Electronic Supplemental Information

Triple-Mode Tunable Long-persistent Luminescence in a 3D Zinc-Organic Hybrid

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Contents

Experimental Section

Materials and methods

All chemicals were reagent grade and used as purchased without further purification.

Synthesis of 1: $Zn(NO_3)_2 \cdot 6H_2O$ (0.09g, 0.30 mmol), D-Cam (0.03 g, 0.15 mmol), tib (0.027g, 0.10 mmol) was added to mixed solution of 14 mL water and 1 mL DMF with a drop of concentrated HNO_3, then sealed in a Teflon-lined autoclave (20 mL) and heated to 140 °C for 3 days, colorless crystals were obtained and washed with deionized water. Yield: ca. 31% based on tib. IR of **1** (KBr pellets, cm^{-1}): 3422(s), 2963(w), 2876(w), 1605(s), 1508(s), 1385(s), 1287(m), 1242(m), 1076(s), 1018(m), 943(m), 872(m), 766(m), 687(m), 652(s), 536(w), 446(w).

The SHG measurements of the crystals samples were completed by a Nd:YAG laser with 1064 nm as fundamental frequency light. IR spectra was recorded on a Shimadzu IRAffinity-1 FT-IR spectrometer with KBr pellet. All luminescence data were measured on an FLS 980 fluorescence spectrometer. The absorption spectra were carried out on a Puxi Tu-1901 spectrophotometer with $BaSO_4$ reference. Thermogravimetric (TG) analysis was measured using a powder sample with a heating rate of 10℃ K^{-1} under N_2 atmosphere on a METTLER TOLEDO Thermogravimetric Analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Shimadzu XRD-7000 (3KW) X-ray diffractometer. Simulated curve of PXRD was exported by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org.

X-ray Crystallography.

The single-crystal X-ray diffraction data of **1** was collected on a Rigaku XtalLAB Synergy diffractometer at 100(10) K with Cu-Kα radiation (λ = 1.54184 Å). SHELX-2016 software was used to solve and refine the structure.[1] Crystallographic data for **1** are listed in Table S1, and selected bond lengths and angles are listed in Table S2. Full crystallographic data for **1** has been deposited with the CCDC (2079214).

Calculation Details

All DFT calculation were carried out with the D.01 revision of the Gaussian 09 program package[2], using the cam-b3lyp functional with the 6-311G* basis set for C, H, O and N, and lanl2dz basis set for the Zn element. The D3 Grimme's dispersion term with Becke-Johnson damping was added to the cam-B3LYP functional to get a better description of the intramolecular non-covalent interactions. In this work, the frontier orbitals were analyzed by Multiwfn[3] and VMD[4].

References

[S1] G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

[S2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.

[S3] T. Lu; F. Chen, Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.*, 2012, **33**, 580-592

[S4] W. Humphrey; A. Dalke; K. Schulten, VMD: Visual molecular dynamics. *J. Mol. Graph.*, 1996, **14**, 33-38.

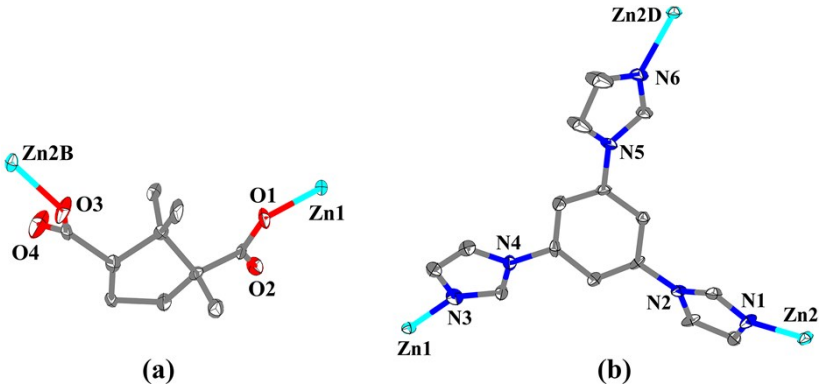

Figure S1. The coordination modes of D-Cam (a) and tib (b).

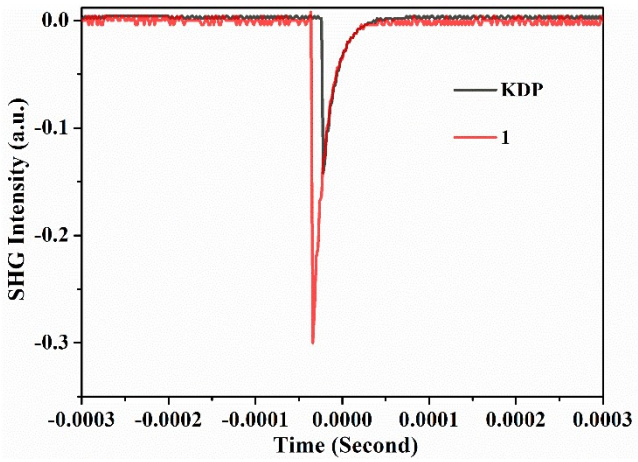

Figure S2. Oscilloscope traces of SHG signals of KDP and **1**.

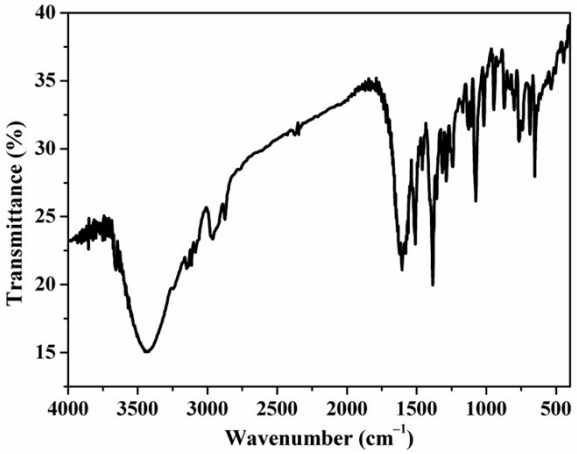

Figure S3. IR plot of **1**.

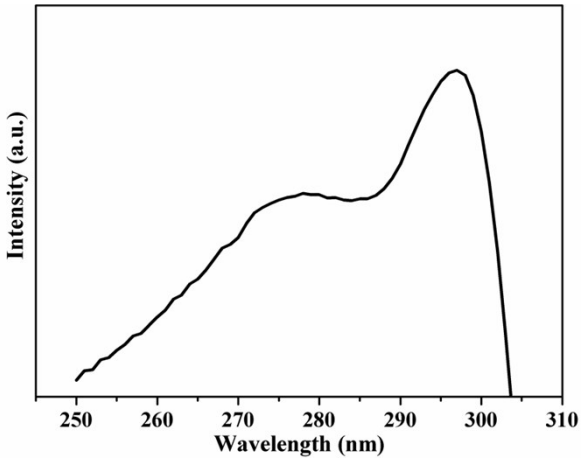

Figure S4. The prompt excitation spectra of **1** at room temperature.

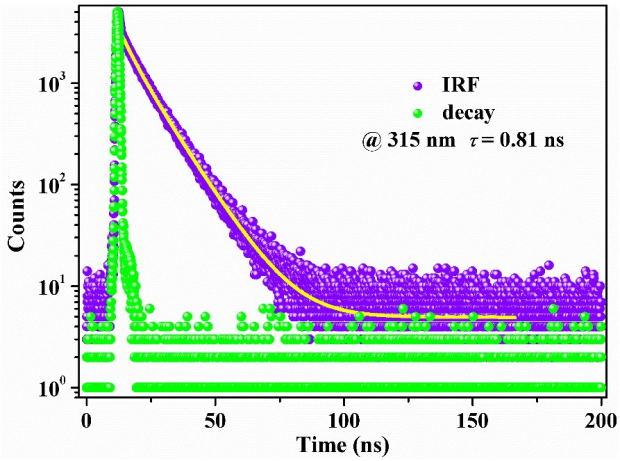

Figure S5. The decay and IRF spectra of **1**.

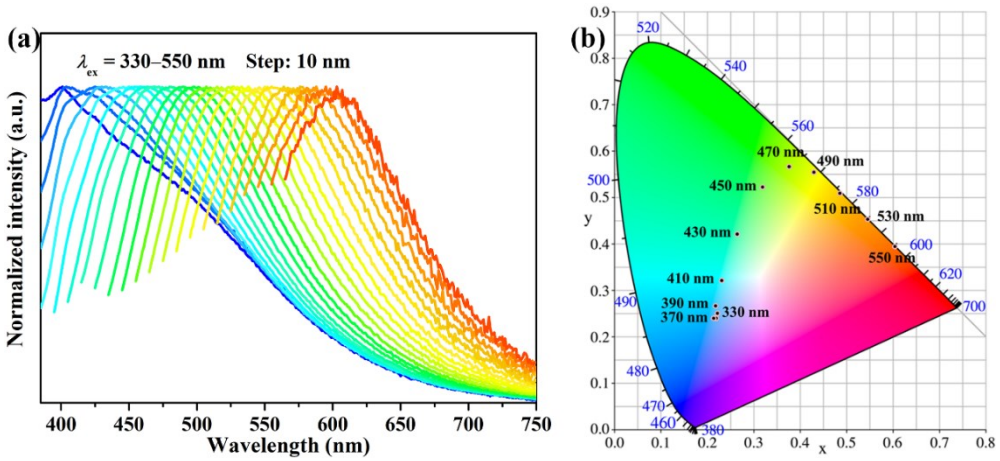

Figure S6. The PL spectra (a) and CIE coordinate (b) of **1** at room temperature.

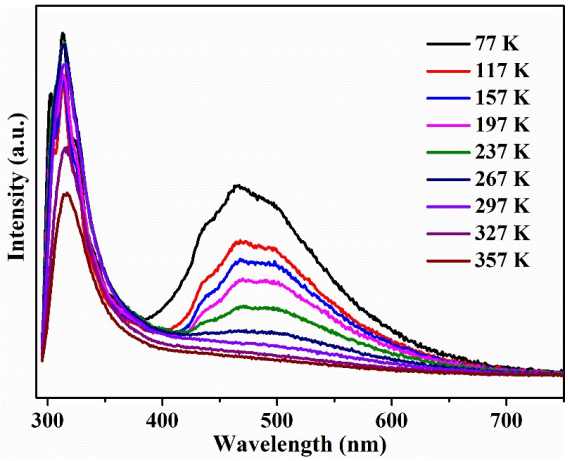

Figure S7. The temperature-dependent emission spectra of **1**.

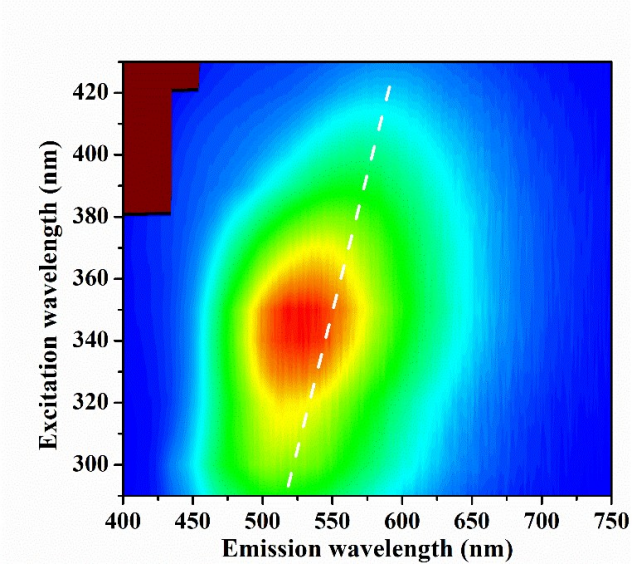

Figure S8. The excitation wavelength-dependent emission spectra.

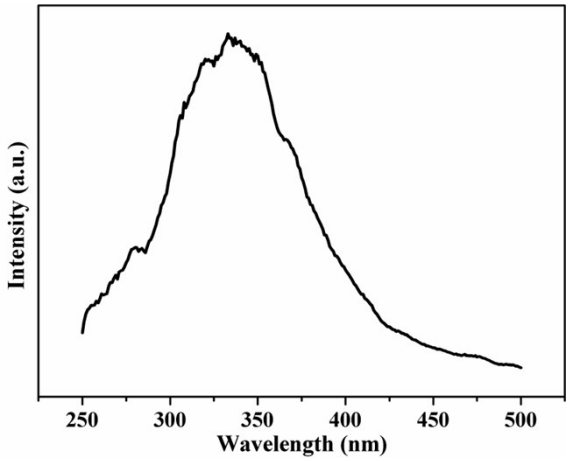

Figure S9. The delayed excitation spectra of **1** at room temperature.

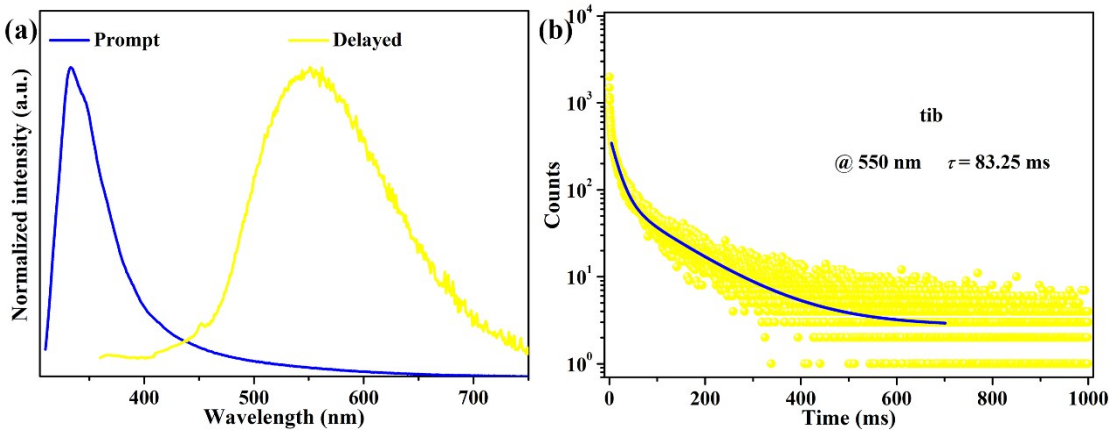

Figure S10. (a) Prompt and delayed PL emission spectra of tib (λ_{ex} = 307 nm, 380 nm). (b) PL decay and fit curves obtained at room temperature.

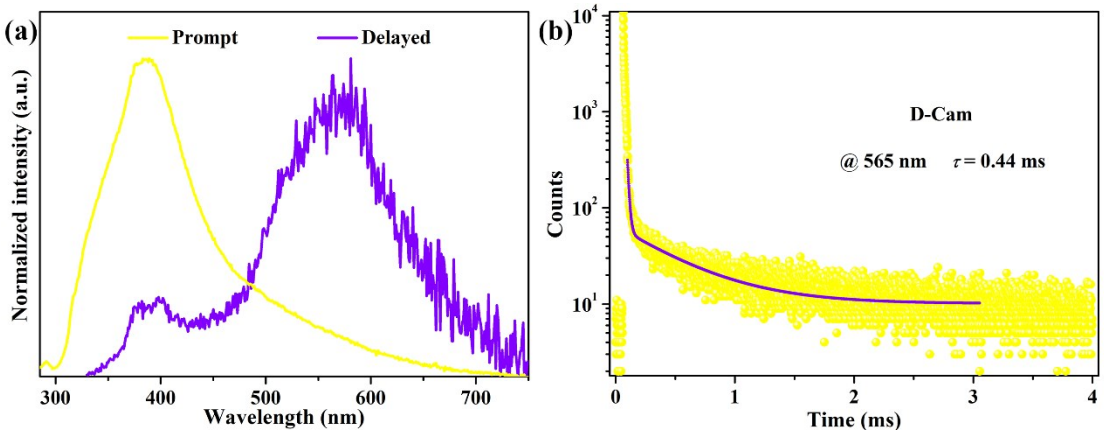

Figure S11. (a) Prompt and delayed PL emission spectra of **D-Cam** (λ_{ex} = 267 nm, 310 nm). (b) PL decay and fitting curves obtained at room temperature.

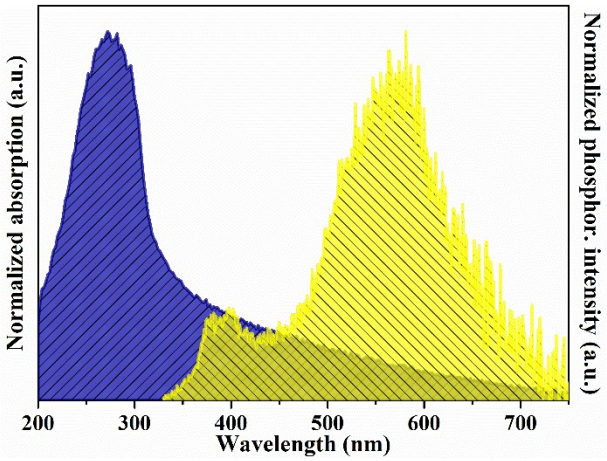

Figure S12. Normalized phosphorescence spectrum of **D-Cam** and absorption spectrum of **tib**.

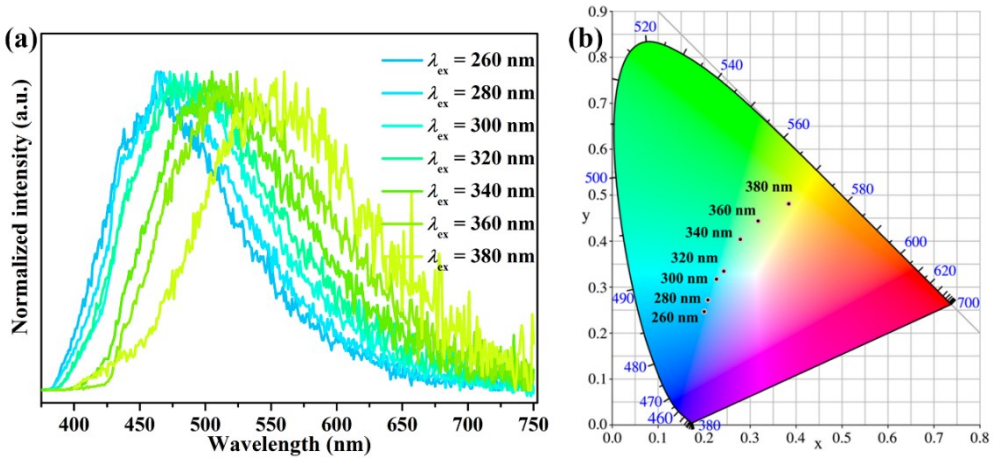

Figure S13. The delayed emission spectra (a) and CIE coordinate (b) of **1** at 77 K.

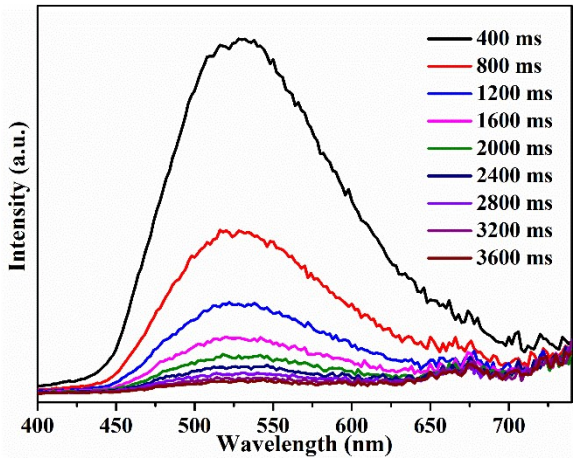

Figure S14. Time-resolved emission spectra (λ_{ex} = 333 nm).

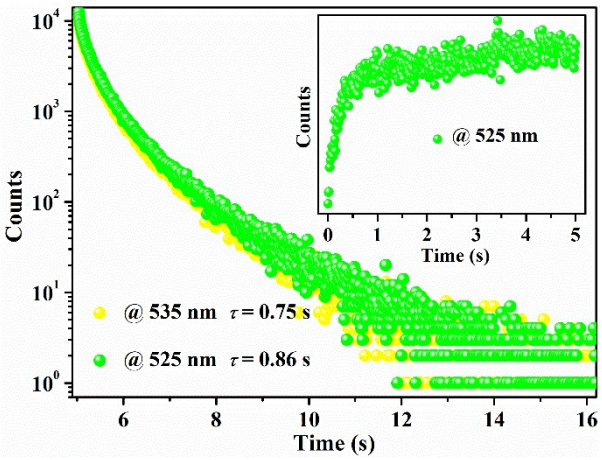

Figure S15. (a) RTP decay at 525 nm and 535 nm of **1** (Insert: photo-activable process).

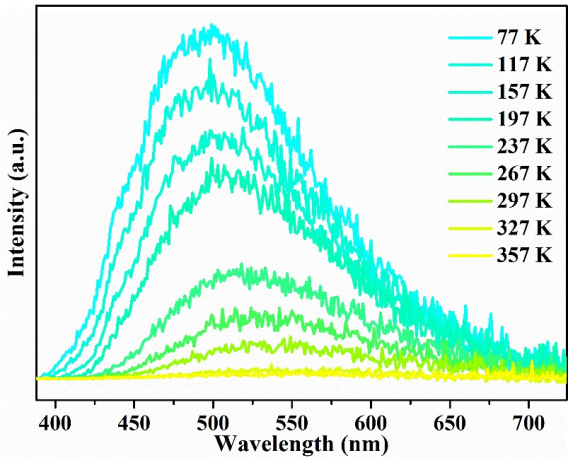

Figure S16. The temperature-dependent emission spectra (λ_{ex} = 333nm).

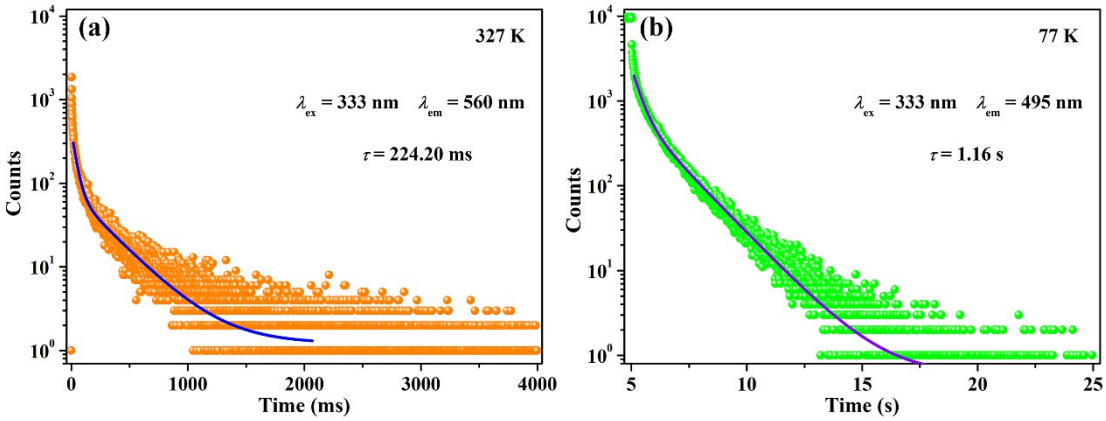

Figure S17. (a) PL decay and fitting curves obtained at 77 K and (b) 327 K.

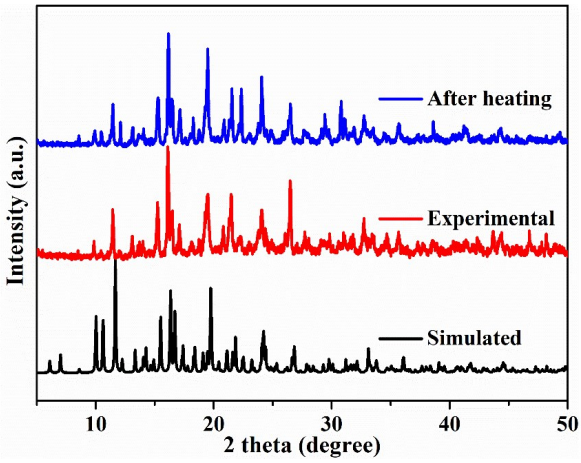

Figure S18. PXRD and simulated profiles of **1**.

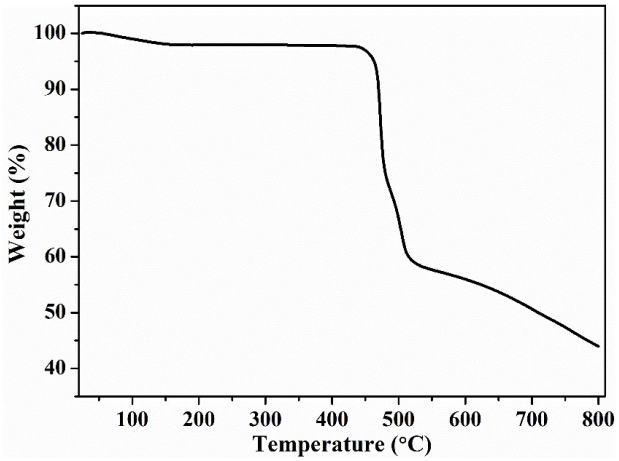

Figure S19. TG profile of **1**.

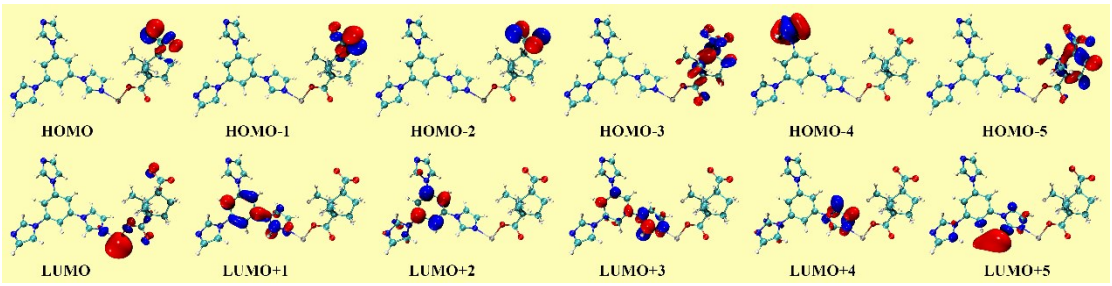

Figure S20. Calculated molecular orbitals.

Table S1. Crystallographic data for **1** at 100K

	1	
Formula	$C_{60}H_{70}N_{12}O_{14}Zn_3$	
*M*r (g·mol^{-1})	1379.39	
Space group	$P2_12_12$	
Crystal system	Orthorhombic	
a (Å)	17.6445(2)	
b (Å)	25.2002(3)	
c (Å)	6.87410(10)	
V (Å^3)	3056.53(7)	
Z	2	
F(000)	1432	
Dc (gcm^{-3})	1.499	
μ (mm^{-1})	2.005	
R_{int}	0.0293	
limiting indices	-21≤h≤21 -30≤k≤21 -8≤l≤8	
Collected reflections	21484	
Unique reflections	5930	
GOF on F^2	1.039	
R_1, wR_2 [$I>2\sigma(I)$]	0.0581	0.1560
R_1, wR_2 [all data]	0.0588	0.1568

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

Table S2. Selected bond lengths (Å) and angles (°) for **1** at 100 K

1			
Zn(1)-O(1)	1.943(5)	Zn(2)-O(5A)	1.965(10)
Zn(1)-O(1)#1	1.943(5)	Zn(2)-O(5)	2.020(12)
Zn(1)-N(3)	2.046(5)	Zn(2)-N(1)	2.021(5)
Zn(1)-N(3)#1	2.046(5)	Zn(2)-N(6)#3	2.024(6)
Zn(2)-O(3)#2	1.940(5)	Zn(2)-O(6A)	2.334(10)
O(1)-Zn(1)-O(1)#1	121.3(3)	O(5A)-Zn(2)-N(1)	109.2(3)
O(1)-Zn(1)-N(3)	90.8(2)	O(5)-Zn(2)-N(1)	104.6(3)
O(1)#1-Zn(1)-N(3)	116.3(2)	O(3)#2-Zn(2)-N(6)#3	99.0(3)
O(1)-Zn(1)-N(3)#1	116.3(2)	O(5)-Zn(2)-N(6)#3	122.8(4)
O(1)#1-Zn(1)-N(3)#1	90.8(2)	N(1)-Zn(2)-N(6)#3	103.6(2)
N(3)-Zn(1)-N(3)#1	124.5(3)	O(3)#2-Zn(2)-O(6A)	87.6(3)
O(3)#2-Zn(2)-O(5A)	114.5(3)	O(5A)-Zn(2)-O(6A)	60.2(4)
O(3)#2-Zn(2)-O(5)	101.9(4)	N(1)-Zn(2)-O(6A)	89.1(3)
O(3)#2-Zn(2)-N(1)	127.0(2)	N(6)#3-Zn(2)-O(6A)	157.4(3)

Symmetry codes: #1: -x+1, -y+2, z; #2: -x+3/2, y-1/2, -z+1; #3: x-1/2, -y+3/2, -z; #4: -x+1, -y+1, z; #5: x+1/2, -y+3/2, -z; #6: -x+3/2, y+1/2, -z+1.

Table S3 Phosphorescence lifetimes (τ) of **1**.

Compound	Temperature	Wavelength (nm)	Excitation light	τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	$<\tau>$ (ms)	χ^2
		525	uF2	150.2	34.72	701.4	65.28	510.0	1.260
	RT	525	Xe	405.2	47.72	1270	52.28	857.3	1.217
1		535	Xe	343.8	50.62	1162	49.38	747.8	1.230
	327 K	550	uF2	40.24	30.28	304.1	69.72	224.2	1.176
	77 K	495	uF2	373.0	32.87	1540	67.13	1156.4	1.147
tib	RT	550	uF2	16.93	34.19	117.7	65.81	83.2	1.237
D-Cam	RT	565	uF2	0.014	14.16	0.502	85.84	0.44	1.141

$<\tau>=\sum A_j\tau_j^2/\sum A_j\tau_j$, j=1, 2, 3...; RT = Room temperature.