Electronic Supplementary Information

Tetranuclear Zn(II) Based Host-Guest MOF Resistant to Thermal Quenching

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A. Experimental Section.

1. Materials and general procedures.

All reagents were of analytical grade and obtained from commercial sources without further purification. Powder X-ray diffraction (PXRD) patterns were measured at room temperature using a Bruker D8-ADVANCE X-ray diffractometer with Cu *Kα* radiation (λ = 1.5418 Å). Intensity data were collected in a 2θ range of 5-50° with a step of 0.02° (2*θ*) and a counting time of 0.2 s/step. Elemental analyses for C, H, and N were carried out on a Flash 2000 organic elemental analyzer. Thermogravimetric analysis (TGA) experiments were carried out using SII EXStar6000 TG/DTA6300 thermal analyzer from room temperature to 700 ^{o}C under a nitrogen atmosphere at a heating rate of 10 ^{o}C min^{-1}. The IR spectrum was recorded in the range of 4000–400 cm^{-1} on a Nicolet 6700 (Thermo) FT-IR spectrometer with KBr pellets. UV-Vis spectra were recorded on Hitachi UH4150 spectrophotometer in the range of 250-800 nm with a slit of 2 nm. Photoluminescence (PL) spectra and decay curve were tested on Edinburgh FLS1000 fluorescence spectrometer equipped with a xenon arc lamp (Xe900) and nanosecond flash-lamp (nF900), respectively. The temperature dependence PL spectra were measured using a temperature controller attached to a cryostat (Oxford Ltd. Optistat DN2) using an FLS1000 fluorescence spectrometer. The morphologies of the title MOF before and after thermal quenching measurements were investigated by a field emission scanning electron microscope (SEM, Zeiss Sigma 500) at 5 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with the Thermo Scientific K-AIpha and equipped with a non-monochromatized source (at 150 W).

Single-crystal X-ray diffraction data for **[AD][Zn_2(IPOIPA)$_2$(μ_3-OH)] (1)** were collected using an Oxford Diffraction SuperNova area-detector diffractometer and mirror optics monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. CrysAlisPro[1] was used for the data collection, data reduction, and empirical absorption correction. The crystal structure was solved by direct methods, using SHELXT-2014[2], and refined by the full matrix on F^2 using the program SHELXL-2014[3]. All other non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The crystallographic data and selected bond lengths and angles for **1** were listed in Tables S1 and S2. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center. CCDC number for **1** is 2456047. This material can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

2. Synthesis of [HAD][Zn_2(IPOIPA)$_2$(μ_3-OH)] (1) crystals

A mixture of IPOIPA (0.2 mmol, 44.81 mg), $Zn(OAc)_2 \cdot 6H_2O$ (0.5 mmol, 109.75 mg), AD (0.2 mmol, 35.84 mg) and H_2O (8 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for two days, and then cooled to room temperature naturally. Greenish-yellow lamellar crystals of **1** were obtained, which were filtered, washed with water and ethanol several times, then dried under room temperature. Yield: 50% (based on Zn). Anal. Calc. (%) for $C_{35}H_{31}NO_{11}Zn_2$: C, 54.42; H, 4.05; N, 1.81; found (%):C, 54.36; H, 3.99; N, 1.67. IR (cm^{-1}): 3429 (w), 2985 (m), 1638 (s), 1585 (s), 1381 (s), 1269 (s), 1026 (s), 908 (m), 785 (s), 726 (s), 598 (m), 467 (m).

3. Preparation of the LED device

A mixture of MOF powders (50 mg) as phosphor and organic silica (about 2 mL) as binder was stirred for 5 min, carefully coated on a commercially available 455 nm blue LED, and then the device was heated at 100 °C for 1 h.

4. Electronic structure calculations

All calculations were performed with the density functional theory (DFT) method using Dmol3 module in Material Studio software package.[4] The structure mode were directly used from the crystal structure file of **1**. The initial configuration was fully optimized by Perdew-Wang (PW91) generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP).

B. Supporting Figures

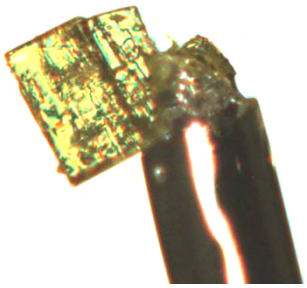


Figure S1. Photograph of the crystal of **1** under day light.

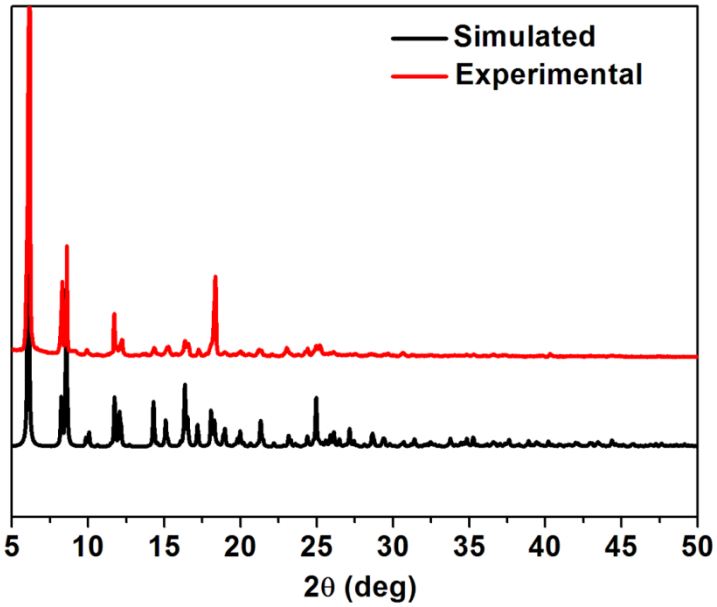


Figure S2. PXRD pattern of **1**.

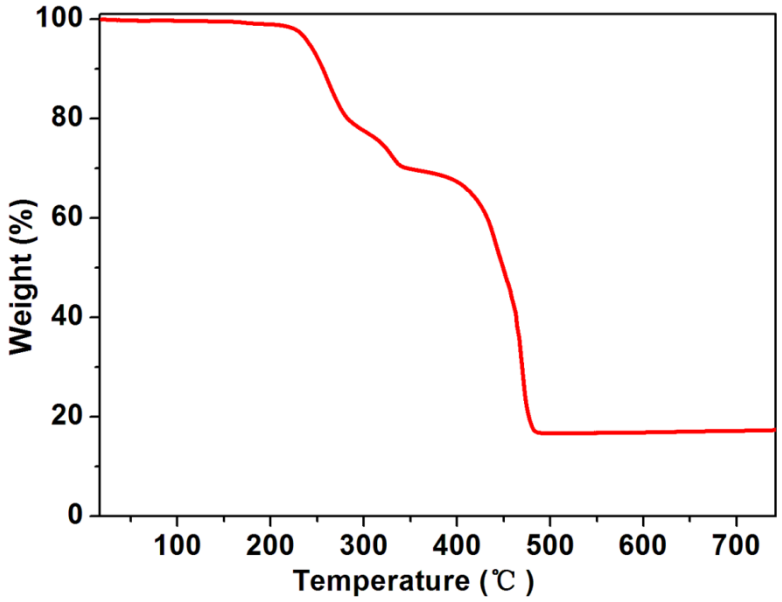


Figure S3. Thermogravimetric analysis (TGA) curve of **1**.

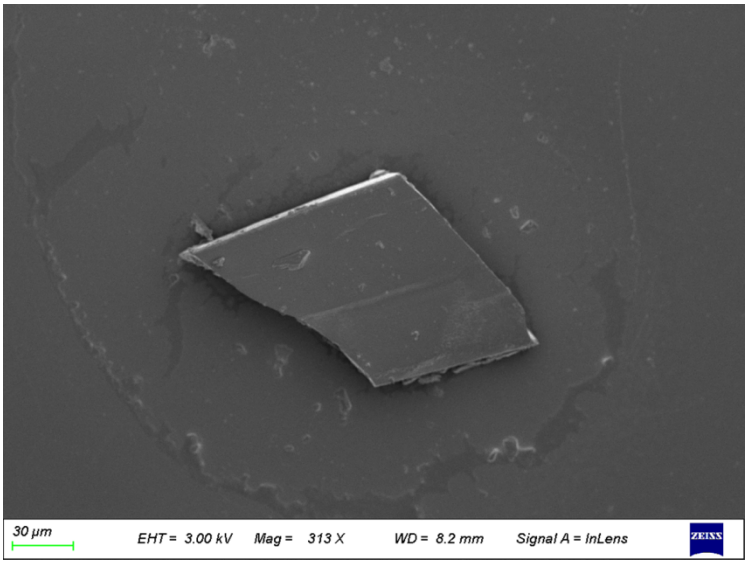


Figure S4. SEM image of **1**.

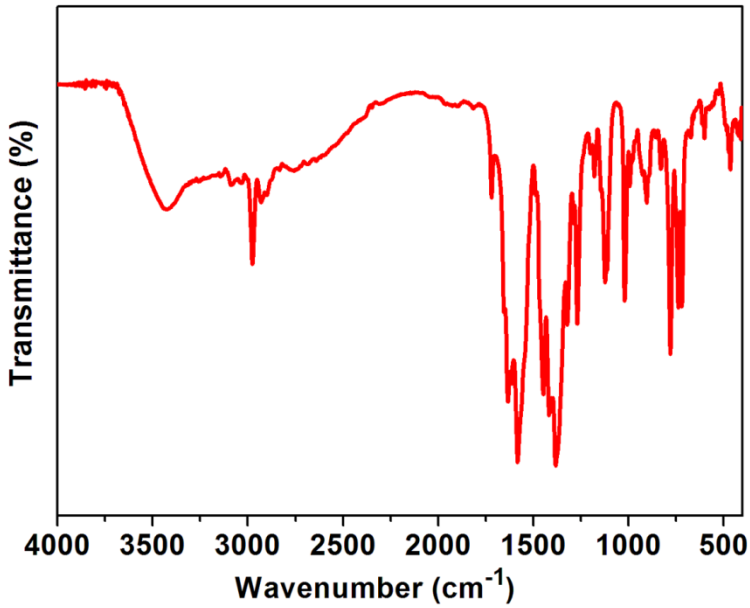


Figure S5. FT-IR spectrum of **1**.

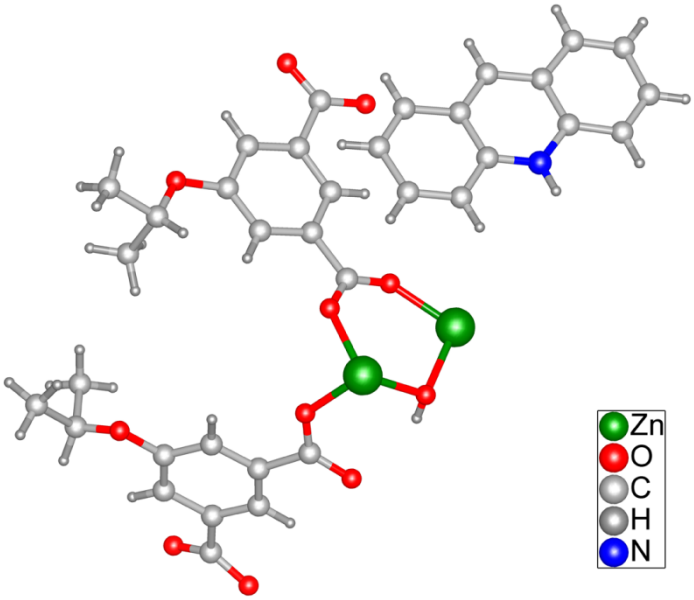


Figure S6. View of the asymmetrical unit of **1**.

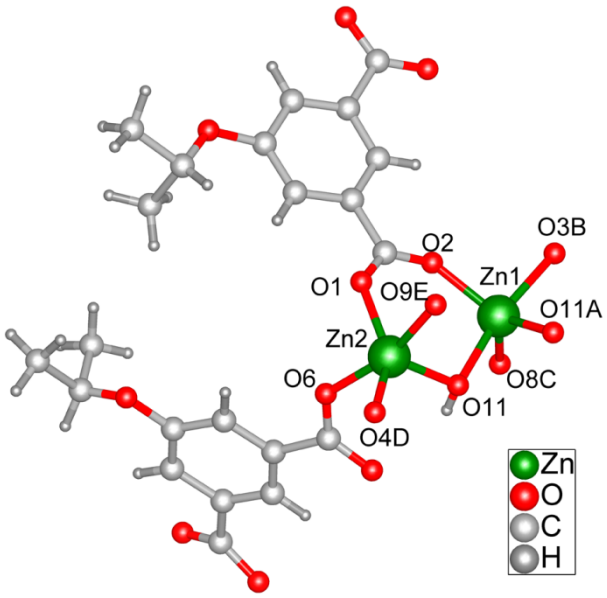


Figure S7. View of the coordination environment of Zn(II) atoms in **1**. Symmetry codes: A: 1-X, -Y, 1-Z; B: 2-X, -Y, 1-Z; C: 1-X, -1-Y, 1-Z; D: -1+X, Y, Z; E: X, 1+Y, Z.

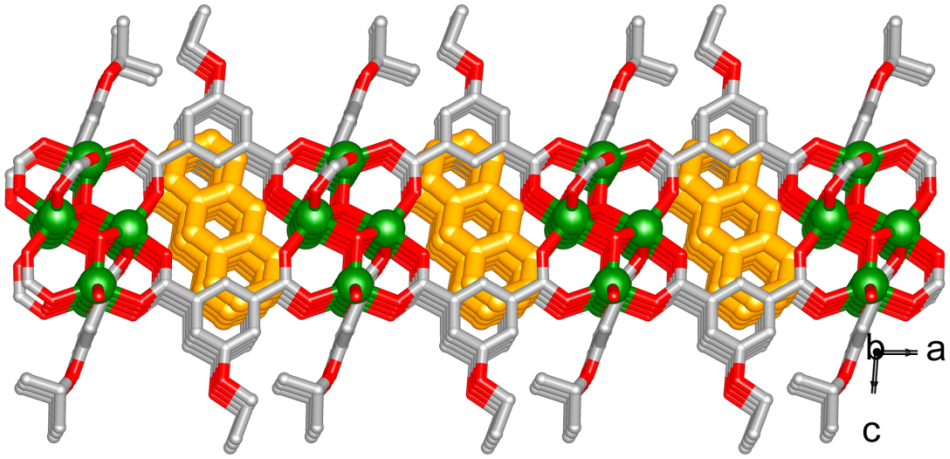


Figure S8. View of the 2D layer structure of **1** along b axis with the protonated AD guests encapsulated in each grids.

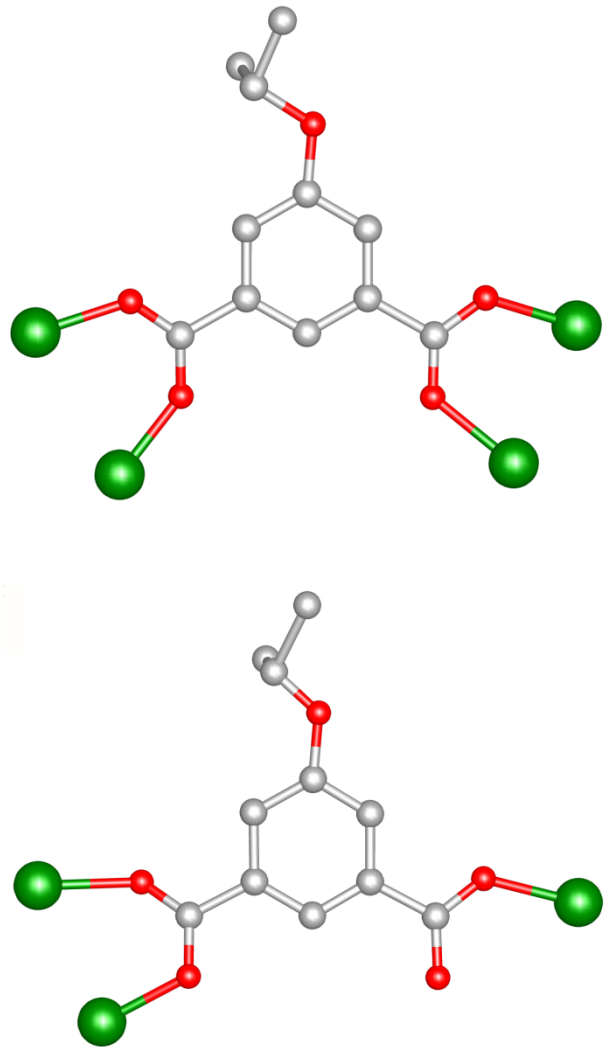
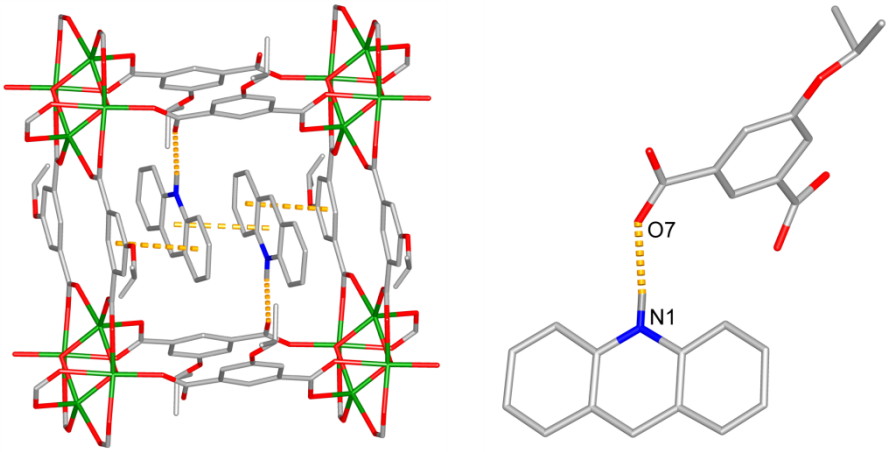
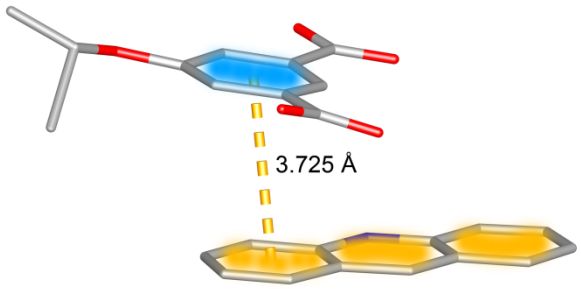


Figure S9. View of the coordination modes of IPOIPA ligands in **1**.



(a)



(b)

Figure S10. View of the N–H···O hydrogen-bonding (a) and π···π stacking between IPOIPA and AD molecules (b) in the host-guest system.

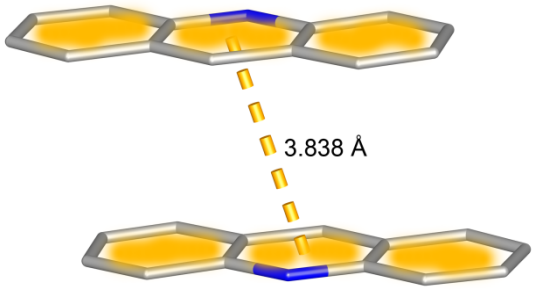
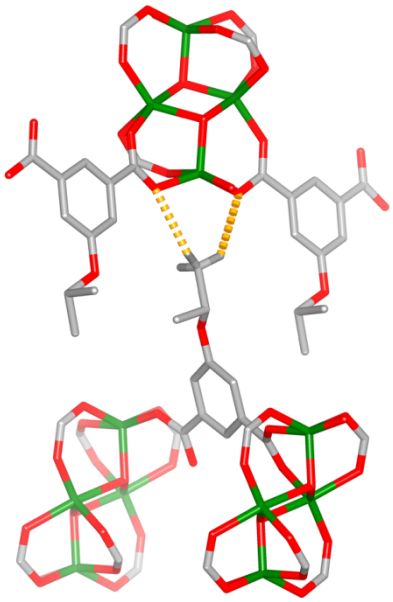
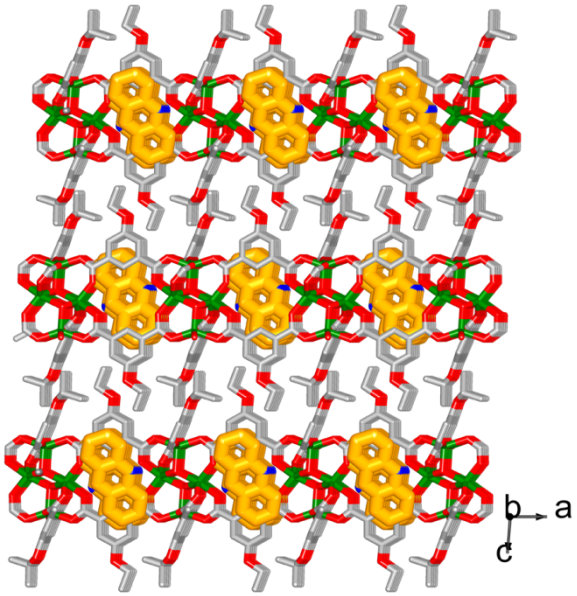


Figure S11. View of the π···π stacking between AD and AD molecules in the host-guest system.



(a)



(b)

Figure S12. (a) C-H···O hydrogen bonding (O21-H21B···O1 and O21-H21C···O4) between carboxyl and isopropoxy groups from adjacent 2D layer. (b) View of the 3D supramolecular network of a b axis.

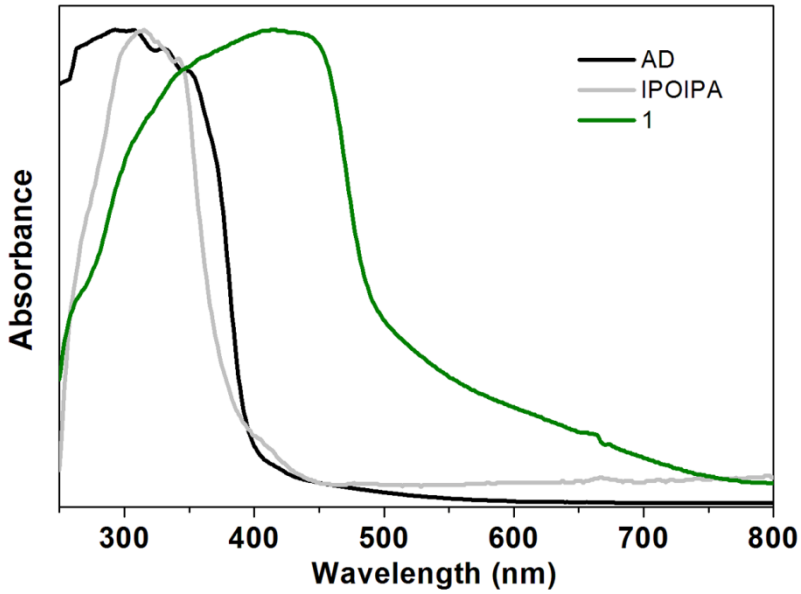
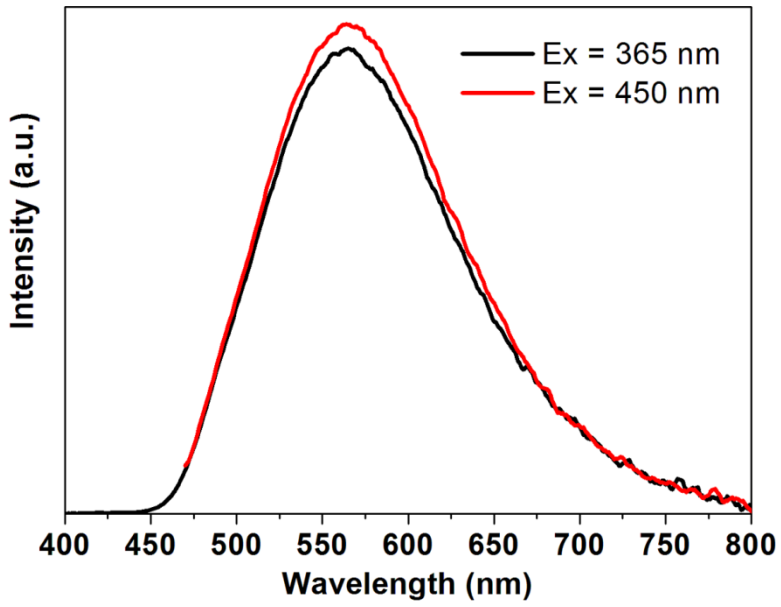
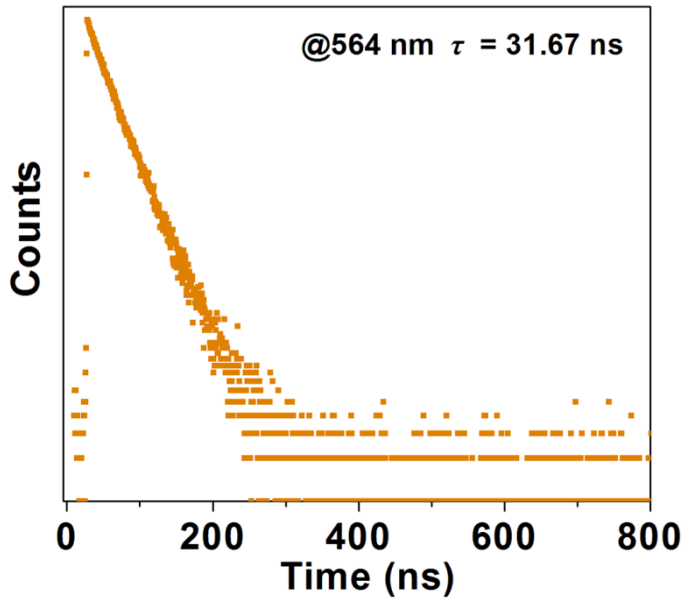


Figure S13. UV−vis absorption spectrum of AD, IPOIPA and **1** in solid state recorded at room temperature.



(a)



(b)

Figure S14. (a) PL spectra of **1** excited by 365 and 450 nm in solid state recorded at room temperature. (b) PL decay curve of **1** exited by 450 nm.

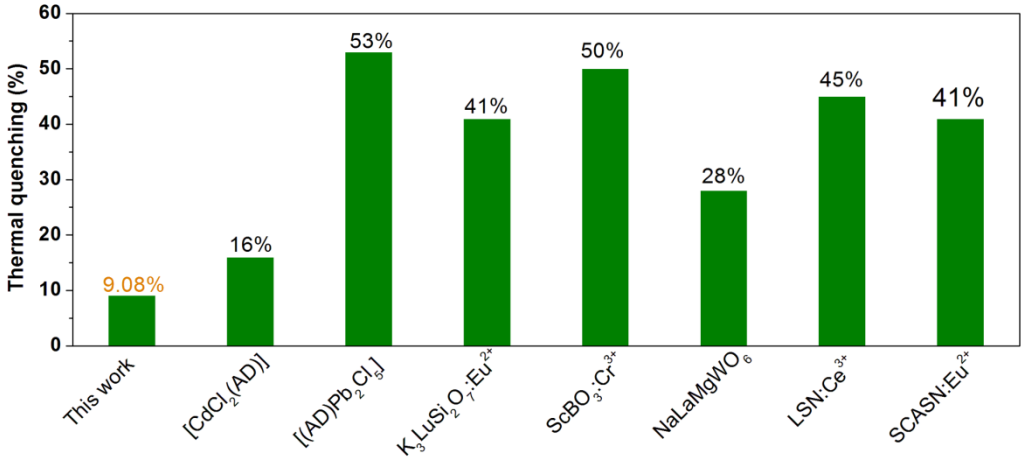


Figure S15. Comparison of thermal quenching for some developed phosphors.

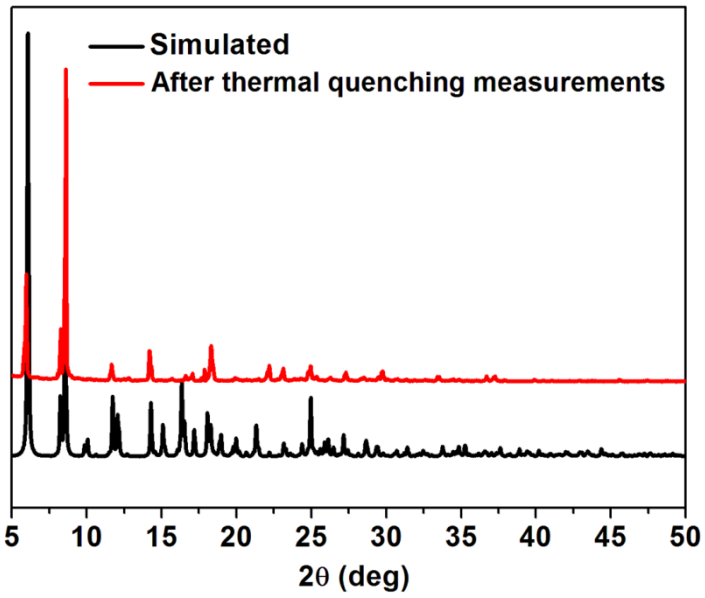
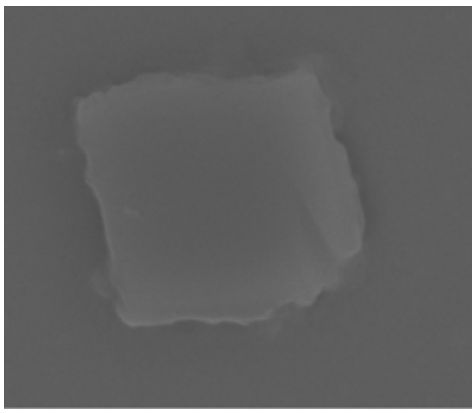
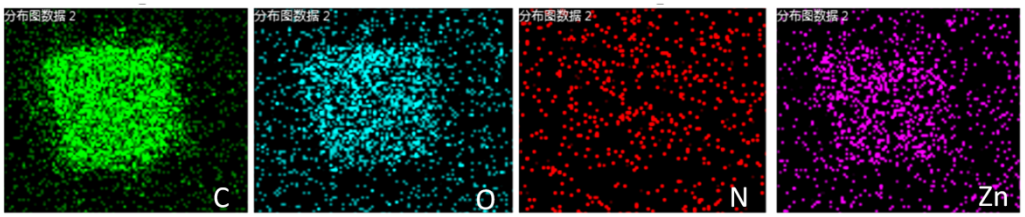


Figure S16. PXRD patterns of **1** after thermal quenching measurements.

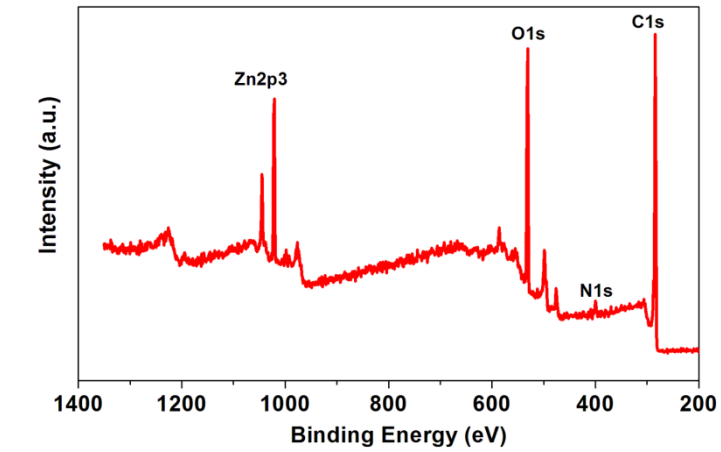


(a)

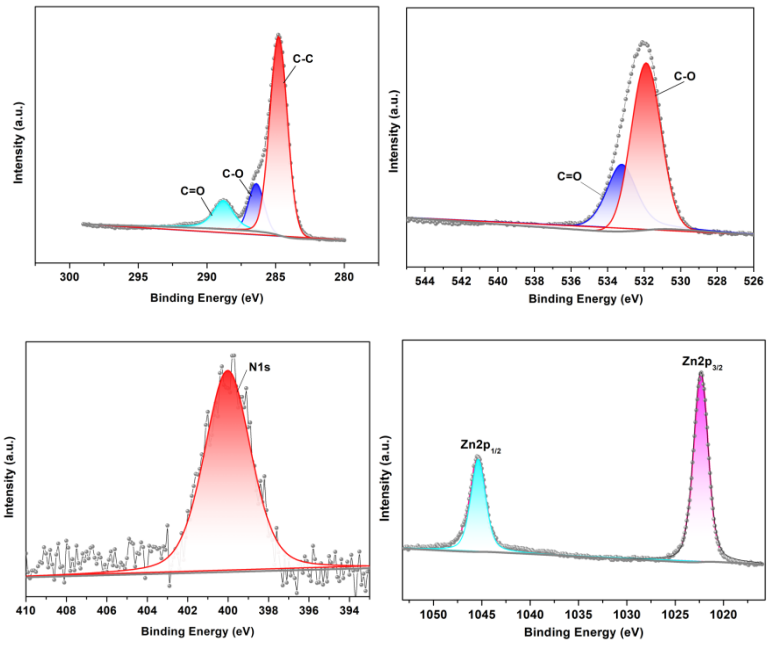


(b)

Figure S17. SEM image (a) and elemental mapping image (b) of **1** after thermal quenching measurements.



(a)



(b)

Figure S18. XPS survey spectrum (a), C 1s, O 1s, N 1s, and Zn 2p (b) of **1** after thermal quenching measurements.

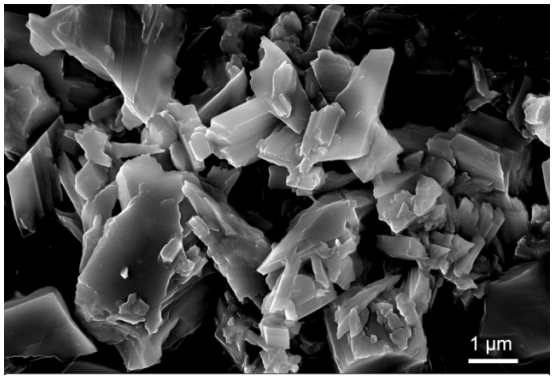


Figure S19. SEM image of **1** after soaking in water for 10 days.

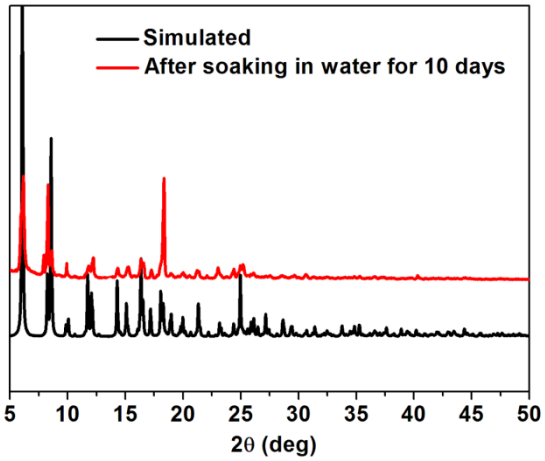


Figure S20. PXRD patterns of **1** after soaking in water for 10 days.

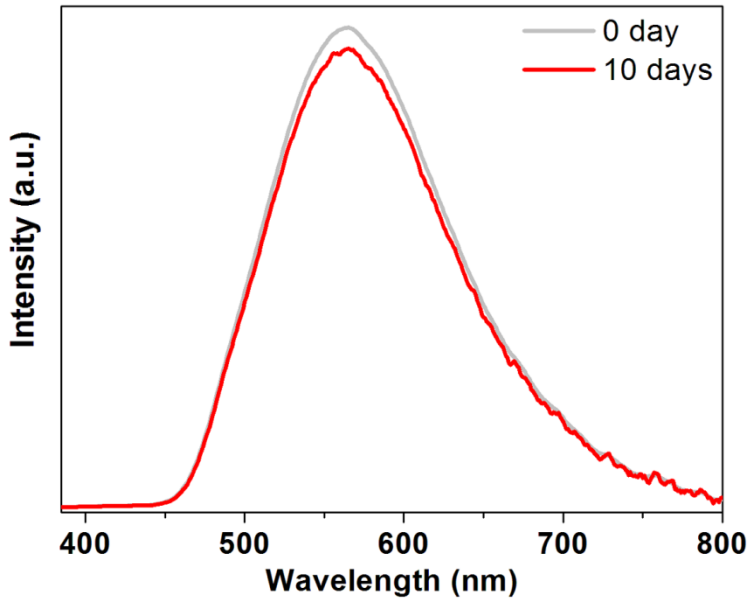


Figure S21. PL spectra 1 before and after being soaked in water for 10 days.

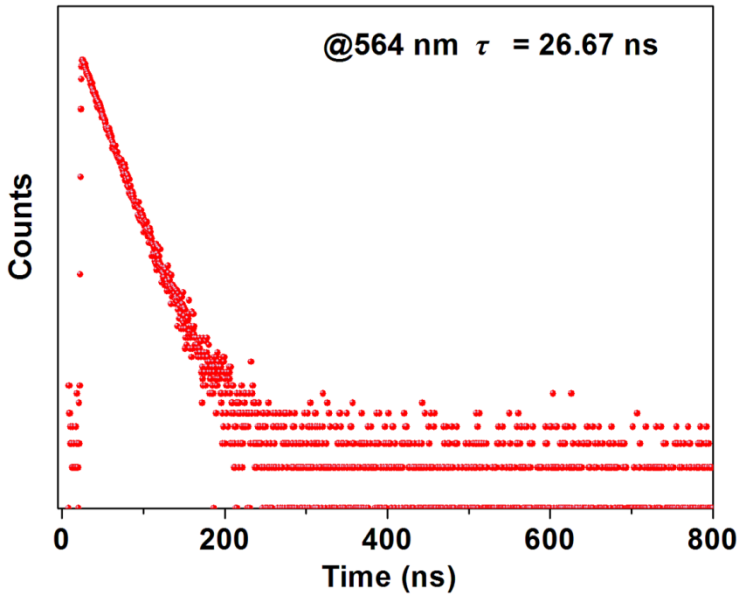


Figure S22. PL decay curve of **1** after soaking in water for 10 days.

D. Supporting Table

Table S1. Crystallographic data for **1**.

Sample	**1**
Chemical formula	$C_{35}H_{31}NO_{11}Zn_2$
Formula weight	772.35
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.7517(7)
b (Å)	11.0322(16)
c (Å)	29.181(3)
V (Å^3)	3451.1(6)
Z	4
D (g cm^{-3})	1.487
μ (mm^{-1})	1.451
T (K)	293(2)
R_{int}	0.0649
Goof	1.075
R_1[a] *(I>2σ (I))*	0.0989
wR_2[b] *(I>2σ(I))*	0.2340

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

D. Supporting References

[1] CrysAlisPro, Rigaku Oxford Diffraction, Version 1.171.39.6a.

[2] G. M. Sheldrick, SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr, A: Found. Adv.* 2015, **71**, 3–8.

[3] G. M. Sheldrick, Crystal structure refinement withSHELXL. *Acta Crystallogr, Sect. C: Struct. Chem*. 2015, **71**, 3–8.

[4] (*a*) B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys*. 1990, **92**, 508–517; (*b*) B. Delley, From molecules to solids with the DMol^3 approach. *J. Chem. Phys*. 2000, **113**, 7756–7764; (*c*) Dmol^3 Module, MS Modeling, Version 2.2; Accelrys Inc.: San, Diego, 2003.