Supporting Information

A Stably Discrete 31-Nuclearity Silver(I) Thiolate Nanocluster Luminescent Thermometer Support by DMF Auxiliary Ligand

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1. Synthetic procedures

General comments: In this paper, all reagents and solvents for synthesis were obtained from commercial sources and used without further purification, such as methanol (Aladdin, >95%), N,N-Dimethylformamide (Aladdin, >95%), dichloromethane (Aladdin, >95%). All other reagents were of analytical grade and used as received. AgS^tBu was synthesized by using Et_3N as organic solvent and reated with equivalent amounts of $AgNO_3$ with HS^tBu according to the literature.[1]

$[Ag_{31}S_3(SBu^t)_{17}(CF_3COO)_7(CO_3)_{0.5}(CF_3COOH)_{0.5}(DMF)_4]\cdot 3DMF\cdot CH_3OH$ (1)

Compound **1** was obtianed by one-pot synthesis, namely, AgS^tBu (0.0653 g, 0.3314 mmol) with CF_3COOAg (0.0293 g, 0.1327 mmol) were dissolved in methanol - N,N-dimethylformamide (DMF) - dichloromethane (V : V : V=1 : 1 : 1) (15 mL) under stir at room temperature to gain a yellow suspension. Then the yellow suspension was uninterruptedly stirred at room temperature for 24h and then was filtered. The filtrate was evaporated slowly in air at room temperature. Compound **1** deposited as yellow block crystals. Yield: *ca.* 63% (based on Ag).

2. Crystallographic studies

Single-crystal X-ray diffraction data for **1** were recorded on a Bruker D8 QUEST with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 150(2) K. Absorption corrections were applied using multi-scan technique and performed by using the SADABS program. The crystal structure was solved by means of direct methods and refined by employing full-matrix least squares on F^2 (*SHELXTL*-2014).[2] Additional CH_3OH solvent molecule was estimated from *PLATON*[3] squeeze and thermal gravimetric (TG) analysis and included in the molecular formula directly. CCDC-1951395 (**1**) 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 for **1**.

Table S1. Crystal data, data collection and structure refinement details for compound **1**

Compound	**1**
Formula*	$C_{104.5}H_{202.5}Ag_{31}F_{22.5}O_{23.5}S_{20}N_7$
Formula weight	6345.895
Crystal system	Monoclinic
Space group	P 2_1/c
a (Å)	32.5856(10)
b (Å)	19.2715(6)
c (Å)	29.1203(9)
α (°)	90
β (°)	97.5290(10)

γ (°)	90
V (Å^3)	18129.1(10)
Z	2
D_c/g cm^{-3}	2.325
μ/mm^{-1}	3.565
F(000)	12184
Reflection collected	179927
Unique reflections	43512
Parameters	2168
R_{int}	0.0474
GOF	1.027
$R_1{}^a$ [I>2σ(I)]	0.0539
$wR_2{}^b$(all data)	0.1191

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

*The formula and D_c is not included the unidentified disordered solvents

Table S2. Selected bond lengths (Å) for compound **1**

Ag(1)-S(1)	2.4123(18)		Ag(11)-S(10)	2.608(2)
Ag(1)-S(3)	2.4415(17)		Ag(11)-S(14)	2.664(2)
Ag(2)-S(1)	2.4678(17)		Ag(11)-S(2)	2.6655(19)
Ag(2)-S(2)	2.4719(18)		Ag(12)-S(11)	2.407(2)
Ag(3)-S(3)	2.4374(17)		Ag(12)-S(10)	2.434(4)
Ag(3)-S(2)	2.4402(18)		Ag(13)-O(2)	2.372(7)
Ag(4)-S(9)	2.4713(19)		Ag(13)-S(11)	2.479(2)
Ag(4)-S(4)	2.517(2)		Ag(13)-S(12)	2.675(2)
Ag(4)-S(1)	2.7066(18)		Ag(13)-S(1)	2.7715(18)
Ag(5)-S(5)	2.399(2)		Ag(14)-S(13)	2.4029(19)
Ag(5)-S(4)	2.430(2)		Ag(14)-S(12)	2.4146(19)
Ag(6)-S(5)	2.399(2)		Ag(14)-S(1)	2.8072(18)
Ag(6)-S(6)	2.427(2)		Ag(15)-S(13)	2.393(2)
Ag(7)-S(7)	2.487(2)		Ag(15)-S(14)	2.396(2)
Ag(7)-O(15)	2.53(2)		Ag(16)-S(15)	2.409(2)
Ag(7)-S(6)	2.548(2)		Ag(16)-S(14)	2.416(2)
Ag(7)-S(2)	2.7043(19)		Ag(17)-S(15)	2.407(2)
Ag(8)-S(7)	2.452(2)		Ag(17)-S(16)	2.411(2)
Ag(8)-S(8)	2.550(2)		Ag(17)-S(2)	2.9429(18)
Ag(8)-S(3)	2.6368(18)		Ag(18)-O(4)	2.351(7)
Ag(9)-S(9)	2.4650(18)		Ag(18)-S(17)	2.449(2)
Ag(9)-S(8)	2.604(2)		Ag(18)-S(2)	2.5458(18)
Ag(9)-S(3)	2.6168(17)		Ag(19)-S(17)	2.520(6)
Ag(10)-O(1)	2.329(6)		Ag(19)-S(10)	2.649(3)
Ag(10)-S(10)	2.5593(19)		Ag(19)-S(18)	2.723(8)
Ag(10)-S(1)	2.5772(18)		Ag(19)-S(3)	2.840(3)
Ag(11)-O(3)	2.348(7)		Ag(20)-O(5)	2.318(8)

	Ag(20)-S(20)	2.373(2)		Ag(27)-O(10)	2.296(8)
	Ag(20)-S(8)	2.467(2)		Ag(27)-O(19)	2.495(8)
	Ag(21)-O(6)	2.371(7)		Ag(27)-S(13)	2.511(2)
	Ag(21)-S(19)	2.391(2)		Ag(27)-S(4)	2.588(2)
5	Ag(21)-S(8)	2.479(2)	25	Ag(28)-O(20)	2.371(10)
	Ag(22)-S(19)	2.3753(19)		Ag(28)-O(11)	2.377(8)
	Ag(22)-S(18)	2.4096(19)		Ag(28)-S(15)	2.478(2)
	Ag(23)-S(20)	2.355(2)		Ag(28)-S(6)	2.579(2)
	Ag(23)-S(18)	2.3859(19)		Ag(29)-O(12)	2.306(8)
10	Ag(24)-O(8)	2.309(5)	30	Ag(29)-O(21)	2.390(9)
	Ag(24)-S(11)	2.515(2)		Ag(29)-S(16)	2.428(2)
	Ag(24)-S(19)	2.5692(19)		Ag(29)-S(6)	2.512(2)
	Ag(24)-S(9)	2.6175(18)		Ag(30)-O(13)	2.332(7)
	Ag(25)-O(7)	2.318(5)		Ag(30)-S(16)	2.447(3)
15	Ag(25)-S(12)	2.4765(19)	35	Ag(30)-S(7)	2.703(6)
	Ag(25)-S(9)	2.5507(19)		Ag(30)-S(17)	2.806(6)
	Ag(26)-O(9)	2.325(9)		Ag(31)-O(14)	2.335(6)
	Ag(26)-O(18)	2.429(9)		Ag(31)-S(20)	2.480(2)
	Ag(26)-S(12)	2.522(2)		Ag(31)-S(17)	2.620(2)
20	Ag(26)-S(4)	2.523(2)	40	Ag(31)-S(7)	2.675(2)

Table S3. All the Ag···Ag interactions (Å) for compound **1**

	Ag(1)-Ag(9)	2.8697(8)		Ag(10)-Ag(12)	3.046(6)
45	Ag(1)-Ag(3)	2.8993(7)	70	Ag(10)-Ag(11)	3.1009(8)
	Ag(1)-Ag(12)	2.9063(17)		Ag(10)-Ag(15)	3.3133(9)
	Ag(1)-Ag(2)	2.9079(7)		Ag(11)-Ag(18)	2.9434(10)
	Ag(1)-Ag(10)	3.0957(8)		Ag(11)-Ag(16)	3.0802(10)
	Ag(1)-Ag(4)	3.1343(8)		Ag(12)-Ag(19)	3.084(5)
50	Ag(1)-Ag(13)	3.1926(9)	75	Ag(12)-Ag(13)	3.321(4)
	Ag(2)-Ag(3)	2.8762(8)		Ag(13)-Ag(25)	3.1454(9)
	Ag(2)-Ag(10)	3.0213(8)		Ag(13)-Ag(14)	3.3427(9)
	Ag(2)-Ag(6)	3.1426(8)		Ag(14)-Ag(26)	2.9474(8)
	Ag(2)-Ag(11)	3.1672(9)		Ag(14)-Ag(27)	3.0372(8)
55	Ag(2)-Ag(5)	3.1871(9)	80	Ag(14)-Ag(15)	3.3012(9)
	Ag(3)-Ag(8)	2.9324(8)		Ag(17)-Ag(29)	3.0458(11)
	Ag(3)-Ag(18)	2.9765(8)		Ag(17)-Ag(18)	3.1827(9)
	Ag(3)-Ag(19)	3.030(6)		Ag(17)-Ag(28)	3.1967(10)
	Ag(3)-Ag(7)	3.0762(8)		Ag(18)-Ag(30)	2.891(7)
60	Ag(4)-Ag(25)	3.0327(8)	85	Ag(19)-Ag(23)	2.966(5)
	Ag(4)-Ag(26)	3.2105(9)		Ag(20)-Ag(21)	2.8875(9)
	Ag(5)-Ag(27)	3.0750(9)		Ag(22)-Ag(23)	3.0118(8)
	Ag(6)-Ag(28)	3.0363(9)		Ag(24)-Ag(25)	2.9939(8)
	Ag(7)-Ag(29)	3.1036(10)		Ag(25)-Ag(26)	3.3356(9)
65	Ag(8)-Ag(20)	3.1177(9)	90	Ag(26)-Ag(27)	3.0167(9)
	Ag(8)-Ag(9)	3.3173(9)		Ag(28)-Ag(29)	3.0688(11)
	Ag(9)-Ag(21)	3.0387(9)		Ag(30)-Ag(31)	2.855(3)
	Ag(10)-Ag(13)	3.0273(9)			

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Table S4. Synthesis methods contrasted

	AgS^tBu	CF_3COOAg	$AgNO_3$	CS_2	Solvent	Yield
$[Ag_{31}S_3(SBu^t)_{17}(CF_3COO)_7(CO_3)_{0.5}(CF_3COOH)_{0.5}(DMF)_4]\cdot 3DMF\cdot CH_3OH$ (Compound **1**, $Ag_{31}S_{20}$-DMF for short)	0.0653 g 0.3314 mmol	0.0293 g 0.1327 mmol	–	–	CH_3OH-DMF-CH_2Cl_2 (V : V : V=1 : 1 : 1) 15 mL	35%
$[Ag_{31}S_3(S^tBu)_{16}(NO_3)_9]_n$ (ref. 15a, $Ag_{31}S_{19}$-NO_3 for short)	0.0197 g 0.1 mmol	–	0.0204 g 0.12 mmol	0.5 mL	CH_3OH-CH_3CN (V : V=1 : 1) 6 mL	40%
$Ag_{31}S_3(S^tBu)_{17}(CF_3COO)_8(CH_3CN)_4$ (ref. 15b, $Ag_{31}S_{20}$-CH_3CN for short)	0.1449 g 0.7355 mmol	0.0810 g 0.367 mmol	–	–	CH_3OH-CH_3CN (V : V=1 : 1) 6 mL	63%

Notes: "–" indicates it has not been involved.

Table S5. The type of auxiliary ligands and their optical properties

	Auxiliary ligand (number)	Emission wavelength	Absorption wavelength	Band gap
$[Ag_{31}S_3(SBu^t)_{17}(CF_3COO)_7(CO_3)_{0.5}(CF_3COOH)_{0.5}(DMF)_4]\cdot 3DMF\cdot CH_3OH$ (Compound **1**, $Ag_{31}S_{20}$-DMF for short)	CF_3COO^- (7) DMF (4) CO_3^{2-}/CF_3COOH (0.5:0.5)	648 nm (77K) 631 nm (298K)	357 nm	2.40 eV
$[Ag_{31}S_3(S^tBu)_{16}(NO_3)_9]_n$ (ref. 15a, $Ag_{31}S_{19}$-NO_3 for short)	NO_3^- (9)	~675 nm (77K) ~590 nm (298K)	~380 nm	–
$Ag_{31}S_3(S^tBu)_{17}(CF_3COO)_8(CH_3CN)_4$ (ref. 15b, $Ag_{31}S_{20}$-CH_3CN for short)	CF_3COO^- (8) CH_3CN (4)	–		2.50 eV

Notes: "–" indicates it has not been involved.

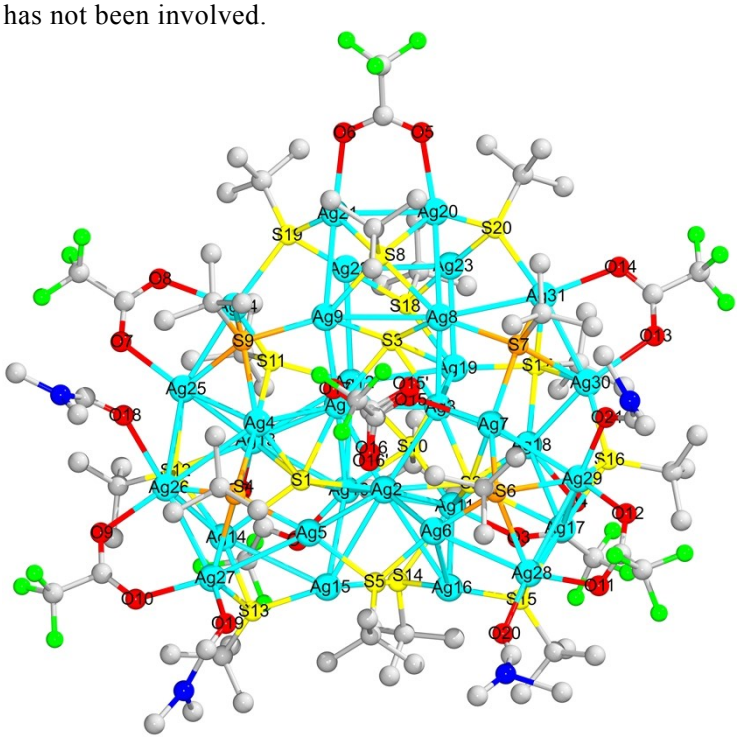

Figure S1. Atomic label of the $[Ag_{31}S_3(S^tBu)_{17}(CF_3COO)_7(CO_3)_{0.5}(CF_3COOH)_{0.5}(DMF)_4]$ cluster. Color code: Ag, turquoise; S, yellow, orange; C, gray-50%; N, blue; O, red; F, bright green.

3. Physical Measurements

The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. PXRD patterns were recorded on a Siemens D 5005 diffractometer with Cu-Kα (λ= 1.5418 Å) radiation in the range of 3-50 ºC. TGA was performed on a Q600 analyzer heated from room temperature to 900 ºC under nitrogen gas with a heating rate of 10 ºC/min. Mass spectra were carried out on a Bruker Daltonics flex Analysis instrument. NMR data were recorded on an AVANCE III HD 400MHz Digital NMR Spectrometer. The UV-Vis absorption spectroscopy and diffuse reflectivity were measured on an UV-3600 UV-VIS-NIR spectrophotometer.

The IR band at 3445 cm^{-1} is due to the O–H vibration; the band at 2954 cm^{-1} is due to the C–H vibration; the band at 1678 cm^{-1} is ascribed to the C=O vibration; the band at 1454 cm^{-1} is attributed to the C–N vibration; the band at 1364 cm^{-1} is attributed to the C–F vibration; the bands at 1221 and 1158 cm^{-1} confirmed the presence of the C–S group, and the band at 838 cm^{-1} is attributed to the N–H vibration.

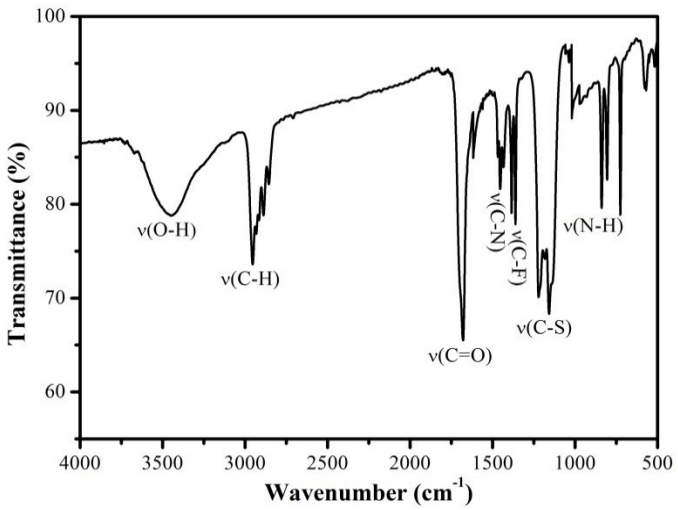

Figure S2. The IR spectrum of **1**

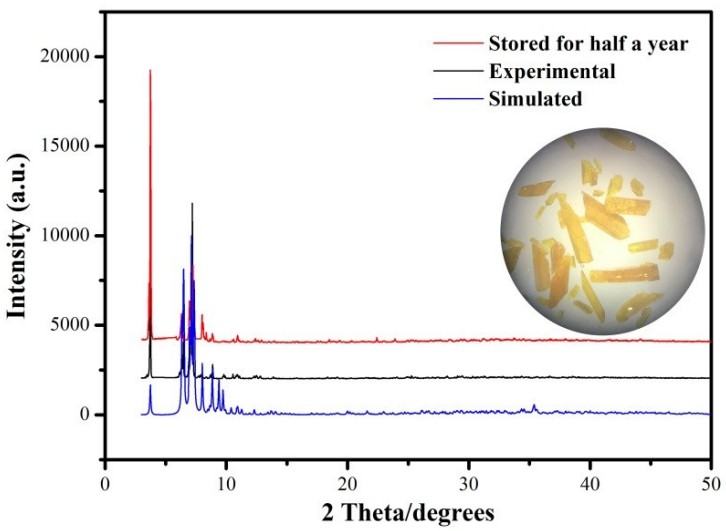

Figure S3. X-ray powder diffraction patterns of **1,** insert: the crystal photo of **1** stored for half a year.

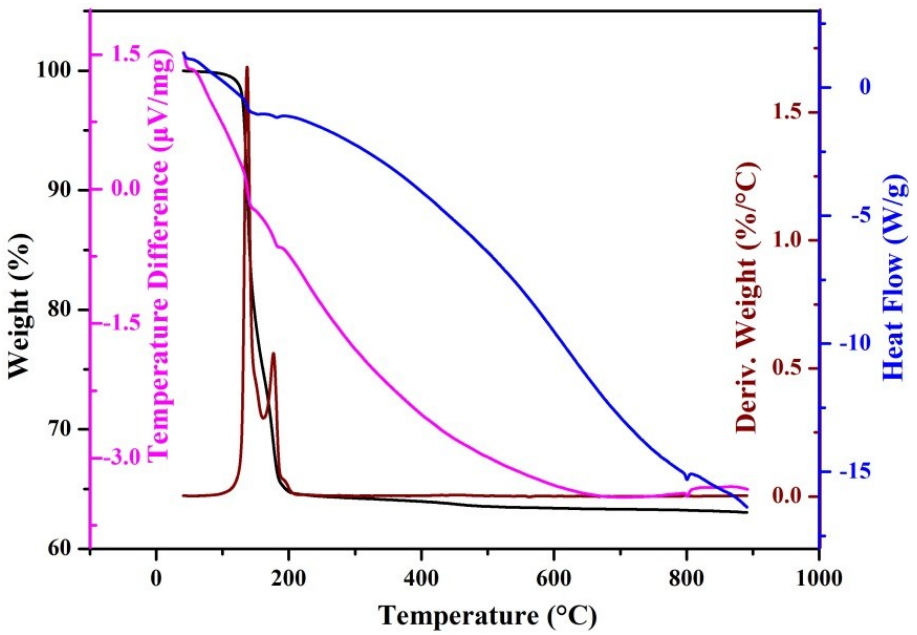

Figure S4. TGA/DSC curve of **1** (in N_2)

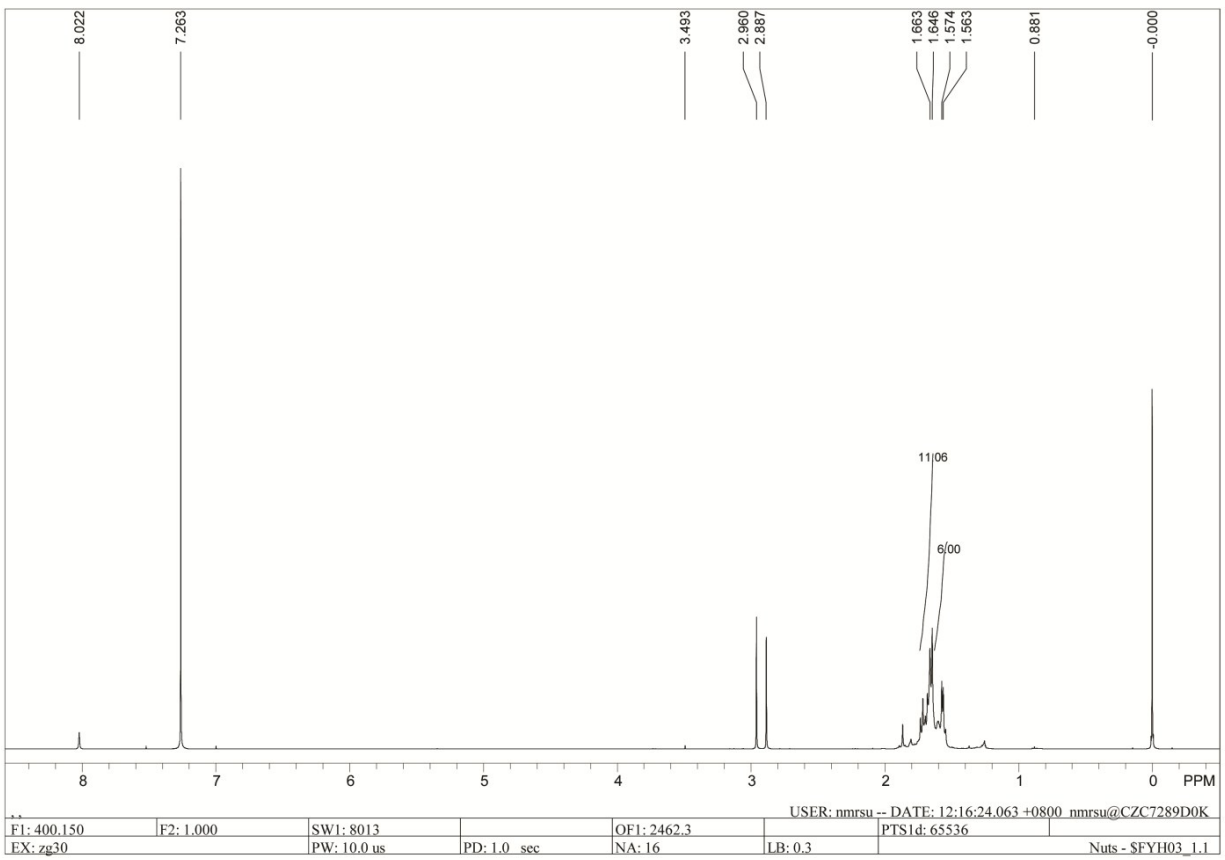

Figure S5. ^{1}H NMR spectrum of **1** (400MHz, $CDCl_3$, RT)

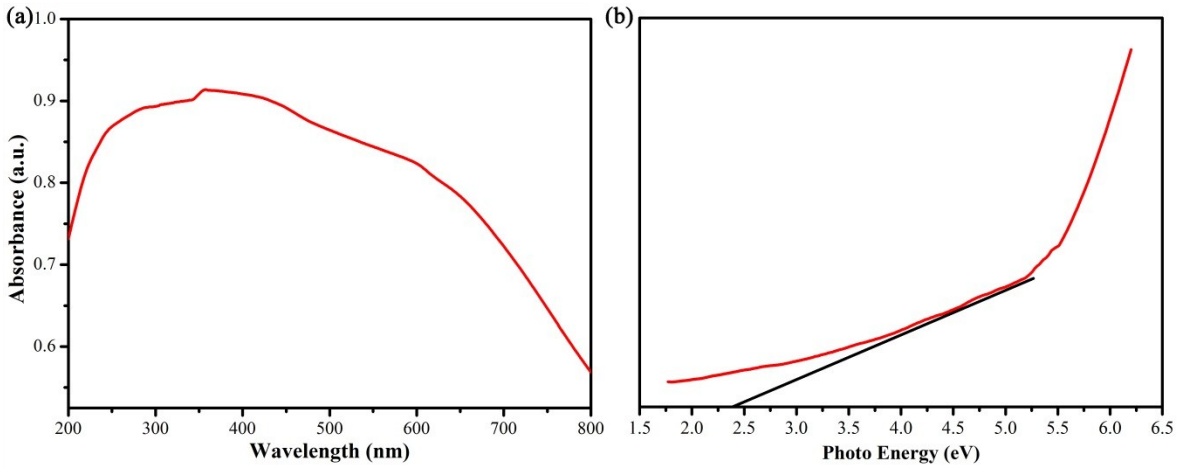

Figure S6. (a) Electronic absorption spectrum of compound **1**; (b) Diffuse reflectance spectrum of compound **1** (Band gap: 2.40 eV).

Figure S7. The photograph of the luminescence of **1** taken at 77 K (soaked in liquid nitrogen) excited with a hand-held UV lamp (365 nm).

Reference:

1 G. Li, Z. Lei, Q.-M. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 17678–17679.

2 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.

3 A. L. Spek, *Acta. Crystallogr. C*, 2015, **71**, 9–18.