Supporting Information

Rational Fabrication of Anionic Zinc Carboxylate Framework as Fluorescent Probe of 2,6-Pyridinedicarboxylic Acid

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Instruments and methods

Polycrystalline X-ray diffraction (PXRD) patterns were collected on Bruker D8 Advance diffractometer using CuKα radiation. Solution ^{1}H NMR spectrum was recorded on a Bruker AVANCE-III NMR (600 MHz). UV-Visible adsorption spectra were recorded on UV-3900 (HITACHI). The fluorescence measurements were carried out on a fluorescence spectrometer (F-7000, HITACHI). Thermogravimetric analyses (TGA) were performed on a simultaneous thermal analyzer (SDT650) at a heating rate of 10 °C/min under an N_2 atmosphere. Nitrogen adsorption desorption isotherms were analyzed using a surface area and porosimetry system (Kubo-X1000, BIAODE) at 77 K. The samples were pretreated by degassing at 100 °C for 5 h. IR spectra were recorded in the range of 4000-550 cm^{-1} using a FTIR spectrometer (Nicolet iS10). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALABMK II spectrometer using a 2 Al Kα (1486.6 eV) photon source. Scanning electron microscopy (SEM) images were taken on EOL JSM-IT500. ICP-OES measurements were carried out on an optical emission spectrometer (OPTMA8000DV, PE).

Single-Crystal Structure Determination

The diffraction intensity data were collected on a Bruker SMART APEX II CCD diffractometer (Mo Kα radiation, λ= 0.71073 Å) at room temperature. SAINT was used for integration of intensity of reflections and scaling.[1] Absorption corrections were carried out with the program SADABS.[2] Crystal structures were solved by direct

methods using SHELXS.[3] Subsequent difference Fourier analyses and least squares refinement with SHELXL-2013 allowed for the location of the atom positions.[4] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the water molecules were located from the difference Fourier map. All hydrogen atoms were refined using a riding model. The crystallographic details are summarized in Table 1. The data have been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition number CCDC 2377451 for compound TTCA-Zn. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Table S1. Selected bond lengths (Å) and bond angles (°).

Zn(1)-O(3)#1	1.933(4)	Zn(2)-O(4)#3	2.059(6)
Zn(1)-O(1)	1.946(5)	Zn(2)-O(4)#4	2.059(6)
Zn(1)-O(5)	1.971(3)	Zn(2)-O(4)	2.059(6)
Zn(1)-O(6)	1.973(5)	Zn(2)-O(5)#5	2.112(5)
Zn(2)-O(4)#2	2.059(6)	Zn(2)-O(5)#6	2.112(5)
O(3)#1-Zn(1)-O(1)	124.0(2)	O(4)#4-Zn(2)-O(4)	92.0(4)
O(3)#1-Zn(1)-O(5)	108.6(2)	O(4)#2-Zn(2)-O(5)#5	86.0(2)
O(1)-Zn(1)-O(5)	107.2(2)	O(4)#3-Zn(2)-O(5)#5	94.0(2)
O(3)#1-Zn(1)-O(6)	103.7(2)	O(4)#4-Zn(2)-O(5)#5	86.0(2)
O(1)-Zn(1)-O(6)	104.2(2)	O(4)-Zn(2)-O(5)#5	94.0(2)
O(5)-Zn(1)-O(6)	108.1(2)	O(4)#2-Zn(2)-O(5)#6	94.0(2)
O(4)#2-Zn(2)-O(4)#3	92.0(4)	O(4)#3-Zn(2)-O(5)#6	86.0(2)
O(4)#2-Zn(2)-O(4)#4	88.0(4)	O(4)#4-Zn(2)-O(5)#6	94.0(2)
O(4)#3-Zn(2)-O(4)#4	180.0	O(4)-Zn(2)-O(5)#6	86.0(2)
O(4)#2-Zn(2)-O(4)	180.0(3)	O(5)#5-Zn(2)-O(5)#6	180.0
O(4)#3-Zn(2)-O(4)	88.0(4)		

Symmetry transformations used to generate equivalent atoms: #1 x, y+1/2, -z+5/2; #2 -x, -y, -z+3; #3 -x, y, z; #4 x, -y, -z+3; #5 x, y-1/2, -z+5/2; #6 -x, -y+1/2, z+1/2.

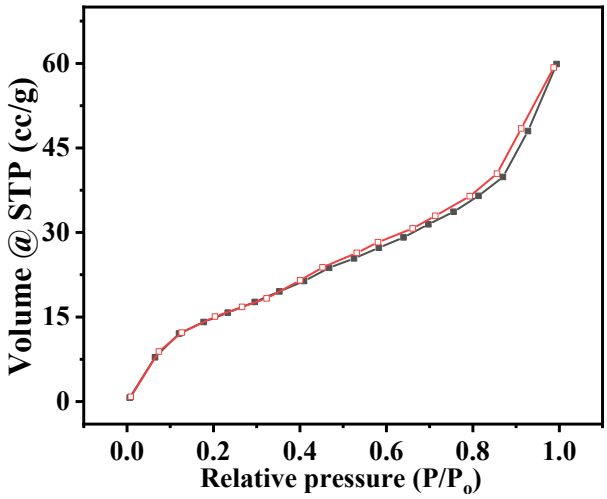

Figure S1. N_2 adsorption-desorption isotherms of TTCA-Zn.

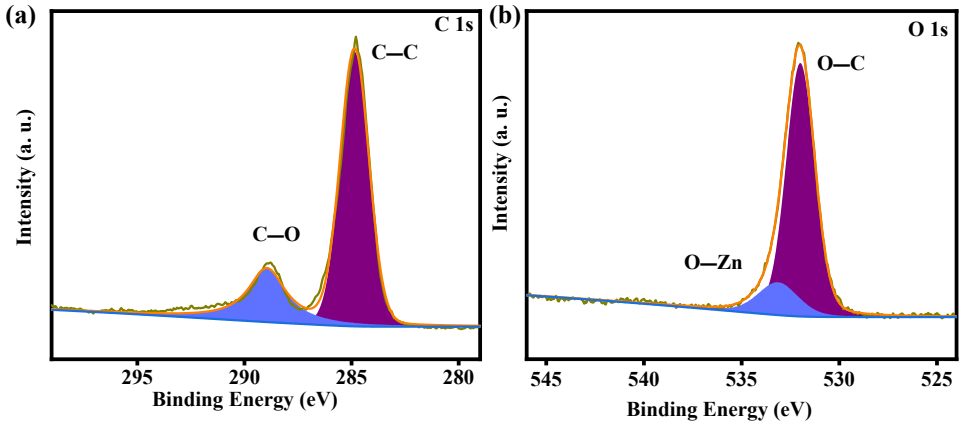

Figure S2. XPS C1s and O1s spectra of TTCA-Zn.

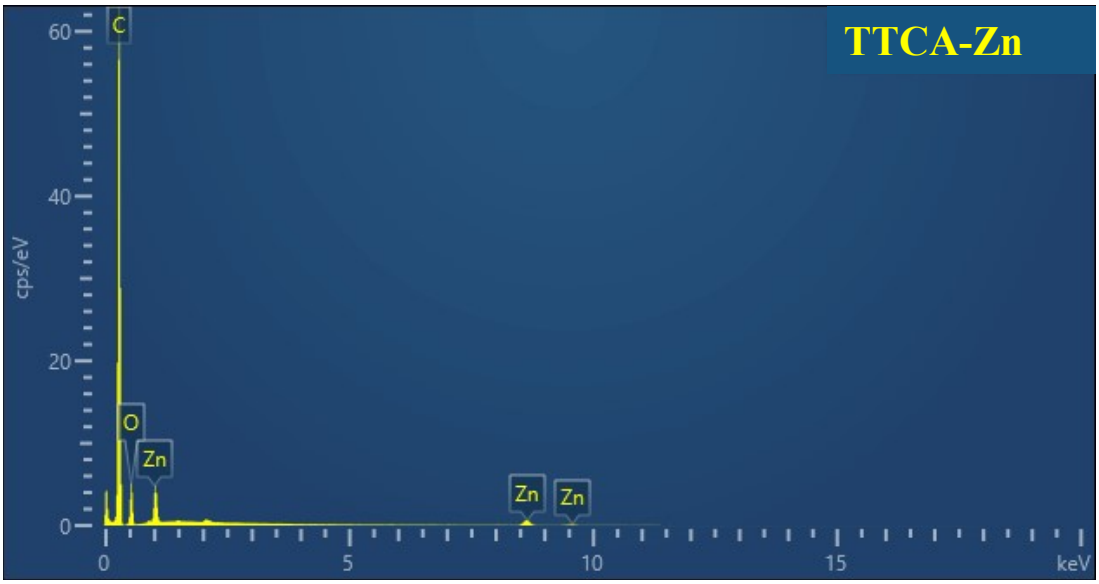

Figure S3. EDX spectrum of TTCA-Zn.

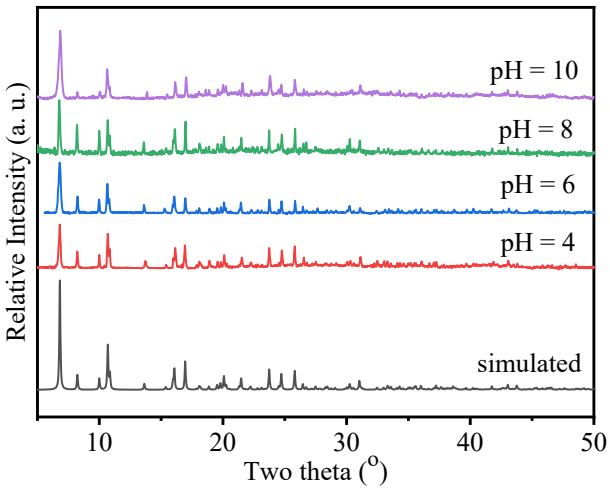

Figure S4. XRD patterns of TTCA-Zn recovered from solutions of different pH values.

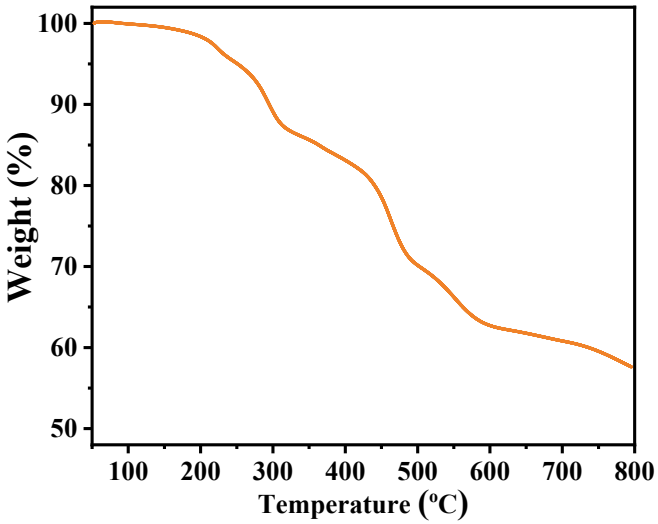

Figure S5. TGA curves of as-prepared TTCA-Zn.

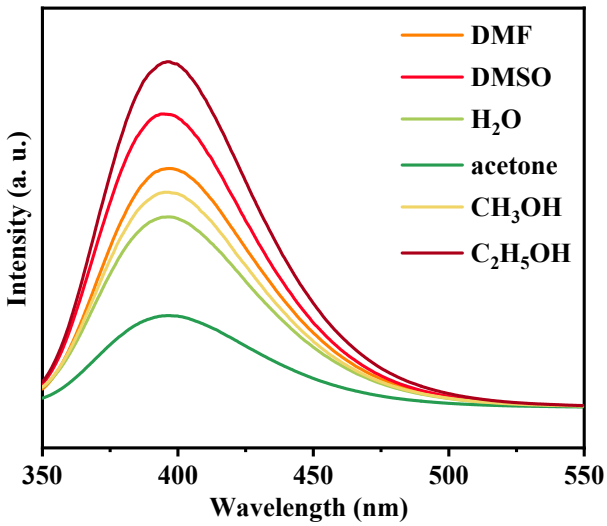

Figure S6. Emission spectra of TTCA-Zn in different solvents (2 mg TTCA-Zn dispersed in 2 mL of solvent).

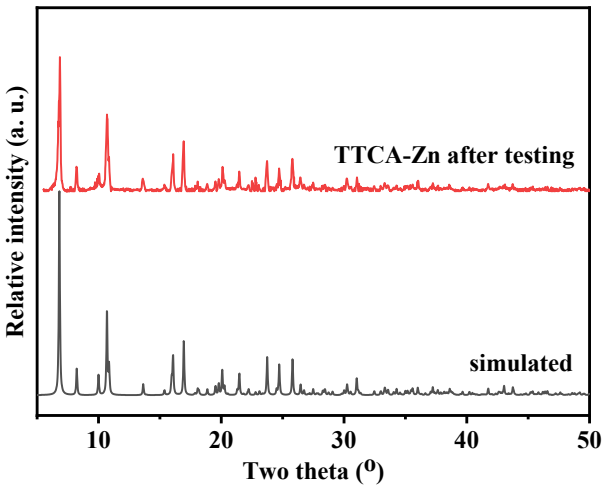

Figure S7. Comparison of the XRD patterns of simulated and TTCA-Zn after testing.

Table S2. The Zn content of TTCA-Zn and the recovered sample tested by ICP-OES.

probe	theoretic concentration of Zn (mg/L)	experimental concentration of Zn (mg/L)
TTCA-Zn	97.774	92.056
TTCA-Zn (in the supernatants after sensing)	--	1.679

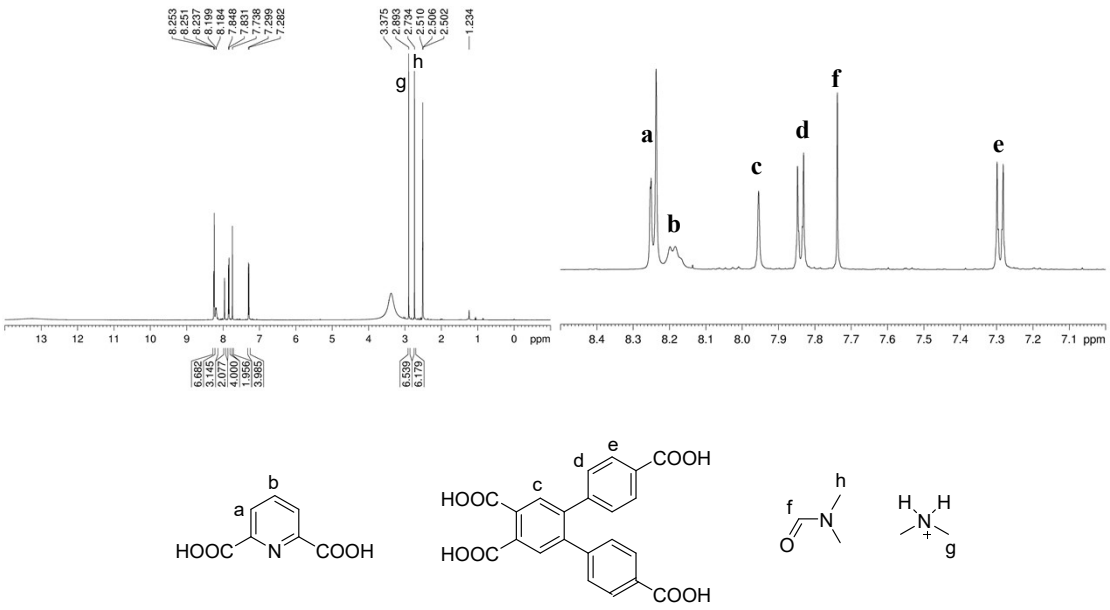

Figure S8. ^{1}HNMR spectra of the suspension in D_6-DMSO.

Ten milligrammes of powdered TTCA-Zn was added to 2 mL of D_6-DMSO and sonicated for 1 min. Afterward, 10 mg of DPA was added and sonicated for additional 1 min to form a homogeneous solution. The solution was then filtered with syringe filter (0.22 μm) and the ^{1}HNMR spectrum was recorded.

REFERENCES

(1) SAINT, Version 6.45; Bruker Analytical X-ray Systems Inc.: 2003.
(2) G. M. Sheldrick. SADABS, Version 2.10; Bruker AXS Inc.: Madison, WI, 2003.
(3) G. M. Sheldrick. SHELXS-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.
(4) G. M. Sheldrick. SHELXL 2013, University of Göttingen, 2013.