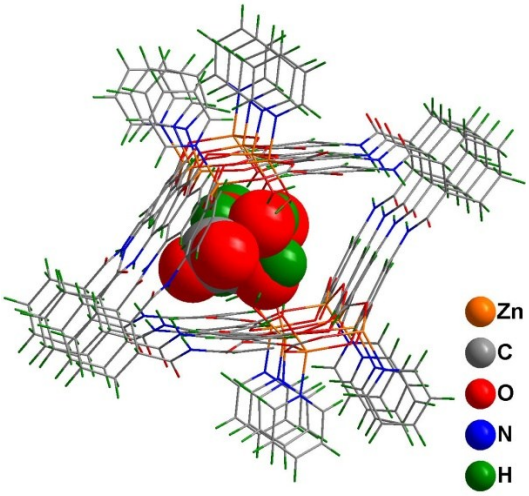



**Fig. S22** Fluorescence spectra of free organic ligand in $CH_3CN$ upon titration with different concentration of D-tartaric acid (left) and L-tartaric acid (right)

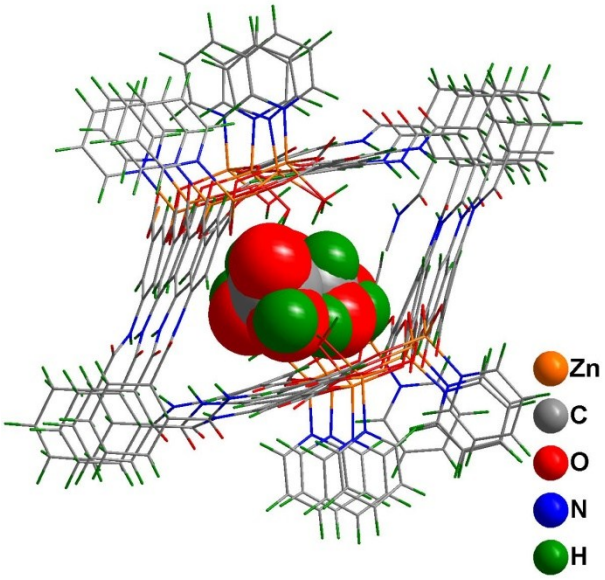
**Computational Details**

1. Monte Carlo Simulations:

Monte Carlo Simulations of interaction of HMOF-2 with α-hydroxy carboxylic acids have been performed by Adsorption Locator module of Accelrys Materials Studio[1] 8.0 package. A quadruple supercell along to B axis is built and the length of the resulting supercell along to A, B and C axis is 30.3390 × 40.3756 × 16.2638 Å. Fixed loading of one α-hydroxy carboxylic acid molecule was used to simulate electrostatic, hydrogen bond and van der Waals interactions. All LJ parameters to model the framework atoms were taken from the dreiding force field. The selection of forcefield type include hydrogen bond and all of potential interaction. In fact, hydrogen bond is largely an electrostatic phenomenon.[2] Atom based summation method, cubic spline truncation method, cut off distance of 7.53 Å, spline width of 1 Å and buffer width 0.5 Å were used during simulation of electrostatic and van der Waals interaction. Ultimately, the bonding energy and binding sites of HMOF-2 with α-hydroxy carboxylic acids is acquired. Molecule Dynamics Simulations of interaction of HMOF-1 with α-hydroxy carboxylic acids have been also performed by Forcite module of Accelrys Materials Studio package. We also find almost equal binding sites and bonding energy change law of HMOF-2 with α-hydroxy carboxylic acids.




(a)




(b)

**Fig. S23** Binding sites maps. (a,b) D-, L-TA in HMOF-**2**.

2. DFT calculation:

To clarify fluorescence attribution, we extract one fragment as model compound with six zinc cores, four organic ligands RR-CHCAIP and six pyridyl, which simulate the intact structure of metal-organic nanotubes. The calculation results show that both

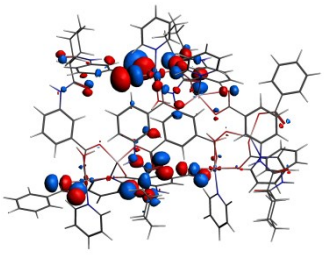
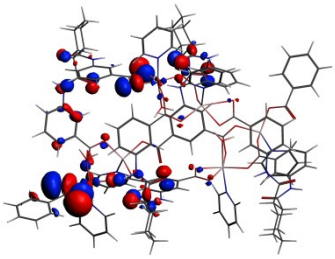
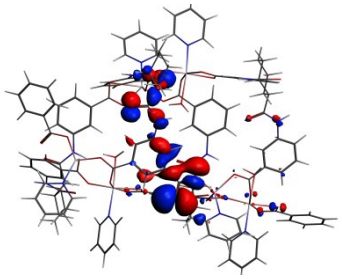
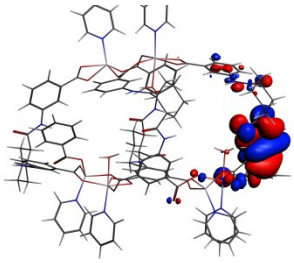
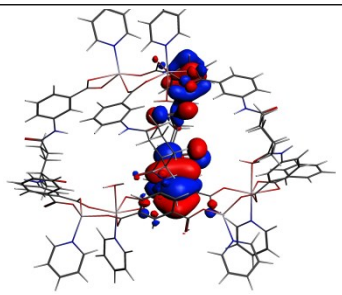
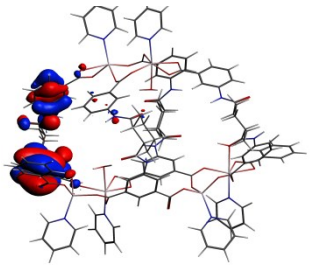
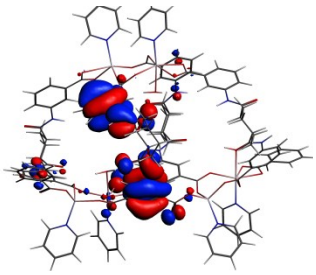
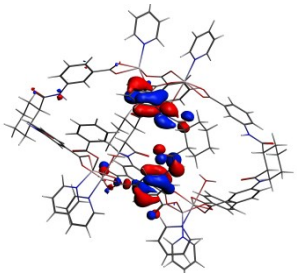
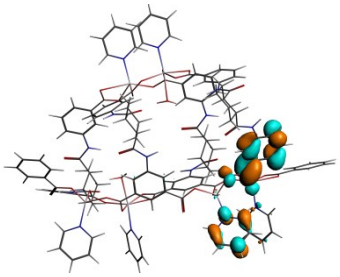
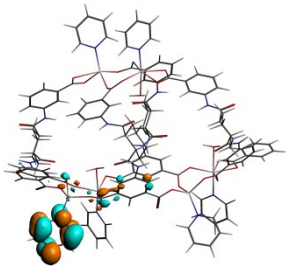
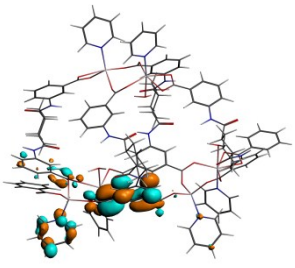
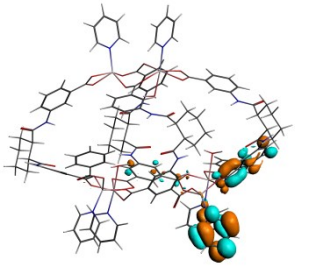
n-π* and π-π* transition processes contribute to the overall emission, in which a emission at λ = 410 nm assigned to a ligand-centered n→π* process. Computation details are as follows:

All of the calculations were performed at the DFT level by using the ADF2016 suite of programs.[3] The exchange and correlation energies were calculated using the BP86 density functionals within the framework of the generalized gradient approximation (GGA). The basis functions to describe the valence electrons of each atom were triple-ξ plus polarization Slater basis sets (TZP) which described by means of single Slater functions. The zero-order regular approximation (ZORA)[4] was adopted in all of the calculations to account for the scalar relativistic effect. The value of the numerical integration parameter used to determine the precision of numerical integrals was 5.5. The lower 60 transitions including singlet→singlet and singlet→triplet (the oscillator strengths are all zero) were considered by using TDDFT method. Spin-restricted calculations were performed for all of the calculations.

**Table S5** Wavelengths, oscillator strengths and transition types of model compound at the level of TZP/BP86 (TDDFT) level

| Singlet→ Singlet | Wavelength (nm) | Strength | Transition type |
|---|---|---|---|
| 519→531(39.9%)<br>520→531(38.0%) | 369.4 | 0.007 | n→π*<br>n→π* |
| 520→532(37.0%)<br>522→534(12.6%) | 368.5 | 0.002 | n→π*<br>n→π* |
| 523→531(46.0%)<br>523→535(31.4%) | 373.5 | 0.002 | π→π*<br>π→π* |
| 524→537(58.0%) | 369.7 | 0.003 | π→π* |

| | | | |
|---|---|---|---|
| 524→536(10.0%) | | | π→π* |
| 524→534(67.1%) | 385.7 | 0.001 | π→π* |
| 525→532(24.2%) | | | π→π* |
| 524→535(32.1%) | 374.7 | 0.001 | π→π* |
| 525→536(30.6%) | | | π→π* |
| 526→537(13.2%) | | | π→π* |

| | | |
|---|---|---|
|  |  |  |
| 519(HOMO-11) | 520(HOMO-10) | 522(HOMO-8) |
|  |  |  |
| 523(HOMO-7) | 524(HOMO-6) | 525(HOMO-5) |
|  |  |  |
| 526(HOMO-4) | 530(HOMO) | 531(LUMO) |
|  |  |  |
| 532(LUMO+1) | 534(LUMO+3) | 535(LUMO+4) |

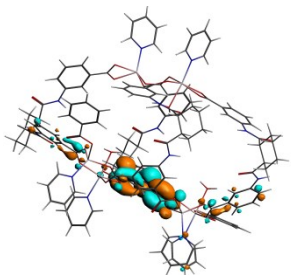
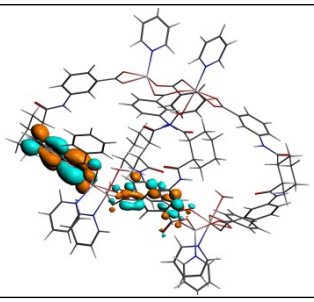
| | | |
|---|---|---|
|  |  | |
| 536(LUMO+5) | 537(LUMO+6) | |

**Fig. S24** orbitals representations of metal-organic nanotubes

**Reference**


1. Materials Studio, version 8.0 V; Accelrys Sofware Inc.: San Diego, CA, 2015.
2. R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320-326.
3. Delley, B. J. Chem. Phys. 1990, 92, 508-517. (b) Delley, B. J. Chem. Phys. 2000, 113, 7756-7764.
4. Chang, C.; Pelissier, M.; Durand, M. Phys. Scr. 1986, 34, 394-404; van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. J. Chem. Phys. 1999, 110, 8943-8953.


**Optimized coordinate of model compound at TZP/BP86 level**

O 3.5203360000 -5.0058150000 -1.4776300000

Zn 6.0814670000 -4.0626350000 -2.9144540000

C 4.4915220000 2.9797170000 -3.0364040000

H 5.5519420000 2.8447350000 -2.8203660000

C 1.7760120000 3.3428310000 -3.6360590000

C 2.3286100000 3.8932030000 -2.4680710000

C 2.5837840000 2.5749450000 -4.4877330000

H -1.0059470000 2.1096550000 -7.9550210000

| | | | |
|---|---|---|---|
| C | 3.6821470000 | 3.7008190000 | -2.1553760000 |
| H | 4.0900620000 | 4.1429030000 | -1.2462450000 |
| C | 3.9506220000 | 2.4150830000 | -4.1899540000 |
| H | 4.5832360000 | 1.8348020000 | -4.8645170000 |
| C | 0.8179140000 | 1.6331130000 | -6.0132680000 |
| C | 0.6863330000 | 0.9017480000 | -7.3507320000 |
| H | 1.6889330000 | 0.6574290000 | -7.7351570000 |
| N | 2.1052880000 | 1.9506110000 | -5.6615680000 |
| H | 2.8293520000 | 1.5745050000 | -6.2704930000 |
| H | 0.7062320000 | -1.4263020000 | -8.9274120000 |
| H | 0.7566840000 | 0.9136980000 | -10.1778410000 |
| O | 1.8927970000 | -1.5481270000 | -6.3193050000 |
| C | 0.6674050000 | -1.3690010000 | -6.2284490000 |
| C | 1.5535710000 | -3.3026490000 | -4.0309430000 |
| H | 2.3667740000 | -2.8775730000 | -4.6097530000 |
| C | 1.8214760000 | -4.1971990000 | -2.9808940000 |
| C | 3.2484390000 | -4.5007890000 | -2.6179420000 |
| O | 4.1475140000 | -4.2092820000 | -3.4863100000 |
| N | 6.9407580000 | -5.8382570000 | -2.3709760000 |
| C | 8.2594930000 | -6.0605750000 | -2.5847520000 |
| H | 8.8185610000 | -5.2199820000 | -2.9962540000 |
| C | 6.1845780000 | -6.8366270000 | -1.8562940000 |

| | | | |
|---|---|---|---|
| H | 5.1323840000 | -6.5998750000 | -1.6956280000 |
| C | 8.0787860000 | -8.3118220000 | -1.7645570000 |
| H | 8.5230010000 | -9.2788170000 | -1.5281980000 |
| C | 8.8584290000 | -7.2821300000 | -2.2933240000 |
| H | 9.9226760000 | -7.4154930000 | -2.4822120000 |
| C | 6.7201450000 | -8.0812100000 | -1.5417060000 |
| H | 6.0746670000 | -8.8554480000 | -1.1294280000 |
| O | 5.4296010000 | -3.4014530000 | 0.7177350000 |
| Zn | 3.4744170000 | -4.0101340000 | 0.3794910000 |
| C | 6.2561020000 | -2.8900440000 | -0.0959760000 |
| C | 9.8389010000 | -1.6690450000 | 0.1432010000 |
| N | 3.7608260000 | -5.8232270000 | 1.4759650000 |
| H | 10.7082610000 | -1.5218500000 | -0.4987230000 |
| C | 7.6317230000 | -2.0678250000 | 1.8232780000 |
| H | 6.7748080000 | -2.2274550000 | 2.4693780000 |
| C | 7.5482760000 | -2.3649860000 | 0.4530470000 |
| C | 8.8181410000 | -1.5343560000 | 2.3459460000 |
| O | 2.6405180000 | -2.8822630000 | 2.2735870000 |
| C | 8.2425210000 | -1.4555340000 | 7.1654440000 |
| H | 7.1562470000 | -1.6386770000 | 7.1805790000 |
| H | 8.7288500000 | -2.4221620000 | 6.9643330000 |
| C | 8.6452410000 | -2.1572900000 | -0.3955680000 |

H 8.5661790000 -2.3928470000 -1.4579600000

C 9.9277090000 -1.3526450000 1.4972410000

H 10.8581360000 -0.9525960000 1.9054800000

C 7.9324700000 0.9175680000 6.2846320000

H 6.8373480000 0.7964210000 6.2981900000

C 3.9686730000 -8.1474380000 3.0112740000

H 4.0480310000 -9.0541210000 3.6113760000

O 6.8354200000 -1.3394580000 4.5332380000

C 8.0303130000 -1.0381290000 4.6869110000

C 8.5589100000 -0.4815120000 6.0112960000

H 9.6501100000 -0.3449810000 5.9459070000

N 8.9739500000 -1.1540210000 3.6970440000

H 9.9099720000 -0.8406380000 3.9469730000

C 3.1320090000 -6.9573950000 1.1009500000

H 2.5542080000 -6.9039450000 0.1783260000

C 4.4925740000 -5.8380750000 2.6105830000

H 4.9850500000 -4.9031360000 2.8762240000

C 3.2115470000 -8.1365230000 1.8379450000

C 4.6207460000 -6.9766040000 3.4027090000

H 5.2230730000 -6.9384660000 4.3094360000

C 8.3955580000 1.4619180000 7.6541990000

H 9.4805800000 1.6481860000 7.6056490000

| | | | |
|---|---|---|---|
| H | 7.9097840000 | 2.4319510000 | 7.8394370000 |
| C | 8.6984700000 | -0.8981810000 | 8.5195990000 |
| H | 8.4240590000 | -1.6032770000 | 9.3187140000 |
| H | 9.7988950000 | -0.8180910000 | 8.5318550000 |
| C | 8.0842990000 | 0.4805070000 | 8.7905300000 |
| H | 8.4614380000 | 0.8883720000 | 9.7405760000 |
| H | 6.9910050000 | 0.3803850000 | 8.8997760000 |
| O | 3.4147030000 | -2.0089640000 | -0.7639880000 |
| H | 4.2837320000 | -2.1048180000 | -1.2357410000 |
| H | 2.7365130000 | -1.9580440000 | -1.4658070000 |
| O | 9.5246050000 | 2.1294720000 | 4.9184520000 |
| C | 8.3323530000 | 1.8947780000 | 5.1772870000 |
| N | 7.2826790000 | 2.4695610000 | 4.5089060000 |
| H | 6.3548980000 | 2.2162260000 | 4.8433430000 |
| C | 7.2963320000 | 3.3684870000 | 3.4195880000 |
| C | 6.0613250000 | 3.9003300000 | 3.0115400000 |
| H | 5.1484490000 | 3.6381590000 | 3.5482400000 |
| C | 8.4683270000 | 3.7225680000 | 2.7268220000 |
| H | 9.4231150000 | 3.3184440000 | 3.0493290000 |
| C | 8.3847330000 | 4.5831150000 | 1.6287260000 |
| C | 5.9877290000 | 4.7528350000 | 1.9051550000 |
| O | 4.5779180000 | 5.8495480000 | 0.3097260000 |

O 6.0279050000 -2.7390940000 -1.3655940000

C 4.6719380000 5.3116050000 1.4485950000

O 3.6515370000 5.2342010000 2.2455610000

H 9.2979340000 4.8518700000 1.0958250000

H 4.4648840000 8.0023720000 0.4111960000

H 4.8578940000 10.4690220000 0.2472530000

C 7.1578510000 5.0916270000 1.2053640000

H 7.0897370000 5.7530880000 0.3426210000

H -8.1831330000 5.0851060000 -1.1285500000

C -10.0441390000 -1.4146420000 -2.0954560000

C -10.1193560000 -1.9941640000 -0.8318060000

H -11.0295720000 -1.8797390000 -0.2425150000

C -9.0416700000 -2.7240290000 -0.3222140000

H -12.8473750000 -2.5840960000 5.3280810000

C -9.4356410000 -2.5370320000 5.1331070000

C -11.5234370000 -1.8896580000 6.8925480000

H -12.3351560000 -1.6387340000 7.5774160000

C -11.8114390000 -2.4212150000 5.6294250000

C -10.1930520000 -1.6811530000 7.2767840000

C -10.7724260000 -2.7435200000 4.7537090000

H -10.9832470000 -3.1582630000 3.7680450000

O -6.8048320000 -4.2178300000 0.5804460000

| | | | |
|---|---|---|---|
| Zn | -4.2415400000 | -4.9252750000 | -0.4920710000 |
| Zn | -1.2658390000 | 5.8705790000 | -1.0183640000 |
| O | 1.7573230000 | 4.6807180000 | -0.2858060000 |
| O | 0.4402900000 | 5.2711520000 | -2.0347640000 |
| C | 1.4541880000 | 4.6867300000 | -1.5404640000 |
| O | -3.3499210000 | 5.7270760000 | -0.6820230000 |
| C | -4.9519200000 | 4.6924900000 | -2.1401080000 |
| N | -1.2834240000 | 7.7943390000 | -1.9538450000 |
| C | -3.5519850000 | 5.1000470000 | -1.7871710000 |
| C | -7.5629330000 | 3.9042800000 | -2.8150960000 |
| H | 0.7251950000 | 3.4924800000 | -3.8640660000 |
| C | -7.3326180000 | 4.7418580000 | -1.7192450000 |
| C | -6.4728750000 | 3.4550180000 | -3.5823490000 |
| O | -2.5835790000 | 4.8252530000 | -2.5676260000 |
| C | -0.0294390000 | 1.8153270000 | -8.3723340000 |
| H | -8.8410950000 | 2.2635740000 | -7.7642260000 |
| H | 0.5563500000 | 2.7375170000 | -8.5043310000 |
| C | -6.0403150000 | 5.1346220000 | -1.3703350000 |
| H | -5.8598580000 | 5.7816350000 | -0.5128040000 |
| C | -5.1725080000 | 3.8604110000 | -3.2416020000 |
| H | -4.3189420000 | 3.5223070000 | -3.8308610000 |
| C | -0.0849830000 | -0.4300470000 | -7.1736630000 |

| | | | |
|---|---|---|---|
| H | -1.0737920000 | -0.1957200000 | -6.7479490000 |
| C | -1.3558650000 | 10.3055770000 | -3.1770790000 |
| H | -1.3849340000 | 11.2846760000 | -3.6558690000 |
| O | -0.1725790000 | 1.9241700000 | -5.3229330000 |
| C | -7.7269490000 | 2.1195870000 | -5.3122830000 |
| C | -7.4569390000 | 1.1879010000 | -6.4961520000 |
| H | -6.3920990000 | 0.9040380000 | -6.5092180000 |
| N | -6.6002120000 | 2.5839240000 | -4.6859350000 |
| H | -5.7164030000 | 2.2706470000 | -5.0829320000 |
| C | -2.3324230000 | 8.6245690000 | -1.7665600000 |
| H | -3.1318770000 | 8.2480460000 | -1.1281290000 |
| C | -0.2703050000 | 8.2069840000 | -2.7454470000 |
| H | 0.5525190000 | 7.5038450000 | -2.8722160000 |
| C | -2.4051290000 | 9.8831770000 | -2.3583220000 |
| H | -3.2732100000 | 10.5158650000 | -2.1767900000 |
| C | -0.2698780000 | 9.4506410000 | -3.3727350000 |
| H | 0.5716600000 | 9.7367040000 | -4.0025920000 |
| C | -0.2824510000 | -1.1303020000 | -8.5398530000 |
| H | -7.0461050000 | -1.3580230000 | -7.6203670000 |
| H | -0.8615600000 | -2.0544340000 | -8.3936860000 |
| C | -0.2275680000 | 1.1098870000 | -9.7193910000 |
| H | -0.7700240000 | 1.7759420000 | -10.4071300000 |

| | | | |
|---|---|---|---|
| H | -6.5304230000 | 0.7640400000 | -9.1383540000 |
| C | -0.9834460000 | -0.2134070000 | -9.5499180000 |
| H | -1.0700720000 | -0.7322260000 | -10.5165090000 |
| H | -2.0111090000 | -0.0084650000 | -9.2053970000 |
| O | -0.9842590000 | 3.7726470000 | -0.0114270000 |
| H | -0.0330500000 | 3.8468040000 | 0.2389080000 |
| H | -1.4644140000 | 3.6870390000 | 0.8356770000 |
| O | -6.7756550000 | -1.3796580000 | -4.9571680000 |
| C | -7.9020630000 | -0.8764290000 | -5.0995720000 |
| N | -0.1259820000 | -2.0060770000 | -5.3087740000 |
| H | -1.1164510000 | -1.7725140000 | -5.3431900000 |
| C | 0.2279220000 | -2.9354340000 | -4.3083010000 |
| C | -0.8170370000 | -3.4798980000 | -3.5414550000 |
| H | -1.8492290000 | -3.1861150000 | -3.7363200000 |
| C | -7.7904190000 | -2.2764870000 | -2.3692780000 |
| H | -6.8882830000 | -2.3874910000 | -2.9613600000 |
| C | -7.8768690000 | -2.8607980000 | -1.0945650000 |
| C | -0.5493260000 | -4.3921170000 | -2.5169770000 |
| O | -1.4170440000 | -5.9037530000 | -0.8797450000 |
| C | -1.6636790000 | -4.9662890000 | -1.6706910000 |
| O | -2.8337740000 | -4.4134250000 | -1.8232110000 |
| C | -6.7231580000 | -3.6593070000 | -0.5635900000 |

| | | | |
|---|---|---|---|
| O | -5.6870450000 | -3.7831400000 | -1.3122560000 |
| N | -4.7961990000 | -6.9091100000 | -0.5137480000 |
| C | -3.8789180000 | -7.8700390000 | -0.7757350000 |
| H | -2.8535790000 | -7.5182140000 | -0.8971020000 |
| C | -6.0894430000 | -7.2731820000 | -0.3495830000 |
| H | -6.7895310000 | -6.4678910000 | -0.1302850000 |
| C | -5.5583530000 | -9.5877770000 | -0.7134540000 |
| H | -5.8566110000 | -10.6333330000 | -0.7930830000 |
| C | -4.2240490000 | -9.2143420000 | -0.8793460000 |
| H | -3.4501810000 | -9.9513960000 | -1.0894010000 |
| C | -6.5049650000 | -8.5975640000 | -0.4440630000 |
| H | -7.5575460000 | -8.8413880000 | -0.3063410000 |
| C | 0.7748660000 | -4.7497510000 | -2.2354560000 |
| H | 0.9789460000 | -5.4335470000 | -1.4160310000 |
| Zn | 2.2273230000 | 6.1365610000 | 1.0698700000 |
| O | -4.5616960000 | -2.9334750000 | 2.6225500000 |
| Zn | -6.5221600000 | -3.5449950000 | 2.5439000000 |
| C | -3.5010010000 | -3.4395510000 | 2.1277740000 |
| O | 1.4209460000 | -3.8633870000 | 0.6851990000 |
| C | 0.2354090000 | -2.8332510000 | 2.4870060000 |
| N | -6.3113640000 | -5.5098760000 | 3.3619170000 |
| C | 1.5116200000 | -3.2086080000 | 1.7884790000 |

| | | | |
|---|---|---|---|
| C | -2.1472350000 | -2.0839190000 | 3.7730520000 |
| H | -3.0705940000 | -1.7931690000 | 4.2637890000 |
| C | -2.1806520000 | -2.9264580000 | 2.6499150000 |
| C | -0.9124100000 | -1.6276560000 | 4.2619800000 |
| O | -7.1065380000 | -2.6854520000 | 4.5309420000 |
| C | -1.4513650000 | -0.2489930000 | 8.6339960000 |
| H | -2.5375420000 | -0.4216770000 | 8.7080440000 |
| H | -0.9742790000 | -1.2354020000 | 8.5337590000 |
| C | -0.9954550000 | -3.2985110000 | 2.0053100000 |
| H | -1.0266770000 | -3.9467120000 | 1.1314220000 |
| C | 0.2740810000 | -2.0104040000 | 3.6143090000 |
| H | 1.2395640000 | -1.6619370000 | 3.9844710000 |
| C | -1.7897580000 | 1.9951550000 | 7.4851640000 |
| H | -2.8828780000 | 1.8795160000 | 7.5594510000 |
| C | -6.1943400000 | -8.0176300000 | 4.5878480000 |
| H | -6.1499330000 | -8.9952200000 | 5.0683970000 |
| O | -2.9393880000 | -0.1949450000 | 5.8864240000 |
| C | -1.7247960000 | -0.1573750000 | 6.1427970000 |
| C | -1.1703930000 | 0.5853500000 | 7.3603190000 |
| H | -0.0810030000 | 0.7046890000 | 7.2494240000 |
| N | -0.7722320000 | -0.8026890000 | 5.3977090000 |
| H | 0.1908810000 | -0.6386090000 | 5.6840430000 |

| | | | |
|---|---|---|---|
| C | -7.3063510000 | -6.4075450000 | 3.1951600000 |
| H | -8.1433420000 | -6.0876720000 | 2.5744750000 |
| C | -5.2610330000 | -5.8520930000 | 4.1365690000 |
| H | -4.4829850000 | -5.0984340000 | 4.2564330000 |
| C | -7.2841730000 | -7.6674160000 | 3.7882780000 |
| H | 2.6853530000 | -9.0258150000 | 1.4933960000 |
| C | -5.1641430000 | -7.0921720000 | 4.7633950000 |
| H | -4.2952520000 | -7.3195140000 | 5.3797750000 |
| C | -1.2760570000 | 2.7030860000 | 8.7630040000 |
| H | -0.1925310000 | 2.8764190000 | 8.6563930000 |
| H | -1.7535600000 | 3.6906680000 | 8.8481120000 |
| C | -0.9499500000 | 0.4613960000 | 9.8972240000 |
| H | -1.2034870000 | -0.1416830000 | 10.7820270000 |
| H | 0.1505480000 | 0.5318870000 | 9.8646810000 |
| C | -1.5487500000 | 1.8675030000 | 10.0204770000 |
| H | -1.1369070000 | 2.3841500000 | 10.9004150000 |
| H | -2.6378990000 | 1.7902440000 | 10.1781470000 |
| O | -6.7684180000 | -1.3481660000 | 1.7970900000 |
| H | -5.8889980000 | -1.0554700000 | 1.4849080000 |
| H | -7.3427600000 | -1.2932320000 | 1.0056320000 |
| O | -0.3184130000 | 2.8746250000 | 5.7606620000 |
| C | -1.4550240000 | 2.8508430000 | 6.2612480000 |

| | | | |
|---|---|---|---|
| N | -2.5036180000 | 3.6034090000 | 5.7995670000 |
| H | -3.3869320000 | 3.4661240000 | 6.2870000000 |
| C | -2.5663350000 | 4.5119000000 | 4.7225550000 |
| C | -3.8245960000 | 5.0853890000 | 4.4539550000 |
| H | -4.6794740000 | 4.8218400000 | 5.0797850000 |
| C | -1.4647900000 | 4.8585840000 | 3.9249600000 |
| H | -0.4886950000 | 4.4304850000 | 4.1301600000 |
| C | -1.6389200000 | 5.7463340000 | 2.8487860000 |
| C | -3.9832490000 | 5.9751120000 | 3.3945460000 |
| O | -3.4456170000 | -4.3646600000 | 1.2477020000 |
| H | -4.9645100000 | 6.4097930000 | 3.2016640000 |
| C | -0.4726170000 | 6.1027130000 | 1.9725220000 |
| O | -0.6811580000 | 6.6571440000 | 0.8404870000 |
| O | 0.7057110000 | 5.8456980000 | 2.4101130000 |
| N | 2.4272640000 | 8.1778780000 | 0.7477490000 |
| C | 3.6498840000 | 8.7154060000 | 0.5218370000 |
| C | 1.3715970000 | 9.0151640000 | 0.8850280000 |
| H | 0.4056690000 | 8.5388360000 | 1.0462620000 |
| C | 2.7650230000 | 10.9490320000 | 0.5760910000 |
| H | 2.8965640000 | 12.0291900000 | 0.5102420000 |
| C | 3.8538660000 | 10.0888470000 | 0.4305060000 |
| C | 1.5033070000 | 10.3981000000 | 0.8050350000 |

| | | | |
|---|---|---|---|
| H | 0.6220370000 | 11.0275940000 | 0.9216260000 |
| C | -2.8984220000 | 6.3011660000 | 2.5779770000 |
| H | -3.0162110000 | 6.9758430000 | 1.7328020000 |
| H | -8.5693590000 | 3.5934150000 | -3.0800380000 |
| C | -7.7942290000 | 1.9225540000 | -7.8148040000 |
| H | -7.1649260000 | 2.8213870000 | -7.8981130000 |
| C | -8.2941990000 | -0.1145940000 | -6.3680550000 |
| H | -9.3538080000 | 0.1794230000 | -6.3067410000 |
| O | -8.8818380000 | 2.4277190000 | -4.9738160000 |
| C | -8.0929410000 | -1.0149850000 | -7.6051770000 |
| H | -8.7239140000 | -1.9111250000 | -7.5054120000 |
| C | -7.5994450000 | 1.0161900000 | -9.0359130000 |
| H | -7.8846530000 | 1.5629570000 | -9.9470300000 |
| C | -8.4188940000 | -0.2738170000 | -8.9078140000 |
| H | -8.2261820000 | -0.9366720000 | -9.7646860000 |
| H | -9.4945390000 | -0.0292200000 | -8.9319190000 |
| N | -8.8889120000 | -0.9451120000 | -4.1484640000 |
| H | -9.7569160000 | -0.4693840000 | -4.3869240000 |
| C | -8.8793010000 | -1.5533900000 | -2.8766410000 |
| H | -10.8913960000 | -0.8497590000 | -2.4887330000 |
| H | -9.0959520000 | -3.1875280000 | 0.6626720000 |
| O | -8.6051040000 | -3.3931360000 | 3.0464380000 |

| | | | |
|---|---|---|---|
| C | -8.3223270000 | -2.8864890000 | 4.1923900000 |
| C | -9.1533420000 | -2.0023070000 | 6.4011210000 |
| H | -8.1142920000 | -1.8437440000 | 6.6904860000 |
| H | -9.9672760000 | -1.2671000000 | 8.2606780000 |
| H | -8.1127760000 | -8.3556930000 | 3.6257790000 |
| C | 9.4058500000 | -1.0285520000 | -8.2113640000 |
| H | 9.7852670000 | -0.5699240000 | -9.1260350000 |
| C | 10.2770460000 | -1.2989040000 | -7.1487950000 |
| H | 11.3362180000 | -1.0506600000 | -7.2338540000 |
| C | 8.0474990000 | -1.3485610000 | -8.0993200000 |
| C | 7.5617000000 | -1.9385080000 | -6.9298750000 |
| H | 6.5061880000 | -2.1923240000 | -6.8358910000 |
| C | 8.4302350000 | -2.2140350000 | -5.8606440000 |
| O | 8.7123490000 | -3.0969110000 | -3.6467110000 |
| C | 7.9287600000 | -2.8618930000 | -4.5968030000 |
| O | 6.6569390000 | -3.1563620000 | -4.5732730000 |
| C | 9.7912550000 | -1.8876780000 | -5.9794590000 |
| H | 10.4590810000 | -2.1044100000 | -5.1453130000 |
| H | 7.3664210000 | -1.1389030000 | -8.9256330000 |