Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Electronic Supporting Information

H-shaped oxalate -bridging lanthanoid-incorporated arsenotungstates

Hanhan Chen, Zikang Xiao, Bing Yan, Hechen Wu, Pengtao Ma* Jingping Wang and Jingyang Niu*

Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China

Material and physical measurements

All chemicals were commercially purchased and used without further purification. The precursor $K_{14}[As_2W_{19}O_{67}(H_2O)]$ was prepared according to the reference and confirmed by Fourier transform infrared (FT-IR) spectrum. C, H elemental analyses were performed on an Elementar Vario EL cube CHNS analyzer. FT-IR spectra were recorded from solid samples palletized with KBr on a Bruker VERTEX-70 spectrometer in the range 400-4000 cm^{-1}. The thermogravimetric analyses (TGA) cures were performed under flowing N_2 atmosphere on a NETZSCH STA 449 F5 Jupiter thermal analyser with a heating rate of 10 °C min^{-1} from 30 °C to 800 °C. Powder X-ray diffraction (PXRD) data were performed on an X-ray powder diffractometer (Bruker, D8 Advance) using Cu Kα radiation (λ = 1.5418 Å) collected with the angular range (2θ) from 5° to 45° at room temperature. Raman spectra were performed on a Renishaw in Via with a red Spectra-Physics He-Ne laser (wavelength of 532 nm and 500 mW capacity). The UV/vis diffuse reflectance spectra and UV absorption spectra were performed on a UH4150 UV-vis spectrometer.

X-ray Crystallography

Diffraction intensity data of all compounds were collected on a Bruker D8 VENTURE PHOTON II diffractometer at 150(2) K using Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were carried out using a multi-scan absorption correction. All these structures were solved by direct methods and refined by fullmatrix least squares on F^2 using the SHELXL-2018/3 program package. Direct methods (SHELXS97) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms. In the final refinement, the W, As, lanthanoid, K, Na, C and most O atoms were refined anisotropically; the few water O atoms were refined isotropically. All H atoms on water molecules were directly included in the molecular formula but not included in the structural model. The lattice water molecules were determined by TGA results. Crystallographic data and structural refinement for **1**–**3** compounds are listed in Table S1.

Table S1. Crystallographic data and structure refinement parameters for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_2H_{129}As_4K_{17}Na_2O_{204}Sm_2W_{38}$	$C_2H_{121}As_4K_{17}Na_2O_{200}Pr_2W_{38}$	$C_2H_{107}As_4Ce_2K_{17}Na_2O_{193}W_{38}$
Formula weight	11714.90	11623.94	11496.24
Temperature/K	150	150	150
Crystal system	Triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	12.2892(5)	12.3275(2)	12.3104(3)
b [Å]	18.5454(9)	18.5853(3)	18.5826(4)
c [Å]	22.9794(11)	22.9955(4)	22.8935(4)
α [o]	67.218(2)	67.2070(10)	67.1430(10)
β [o]	81.116(2)	81.0460(10)	81.2010(10)
γ [o]	79.915(2)	79.9610(10)	79.8400(10)
V [Å^3]	4732.3(4)	4760.15(14)	4729.56(18)
Z	1	1	1
ρ_{calcd} [g cm^{-3}]	4.065	4.013	3.999
μ [mm^{-1}]	24.792	24.539	24.659
F (000)	5057.0	5019.0	4961.0
Index ranges	$-13 \le h \le 14$ $-22 \le k \le 22$ $-27 \le l \le 27$	$-14 \le h \le 14$ $-22 \le k \le 22$ $-24 \le l \le 27$	$-14 \le h \le 14$ $-22 \le k \le 22$ $-27 \le l \le 25$
Reflections collected	53152	60416	68907
Independent reflections	16793	16910	16820
data/restraints/parameters	16793/78/1096	16910/12/1099	16820/6/1062
Goodness-of-fit on F^2	1.051	1.041	1.017
R_1, wR_2 [$I > 2\sigma(I)$]	0.0533, 0.1246	0.0345, 0.0780	0.0332, 0.0807
R_1, wR_2 [all data]	0.0645, 0.1309	0.0434, 0.0824	0.0399, 0.0848
Largest diff. Peak/hole/e Å^{-3}	3.55/-2.91	3.76/-2.44	2.85/-1.95

Table S2. BVS values for Sm, As, and W atoms in **1.**

Atoms	BVS value	Atoms	BVS value
Sm1	2.829	W9	6.115
As1	2.860	W10	6.132
As2	2.923	W11	6.136
W1	6.143	W12	6.301
W2	5.988	W13	6.125
W3	6.187	W14	6.011
W4	6.007	W15	6.031
W5	6.073	W16	6.015
W6	5.899	W17	6.180
W7	5.958	W18	6.006
W8	6.092	W19	6.166

Table S3. Selected bond lengths (Å) of **1**.

Bond	Length
Sm1-O53	2.401(13)
Sm1-O51	2.424(14)
Sm1-O63	2.439(12)
Sm1-O2W	2.450(13)
Sm1-O68	2.460(13)
Sm1-O69	2.452(13)
Sm1-O42	2.473(11)
Sm1-O3W	2.490(14)
As1-O21	1.809(12)
As1-O26	1.804(12)
As1-O44	1.807(12)
As2-O20	1.800(12)
As2-O23	1.791(11)
As2-O36	1.805(12)

Table S4. Possible geometries of eight coordinated metal centers.

geometry	point group	polyhedron
OP-8	D_{8h}	Octagon
HPY-8	C_{7v}	Heptagonal pyramid
HBPY-8	D_{6h}	Hexagonal bipyramid
CU-8	O_h	Cube
SAPR-8	D_{4d}	Square antiprism
TDD-8	D_{2d}	Triangular dodecahedron
JGBF-8	D_{2d}	Johnson gyrobifastigium (J26)
JETBPY-8	D_{3h}	Johnson elongated triangular bipyramid (J14)
JBTPR-8	C_{2v}	Biaugmented trigonal prism (J50)

BTPR-8	C_{2v}	Biaugmented trigonal prism
JSD-8	D_{2d}	Snub diphenoid(J84)
TT-8	T_d	Triakis tetrahedron
ETBPY-8	D_{3h}	Elongated trigonal bipyramid

Table S5. Deviation parameters calculated by SHAPE from each ideal polyhedron for compounds Sm1.

	Sm1
OP-8	32.167
HPY-8	20.621
HBPY-8	14.708
CU-8	13.043
SAPR-8	4.589
TDD-8	3.531
JGBF-8	13.206
JETBPY-8	27.960
JBTPR-8	3.425
BTPR-8	2.522
JSD-8	5.748
TT-8	13.847
ETBPY-8	21.848

Table S6. Selected bond angles (°) of **1**.

Bond	Angle	Bond	Angle
O53-Sm1-O51	127.4(4)	O63-Sm1-O68	112.4(4)
O53-Sm1-O63	71.2(4)	O63-Sm1-O69	70.9(4)
O53-Sm1-O2W	66.7(4)	O63-Sm1-O42	84.4(4)
O53-Sm1-O68	134.3(4)	O63-Sm1-O3W	135.9(5)
O53-Sm1-O69	74.3(4)	O2W-Sm1-O68	136.3(4)
O53-Sm1-O42	150.7(4)	O2W-Sm1-O69	137.1(5)
O53-Sm1-O3W	73.8(4)	O2W-Sm1-O42	109.5(4)
O51-Sm1-O63	150.7(4)	O2W-Sm1-O3W	77.9(4)
O51-Sm1-O2W	67.0(4)	O68-Sm1-O69	65.4(4)
O51-Sm1-O68	72.5(4)	O68-Sm1-O42	69.7(4)
O51-Sm1-O69	131.9(4)	O68-Sm1-O3W	75.3(54)
O51-Sm1-O42	70.0(4)	O69-Sm1-O42	113.3(4)
O51-Sm1-O3W	73.3(4)	O69-Sm1-O3W	74.5(5)
O63-Sm1-O2W	110.9(4)	O42-Sm1-O3W	135.1(4)

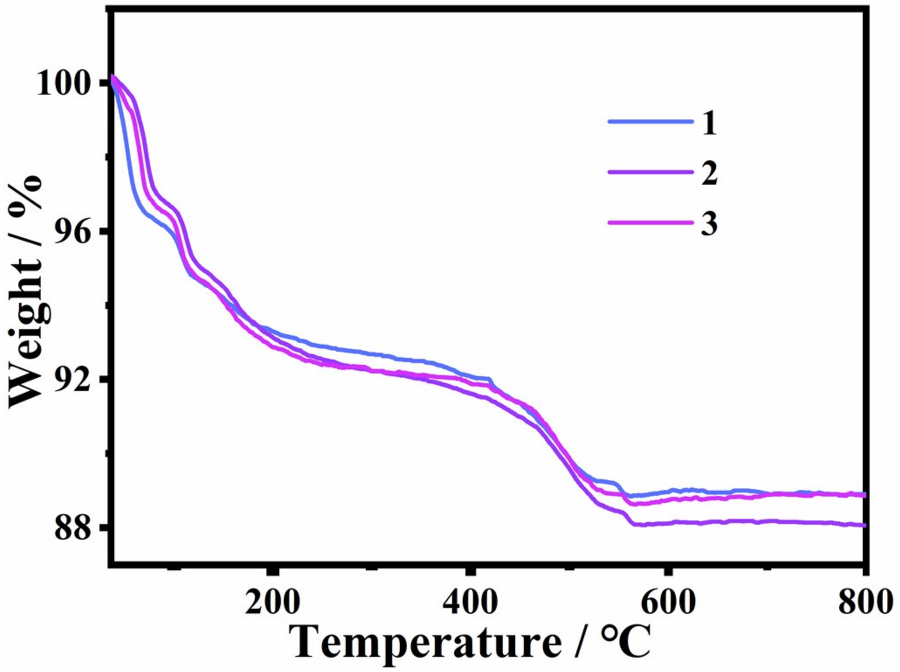

Fig. S1. TGA curves of **1**–**3**.

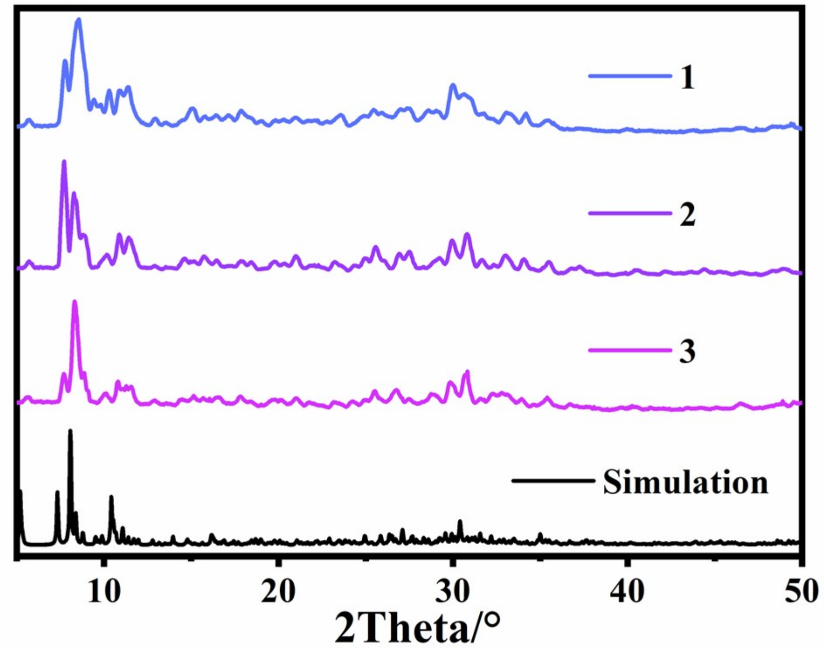

Fig. S2. The experimental and simulated PXRD patterns of **1–3**.

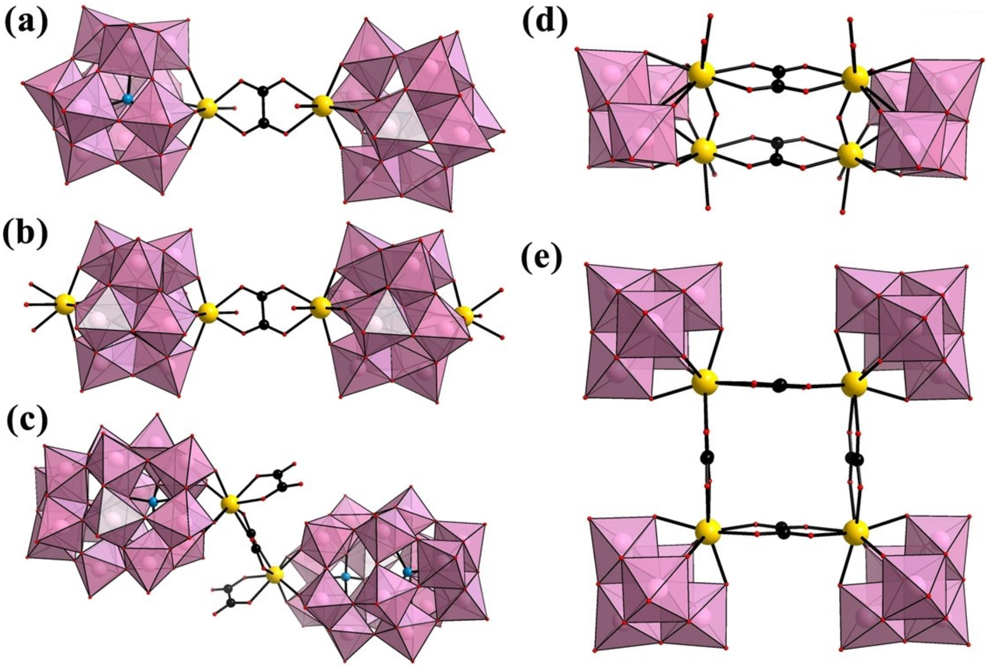

Fig. S3. Some typical oxalate-bridging lanthanoid-incorporated arsenotungstate structures reported in recent years.[16] Color code: {WO_6} rose; W, rose; O, red; Ln, yellow; As, P, turquoise; C, black.

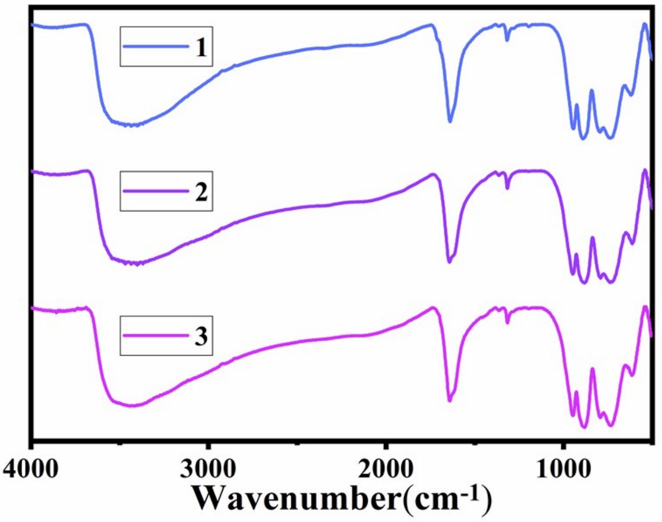

Fig. S4. IR spectra of **1**–**3**.

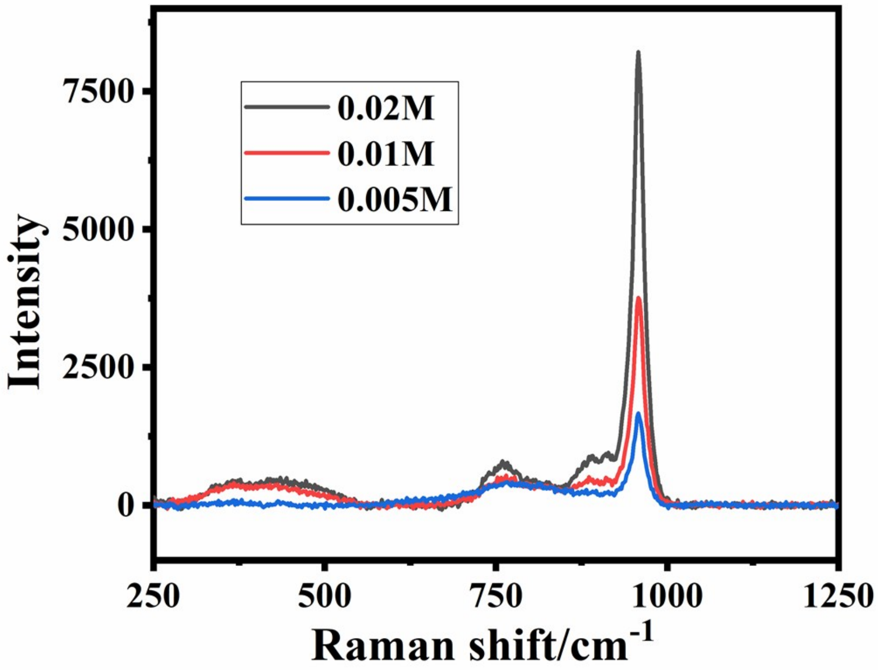

Fig. S5. 2 dissolved in deionized water at different concentrations i.e., 0.02 M, 0.01 M, and 0.005M.

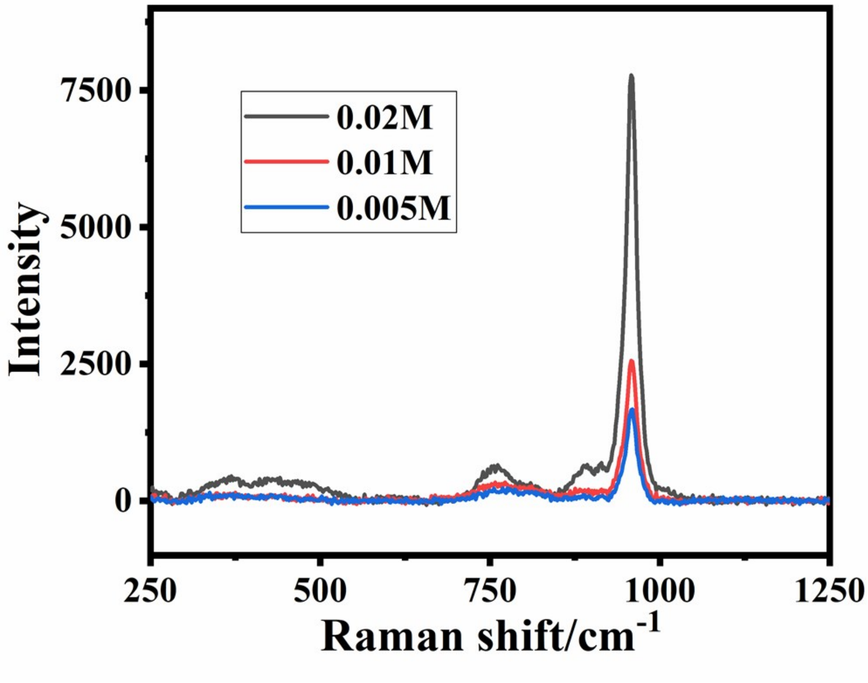

Fig. S6. 3 dissolved in deionized water at different concentrations i.e., 0.02M, 0.01M, and 0.005M.

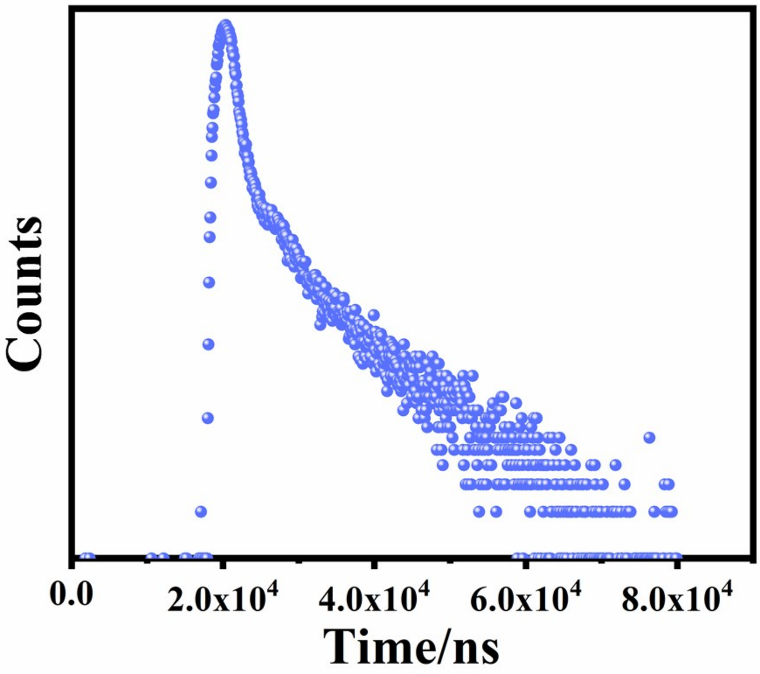

Fig. S7. The lifetime-decay curve of **1** obtained by monitoring the emission at λ= 599 nm upon the excitation at 432 nm.

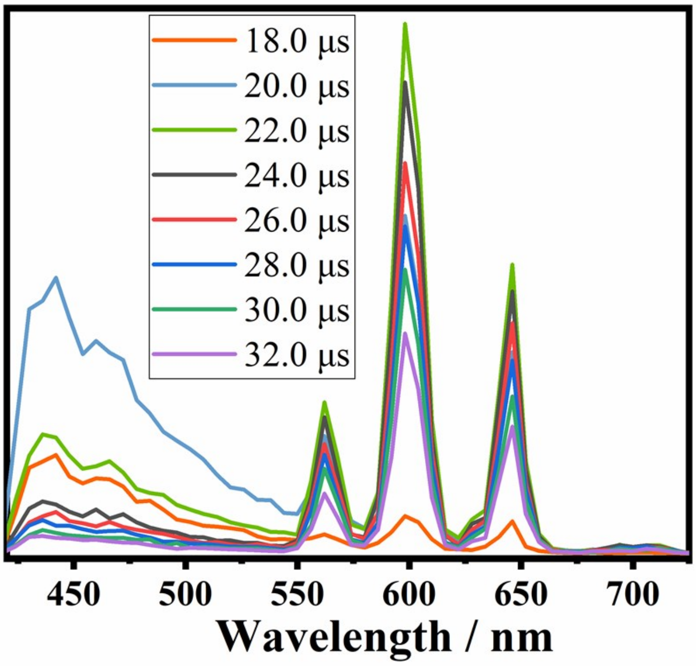

Fig. S8. Reconstructed plots of **1** at room temperature under excitation at 402 nm resolved by microsecond fluorescence: partial spectral temporal evolution.

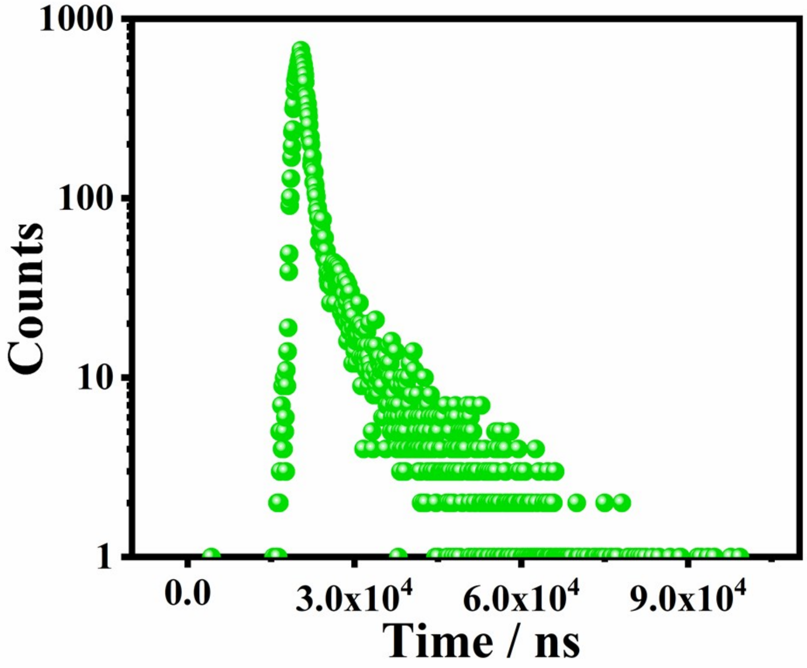

Fig. S9. The lifetime-decay curve of **2** obtained by monitoring the emission at λ= 528 nm upon the excitation at 446 nm.

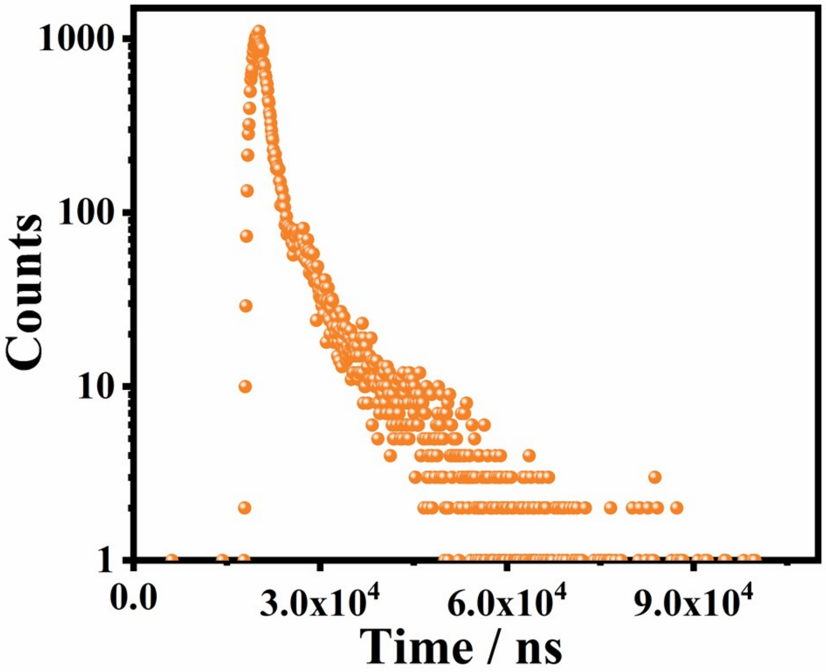

Fig. S10. The lifetime-decay curve of **3** obtained by monitoring the emission at λ= 508 nm upon the excitation at 365 nm.