Electronic Supplementary Information

Coordination tailoring of water-labile 3D MOFs to fabricate ultrathin 2D MOF nanosheets

Yuehong Wen,[a] Qiang Liu,[a,b] Shaodong Su,[a] Yuying Yang,[a,b] Xiaofang Li,[a] Qi-Long Zhu,*[a] and Xintao Wu*[a]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

*Corresponding Authors. E-mail: qlzhu@fjirsm.ac.cn; wxt@fjirsm.ac.cn

Materials. All chemicals such as $Zn(NO_3)_2 \cdot 6H_2O$, 1,4-benzendicarboxylic acid (H_2bdc), N,N-dimethylformamide, ethanol, etc. were purchased commercially and used without further purification. Ligand bdc was in-situ prepared from H_2bdc and NaOH. Ligand 1,2-bis(4′-pyridylmethylamino)-ethane (hsb-2) was synthesized employing previous method.[1]

Synthesis of MOF HSB-W1. A solution of hsb-2 (72 mg, 0.3 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (90 mg, 0.3 mmol) in H_2O/EtOH (6 mL/6 mL) was slowly layered over a solution of bdc (0.3 mmol) in H_2O/DMF (8 mL/4 mL). Colorless crystals HSB-W1 were yielded after one month.[2]

Synthesis of MOF HSB-W5. A solution of hsb-2 (12 mg, 0.05 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol) in H_2O/DMF (6 mL/3 mL) was quickly added a solution of bdc (0.05 mmol) in H_2O/DMF (8 mL/4 mL) under vigorously stirring. Then, the reaction mixture was filtered immediately and the filtrate was evaporated for 6 days to give the colorless and leaf-like single crystals. Elemental analysis calcd (%) for $ZnC_{22}H_{30}N_4O_8$ [Zn(hsb-2)(bdc)·$4H_2O$]: C 48.58, H 5.56, N 10.30; found: C 49.16, H 5.29, N 10.41. IR (KBr): ν = 3398(s), 3276(s), 2948(w), 1944(vw), 1616(m), 1593(s), 1563(s), 1502(m), 1456(w), 1426(m), 1395(s), 1381(s), 1362(s), 1311(vw), 1290(vw), 1254(vw), 1225(m), 1140(w), 1097(vw), 1065(w), 1016(m), 980(w), 965(vw), 924(m), 884(w), 843(m), 818(m), 801(m), 745(m), 628(w), 617(w0, 563(w), 540(w), 505(w).

Synthesis of HSB-W5-Ns. Bulk MOF HSB-W1 (20 mg) was added in 15 mL of water, followed by ultrasonication for 90 min. Then, the milky colloidal suspension was centrifugated at 10,000 rpm for 4 min to remove the water. The residual solid was next

washed with DMF and EtOH, respectively. After drying, 4.0 mg of the nanosheet sample, named as HSB-W5-Ns, was obtained.

Characterization studies. The structural determination of single crystal was performed on Rigaku SCXmini diffractometer with graphite-monochromated Mo-Ka (λ = 0.71073 Å) radiation at room temperature. The structure was solved by the SHELXL-2017 and OLEX2 program package.[3] All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located at their ideal positions. Elemental analyses were performed by Vario MICRO CHNOS Elemental Analyzer. The Fourier-transform infrared spectra with KBr pellet were performed in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR Spectrometer. PXRD data were collected on a DMAX-2500 diffractometer with Cu-Ka. Thermal analyses were performed on a NETZSCH STA 449C apparatus from 20 to 1000 °C with a heating rate of 10 °C min^{-1} under nitrogen flow. SEM characterization was conducted on a JEOL JSM-7800F instrument. TEM images of the samples were gained using FEI Tecnai G^2 F30 instrument equipped with energy-dispersive X-ray (EDX) detector. AFM images of the samples were obtained in a Bruker Dimension ICON atomic force microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Kα source (15 kV, 10 mA). The fluorescent emission and excitation spectra were recorded on a FLS920 fluorescence spectrophotometer.

[CCDC 1990806 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Table S1 Crystallographic data and refinement details for HSB-W5**.**

Empirical formula	$C_{22}H_{30}N_4O_8Zn$
M	543.87
Crystal system	triclinic
Space group	*P*-1
a (Å)	10.854(6)
b (Å)	14.735(6)
c (Å)	17.464(7)
α (°)	67.045(18)
β(°)	79.81(2)
γ(°)	77.424(19)
V/Å^3	2497.0(19)
Z	4
D_c/g cm^{-3}	1.447
μ/mm^{-1}	1.036
$2\theta_{range}$ (°)	6.07 to 49.998
h, k, l, ranges	-12 to 12, -17 to 17, -20 to 20
F(000)	1136.0
R_1,[a] wR_2[b] [$I>2\sigma(I)$]	0.0799, 0.1636
GOF on F^2	1.141

[a] $R = \Sigma(||Fo| - |Fc||)/\Sigma|Fo|$. [b] $Rw = \{\Sigma w[(Fo^2 - Fc^2)^2]/\Sigma w[(Fo^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) of HSB-W5.

Zn1-N3	2.220(4)
Zn1-N4	2.115(4)
Zn1-N8[a]	2.224(4)
Zn1-O1	2.043(4)
Zn1-O5[b]	1.993(4)
Zn2-N1	2.222(4)
Zn2-N5	2.137(5)
Zn2-N6	2.215(5)
Zn2-O3	2.007(4)
Zn2-O7	2.068(4)
N8-Zn1[c]	2.224(4)
N3-Zn1-N8[a]	172.93(18)
N4-Zn1-N3	81.53(17)
N4- Zn1-N8[a]	92.73(17)
O1- Zn1-N3	93.89(16)
O1- Zn1-N4	139.76(17)
O1- Zn1-N8[a]	87.82(16)
O5[b]-Zn1-N3	96.15(17)
O5[b] Zn1-N4	117.23(17)
O5[b] Zn1-N8[a]	90.14(17)
O5[b] Zn1-O1	103.00(17)
N5- Zn2-N1	91.98(19)
N5- Zn2-N6	81.2(2)
N6- Zn2-N1	170.0(2)
O3- Zn2-N1	91.92(16)
O3- Zn2-N5	118.9(2)
O3- Zn2-N6	97.8(2)
O3- Zn2-O7	99.61(16)
O7- Zn2-N1	86.94(16)
O7- Zn2-N5	141.4(2)
O7- Zn2-N6	93.75(18)

Symmetry codes: (a) 1+x, +y, -1+z; (b) -x, 1-y, -z; (c) -1+x, +y, 1+z.

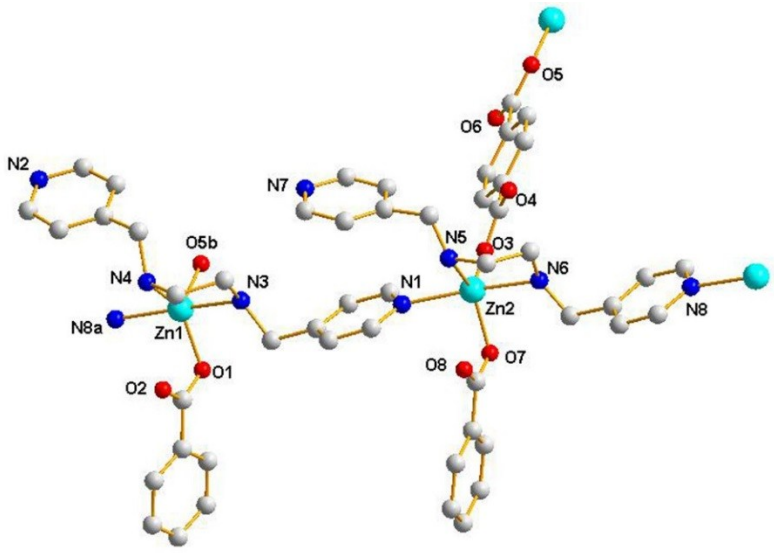

Fig. S1 View of the coordination environment of Zn(II) ion in HSB-W5 (hydrogen atoms and free water molecules have been omitted for clarity).

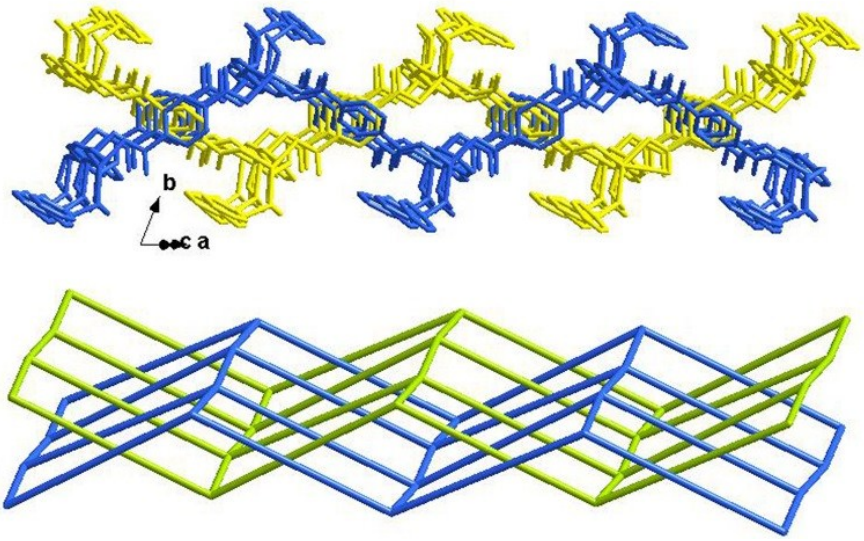

Fig. S2 A single interpenetrated 2D layer of HSB-W5.

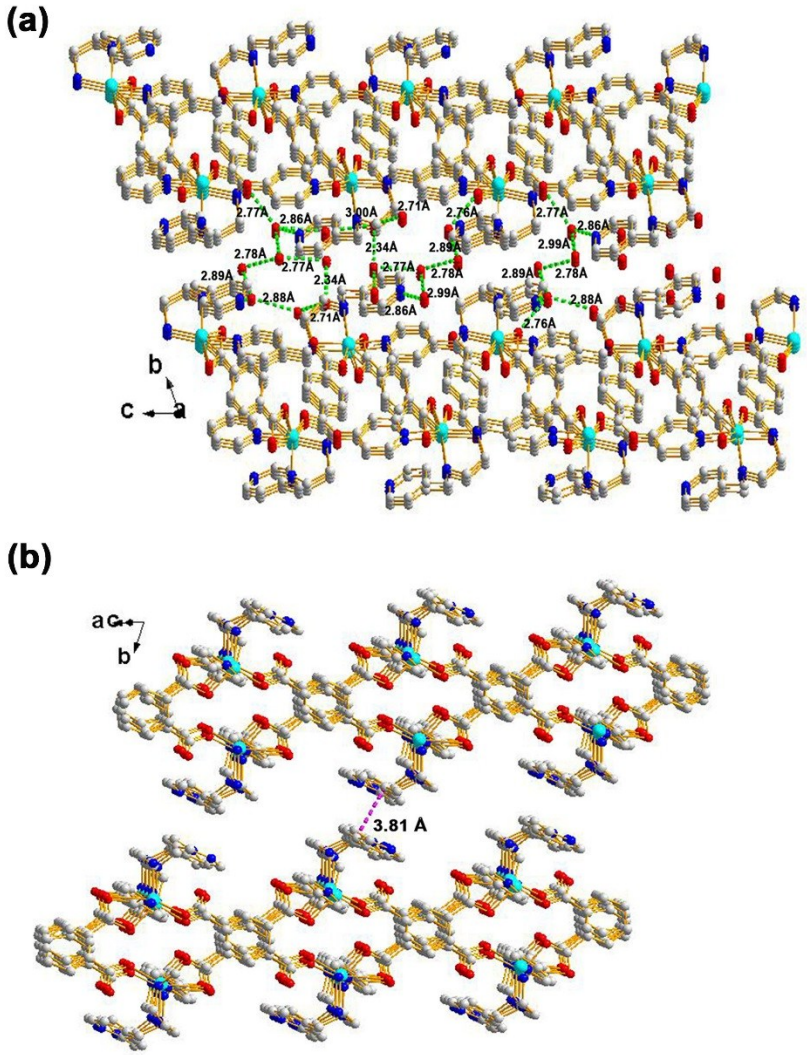

Fig. S3 The hydrogen bonding (a) and π···π stacking (b) interactions between adjacent layers in HSB-W5.

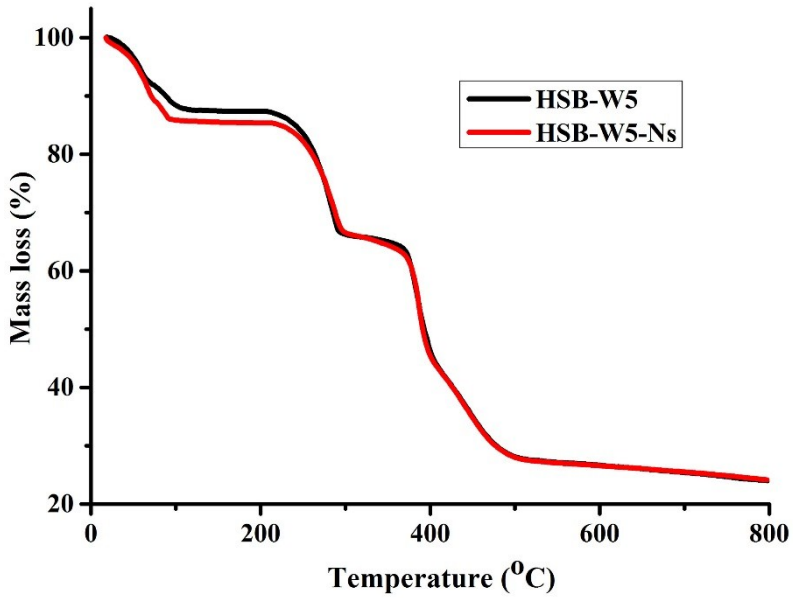

Fig. S4 TGA plots of HSB-W5 and HSB-W5-Ns.

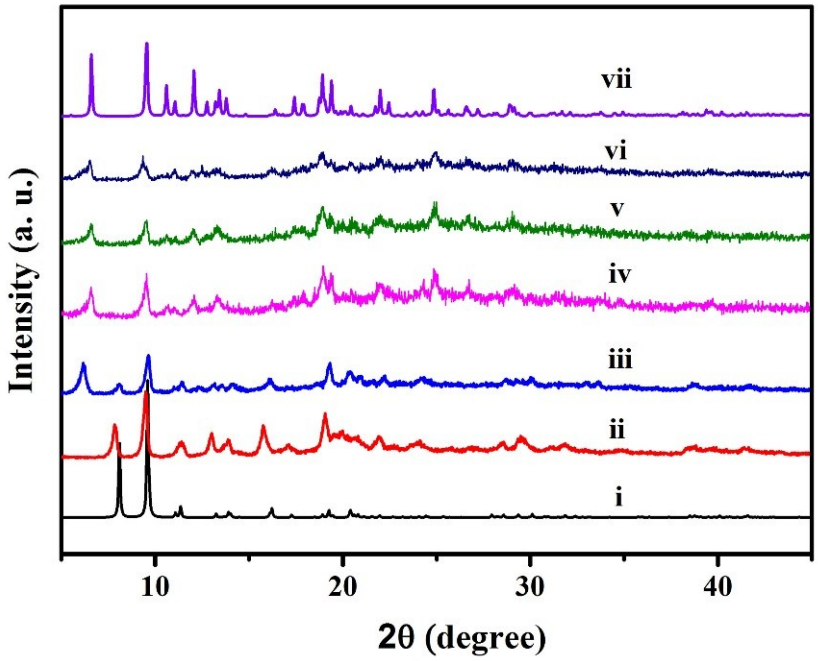

Fig. S5 PXRD patterns of the samples treated with different ultrasonic time in water**.** i) HSB-W1 (simulated); ii) pristine HSB-W1; iii) two min; iv) five min; v) ten min; vi) ninety min; vii) simulated HSB-W5.

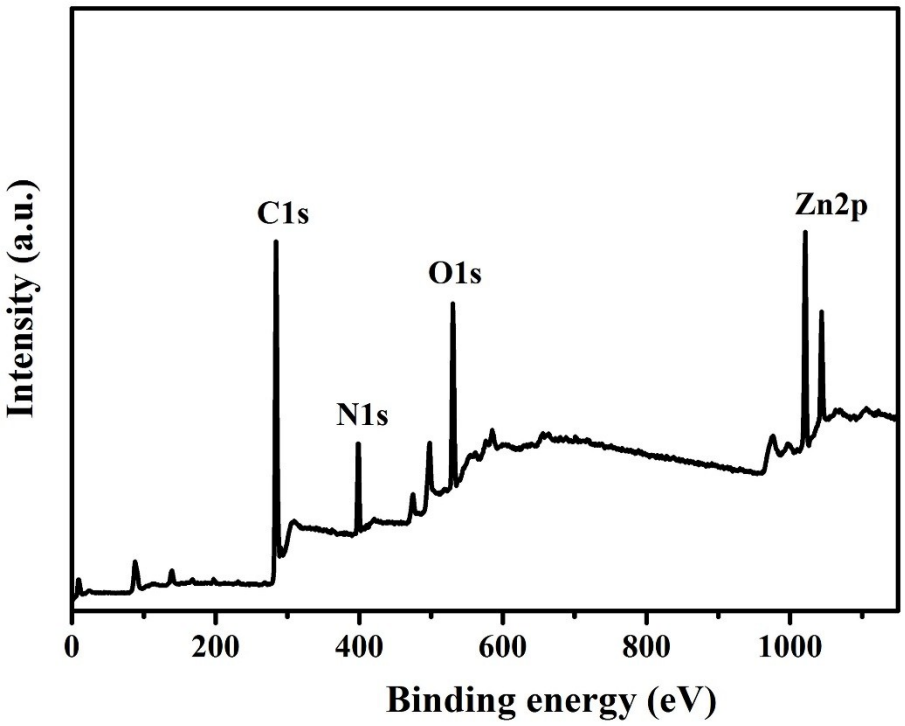

Fig. S6 XPS spectrum of HSB-W5-Ns.

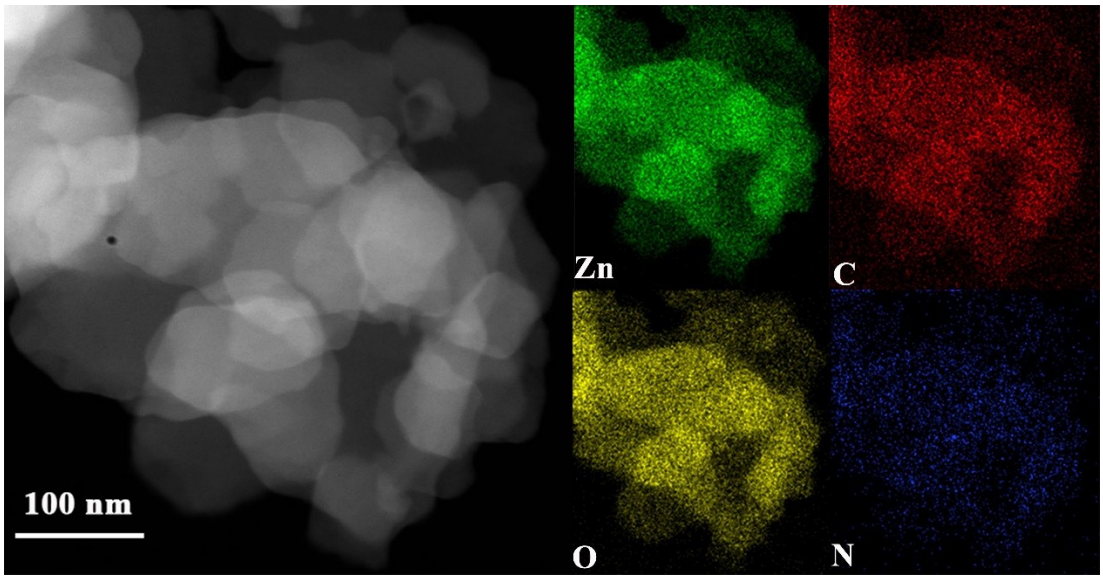

Fig. S7 TEM image and the corresponding EDX elemental mapping images of HSB-W5-Ns for Zn, C, O, and N.

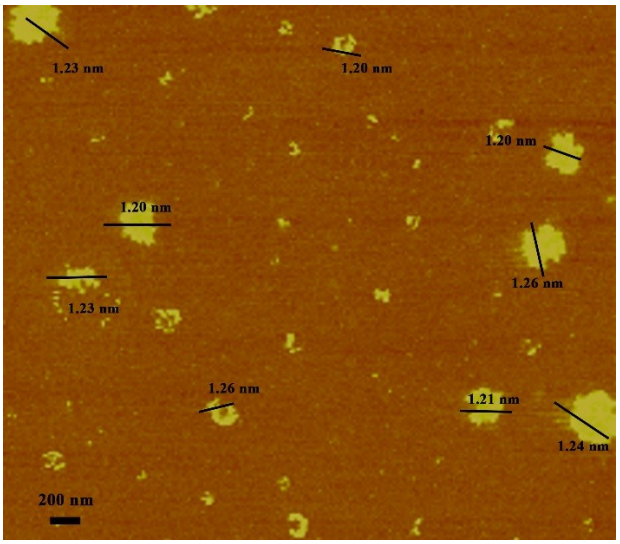

Fig. S8 AFM image of HSB-W5-Ns indicating the average thickness of ~1.2 nm.

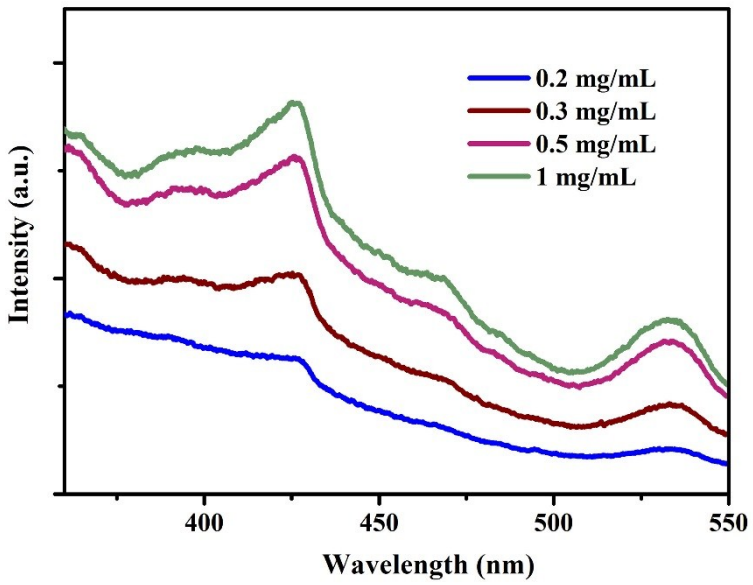

Fig. S9 Relative emission spectra of the HSB-W5-Ns aqueous suspensions with different concentrations.

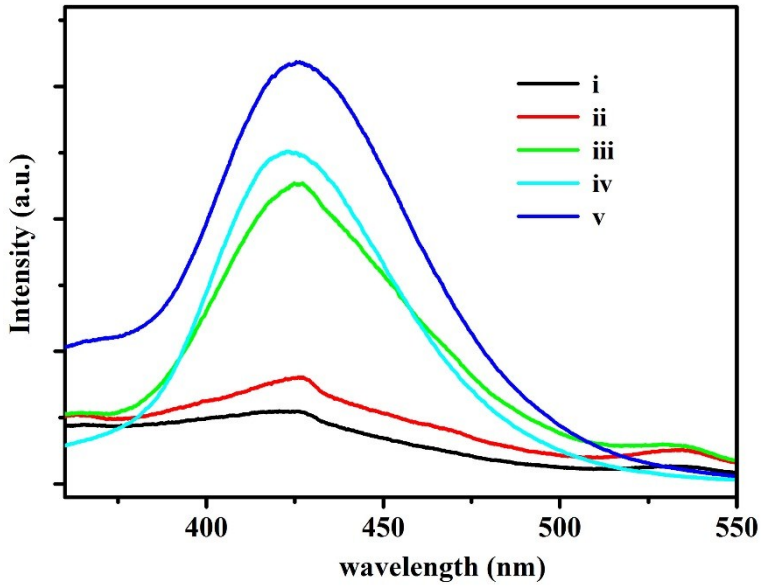

Fig. S10 Comparison of the fluorescent emissions: i) HSB-W5-Ns dispersed in water (0.2 mg·mL^{-1}); ii, iii) ultrasonic irradiation of HSB-W1 in water for 10 and 90 min, respectively; iv) clear reaction solution by remove of the formed HSB-W5-Ns; v) the bdc-Zn(II) mixture obtained by adding a small amount of $Zn(NO_3)_2{\cdot}4H_2O$ to the solution of bdc in water.

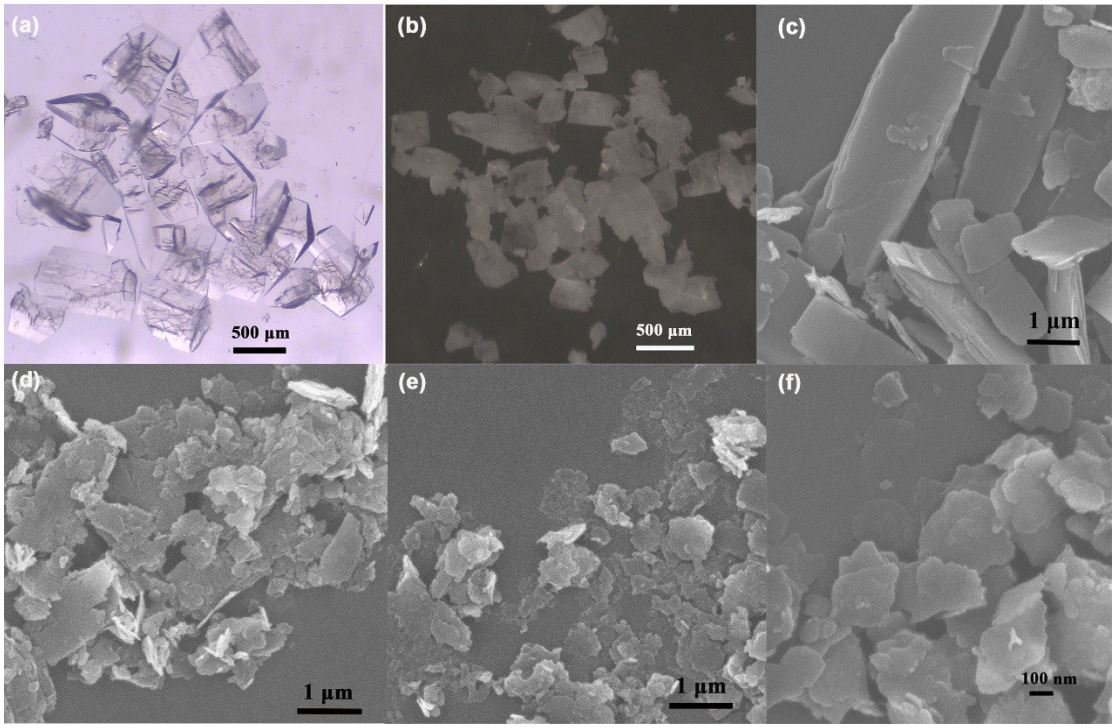

Fig. S11 Photographic and SEM images of the samples: (a, b) pristine HSB-W1; (c) upon ultrasonic irradiation for 10 min; (d) upon ultrasonic irradiation for 30 min; (e) upon ultrasonic irradiation for 60 min; (f) upon ultrasonic irradiation for 90 min.

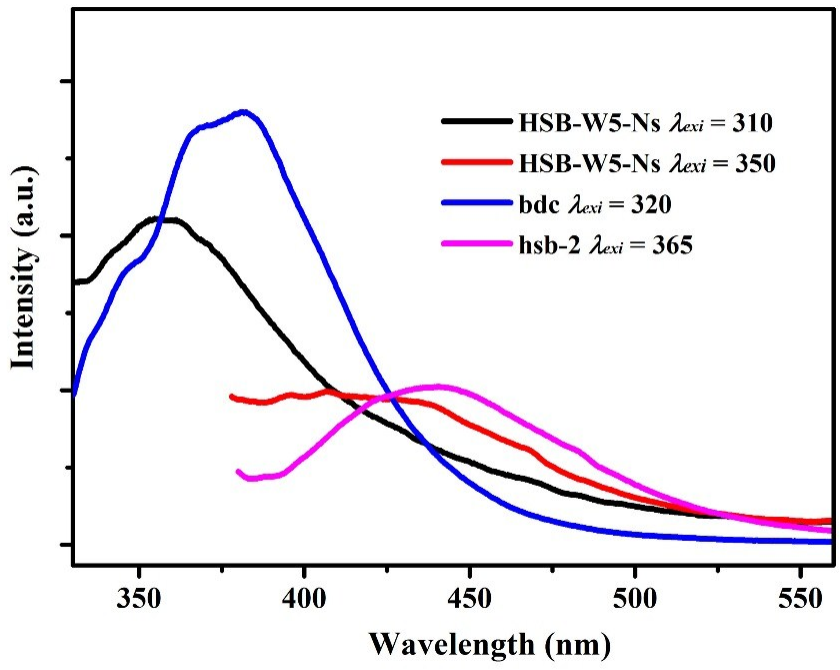

Fig. S12 Fluorescent spectra of solid HSB-W5-Ns and free ligands.

References:

[1] Y.-H. Wen, T.-L. Sheng, S.-M. Hu, Y.-L. Wang, C.-H. Tan, X. Ma, Z.-Z. Xue, Y. Wang and X.-T. Wu, *CrystEngComm* 2013, **15**, 2714.

[2] Y.-H Wen, T.-L Sheng, X.-Q. Zhu, C. Zhuo, S.-D. Su, H.-R. Li, S.-M. Hu, Q.-L. Zhu and X.-T. Wu, *Adv. Mater*. 2017, **29**, 1700778.

[3] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*. 2009, **42**, 339; b) L. J. Bourhis, O. V. Dolomanov, R. J.Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst. A* 2015, **71**, 59; c) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3.