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Supporting Information

An Ultrastable Metal-Organic Material Emits Efficient and Broadband Bluish White-Light Emission for Luminescent Thermometer

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Experimental Section

Materials. Starting materials and solvents were used without further purification from commercial supplier unless otherwise indicated. Antimonous chloride (SbCl3, 99.0%, Adamas), 1,2-Ethylenediphosphonic acid (EDP, >98.0%, Adamas-beta), hydrochloric acid (38.0% in H2O, SCR), ethanol (>99.9%, Aladdin), High vacuum grease (HVG, Dow corning).

Solvothermal synthesis of TJU-12. 0.28 g SbCl3 (1.0 mmol), 0.38 g 1,2-Ethylenediphosphonic acid (2.0 mmol) and hydrochloric acid (1.54 mL) were completely dispersed in 10 mL EtOH by magnetic stirring for 15min. Then, the mixture was transferred to a 15 mL Teflon-lined autoclave reactor, which was statically heated at 175 ℃ for 72 h. After the autoclave was cooled to room temperature, colorless plate-like crystals of TJU-12 were isolated by vacuum filtration. The solids were washed with ethanol and dried under air (yield: 296 mg, ~96% based on Sb). The μm-sized microscopic powders of TJU-12 were prepared via manual grinding the bulk crystals.

Powder X-ray Diffraction (PXRD). ~20 mg TJU-12 crystals were dried under vacuum prior to PXRD analysis. The data collected by using a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ = 1.5418 Å) with a scan speed of 0.1 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5~40 °under room temperature.

Single Crystal X-ray Crystallography. A single crystal of 0.18 ×0.16 ×0.01 cm was mounted to a glass fiber and placed on the detector, then the diffraction data were collected at 297(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube operated at 50 kV and 30 mA on a Bruker SMART APEX II CCD area detector X-ray diffractometer. The initial structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters.

Programs used were APEX-II v2.1.4, SHELXTL v6.14, and Diamond v3.2. Further details of crystallographic data and structural refinement are summarized in Table S2.

Fourier-transform Infrared (FT-IR) Spectroscopy. FT-IR spectra were recorded using a BRUKER ALPHA spectrophotometer in 4000~400 cm-1 region.

Thermal and Chemical Stability Test. ~50 mg of as-synthesized crystals were immersed in water, CH_2Cl_2 solvents, diluted HCl solution (pH=1), diluted NaOH solution (pH=12) or calcined at 260 ^oC in air for 24 h. Then, the remains were isolated by vacuum filtration and washed with ethanol, air-dried before performing PXRD and mass balance measurements.

Thermogravimetry Analysis (TGA). TGA data of TJU-12 were collected using a thermal gravimetric analyzer (TA, Q500). The samples were heated from 20 ℃ to 700 ℃ with a heating rate of 10 ℃/min in N2 atmosphere (60 mL/min).

Optical Imaging. Optical microscope images were captured by using a Nikon ECLPSE LV100NPOL. Photo-images were captured using an OPPO R9S Smartphone under the irradiation from a 4W 250 nm UV lamp (67mW/cm^2).

UV-Vis Absorption Spectra. The absorption spectra were recorded in the region of 200-1000 nm at room temperature on a UV-VIS spectrometer (UV-2600, Shimadzu).

Steady State Photoluminescence Spectra. The steady state photoluminescence spectra of cm-sized TJU-12 single crystals and μm-sized TJU-12 microcrystals was obtained by a FLS980 spectrophotometer (Edinburgh Instruments).

Photoluminescence quantum yield (PLQY). Absolute PLQY measurements of both bulk and microscopic crystals were performed on FLS 920 spectrophotometer with an integrating sphere (BaSO4 coating) using single photon counting mode. The focal length of the monochromator was 300 mm. Samples were excited using a 450W Xenon lamp with 3 mm excitation slits width and detected by a Hamamatsu R928p photomultiplier tube. The emission was obtained using 0.2 nm scan step, 0.2 s scan dwell time, and 0.1 mm emission slit width. The PLQEs were calculated by the equation:

$$\varphi = \frac{k_f}{k_a}$$

in which k_f means the number of emitted photons and k_a means the number of absorbed photons.

Time-resolved Photoluminescence. Time-resolved emission data was collected at room temperature using the FLS980 spectrophotometer. The average lifetime was obtained according to the equation:

$$\tau_{avg} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \quad i=1, 2, 3...$$

where a_i represents the amplitude of each component and τ_i represents the decay time.

Photostability tests. The solid-state samples was treated under continuous irradiation using a 4-W, 365 nm UV lamp in air (~60% relative humidity, room temperature) for a month to test their long-term photostability.

Computational Methods. Density function theory calculations were performed by using the CP2K package. Perdew-Burke-Ernzerhof (PBE) functional with Grimme D3 correction was used to describe the system. Unrestricted Kohn-Sham DFT has been used as the electronic structure method in the framework of the Gaussian and plane waves method. The Goedecker-

Teter-Hutter (GTH) pseudopotentials, DZVP-MOLOPT-SR-GTH basis sets were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed. The lattice parameters were fixed at the experimentally measured values while the atomic positions were optimized. Following Franck-Condon principle, the optical excitation and emission energies were obtained by calculating the total energy differences between the excited and the ground states using optimized ground-state and excited-state structures, respectively.

Supporting Figures and Tables

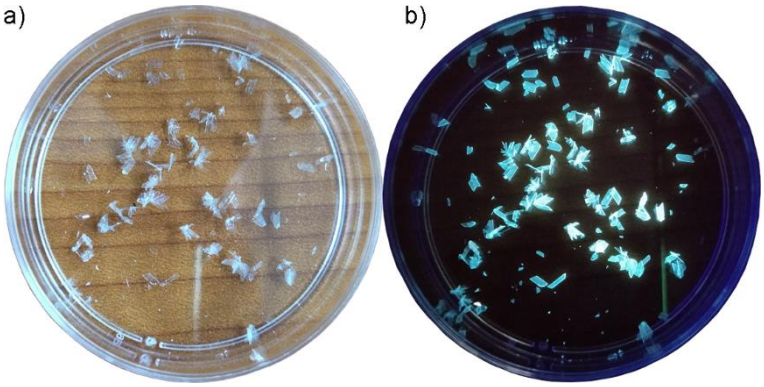

Figure S1. TJU-12 crystals before (a) and after (b) under UV-light.

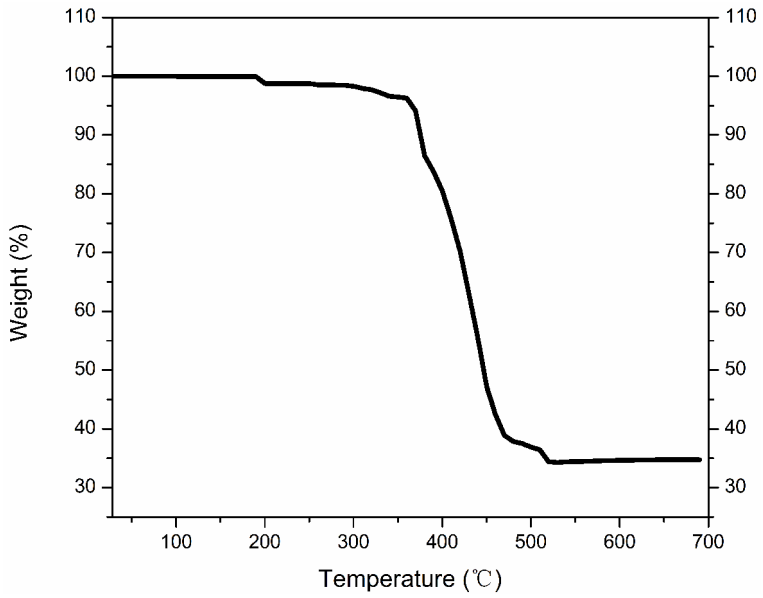

Figure S2. TGA curve of TJU-12.

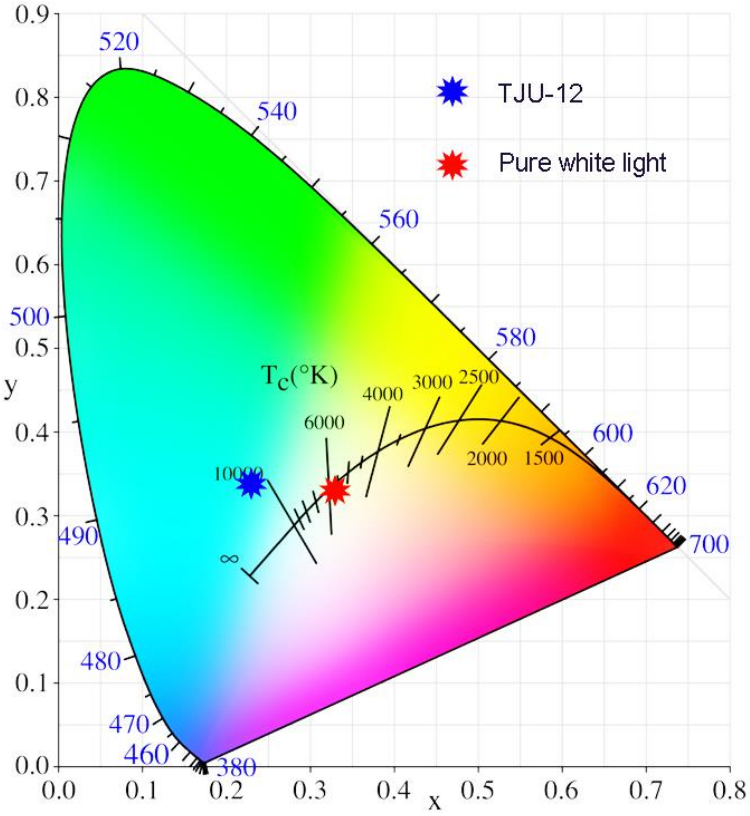

Figure S3. CIE coordinate of TJU-12 (blue) and pure white light (red).

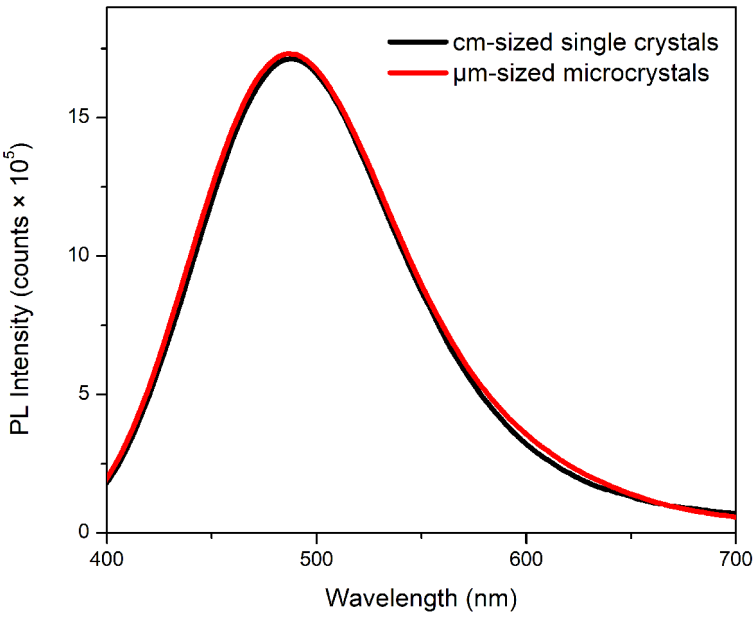

Figure S4. Photoemission of TJU-12 before and after UV-irradiation under atmospheric condition (~60% relative humidity, room temperature) for 30 days.

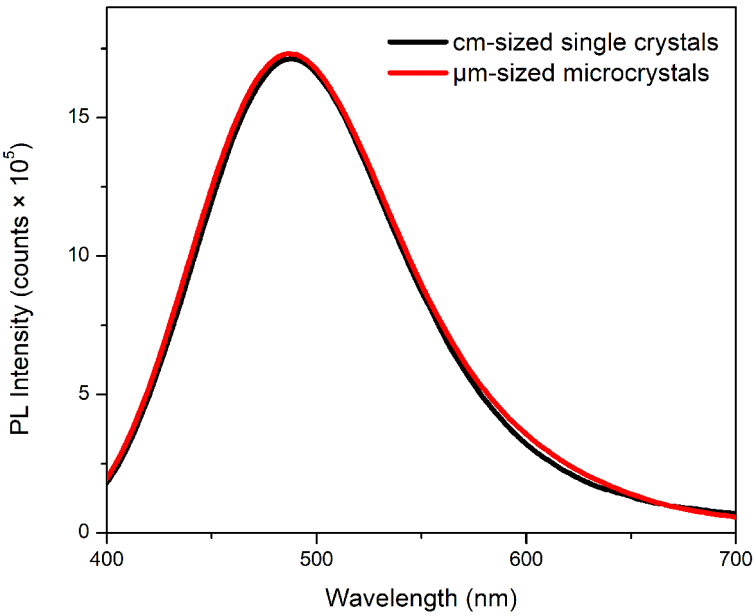

Figure S5. The photoluminescence spectra of cm-sized TJU-12 crystals(black) and μm-sized TJU-12 microcrystals(red).

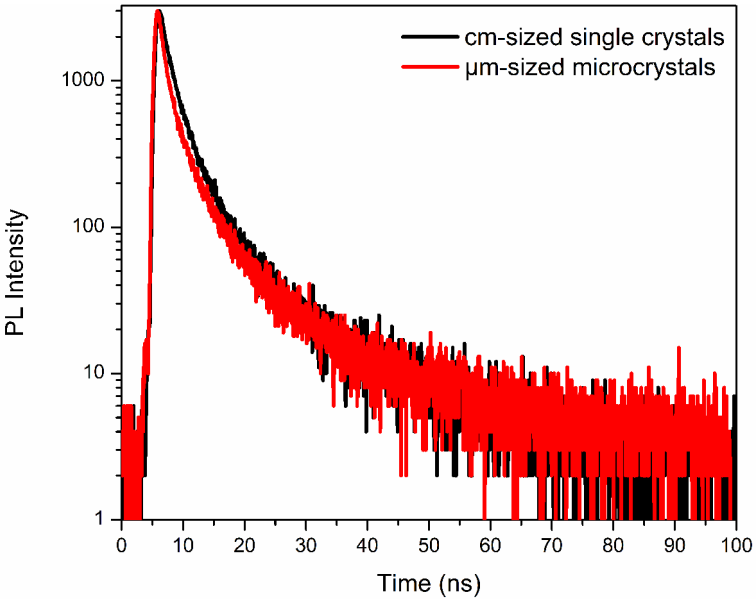

Figure S6. The decay curve of cm-sized TJU-12 single crystals (black) and μm-sized TJU-12 microcrystals (red).

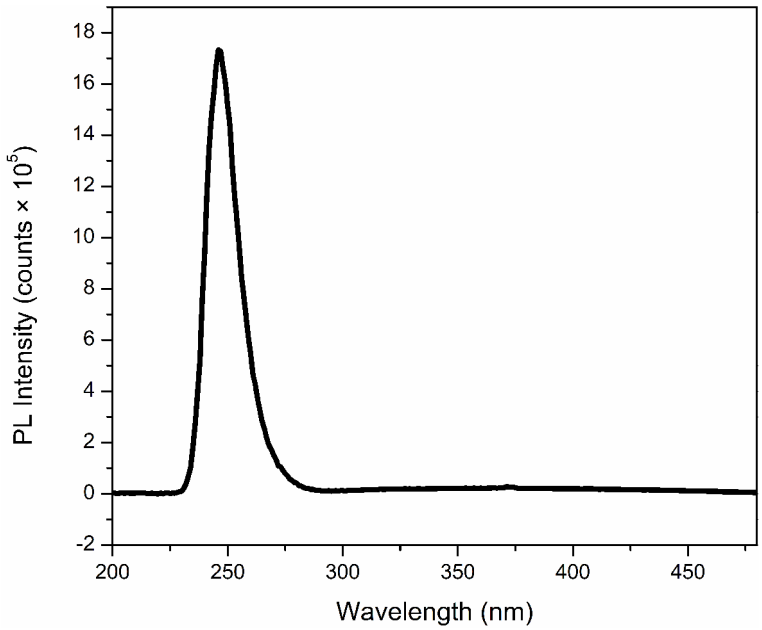

Figure S7. Excitation spectra for the 490 nm emission of TJU-12.

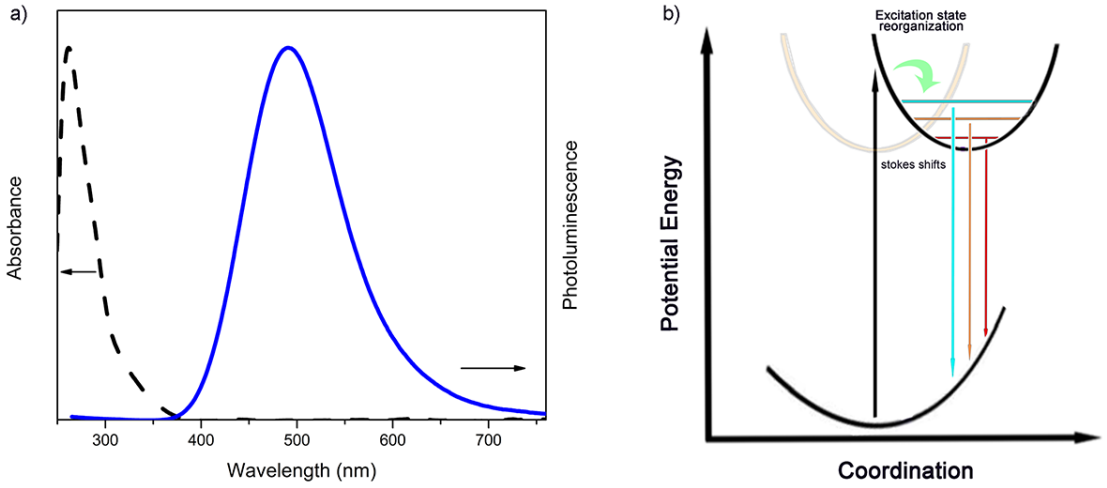

Figure S8. a) Absorption (black) and emission (blue) spectra of TJU-12; b) Schematic of the photophysical processes in Sb^{III}. Upon UV excitation, TJU-12 exhibits a large stokes shift, as a result of shift in the configurational diagram and vibration relaxation upon excitation of the asymmetric structures of SbO_5 polyhedron.

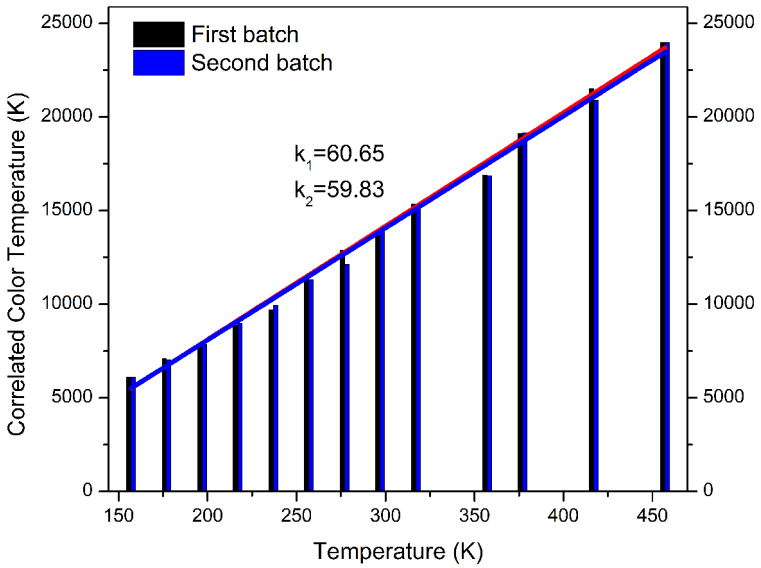

Figure S9. Temperature-dependent correlated color temperature of two different batches of TJU-12.

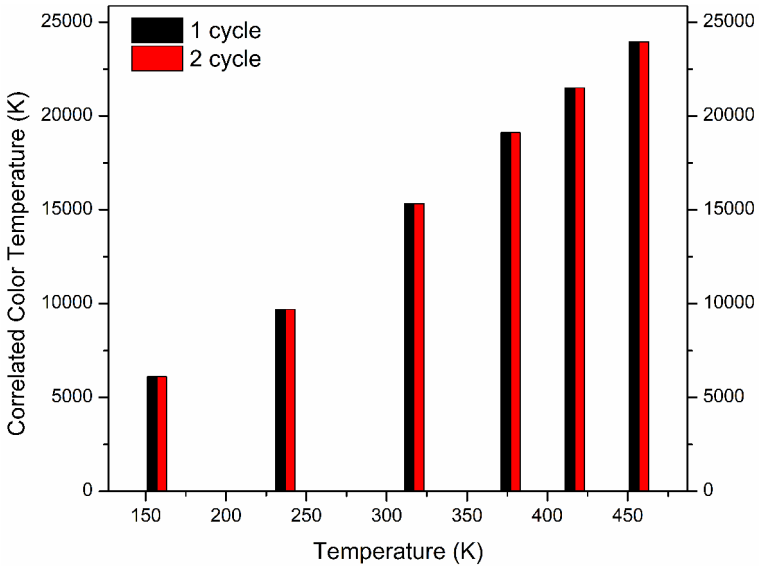

Figure S10. Reversible luminescence changes in two thermo-cycles of TJU-12.

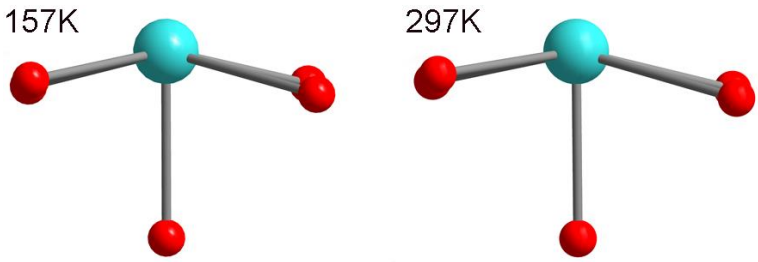

Figure S11. The coordination environment of Sb^{3+} at 157 K and 297 K. Cyan and red spheres represent Sb and O atoms, respectively.

Table S1. O-Sb-O angles at 157K and 297K.

	157K	297K
O-Sb-O angles	77.396	77.779
	78.186	78.515
	80.537	80.813
	84.929	85.103
	80.752	80.931
	89.191	89.162
	89.999	90.093
	93.723	93.864

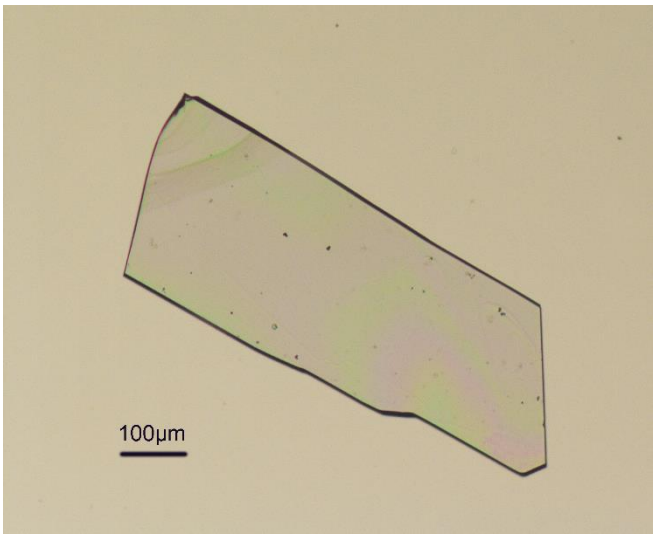

Figure S12. The optical images of TJU-12 crystals**.**

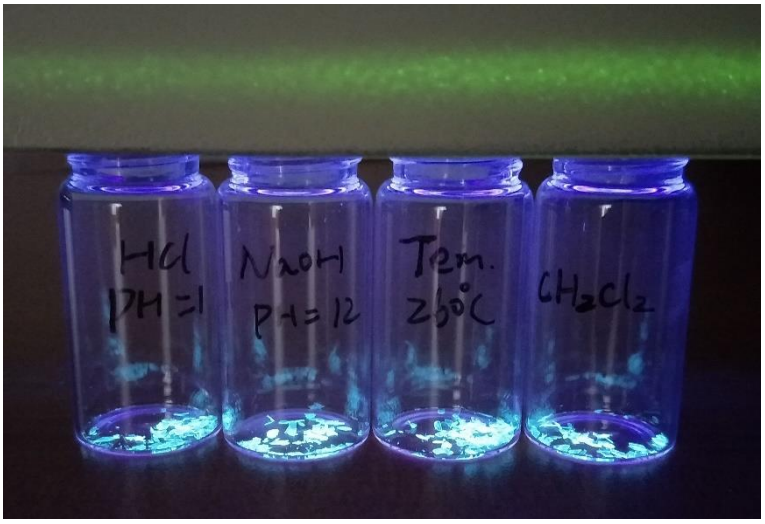

Figure S13. The photo-images of TJU-12 upon UV excitation after chemical or thermal treatment for 24 h.

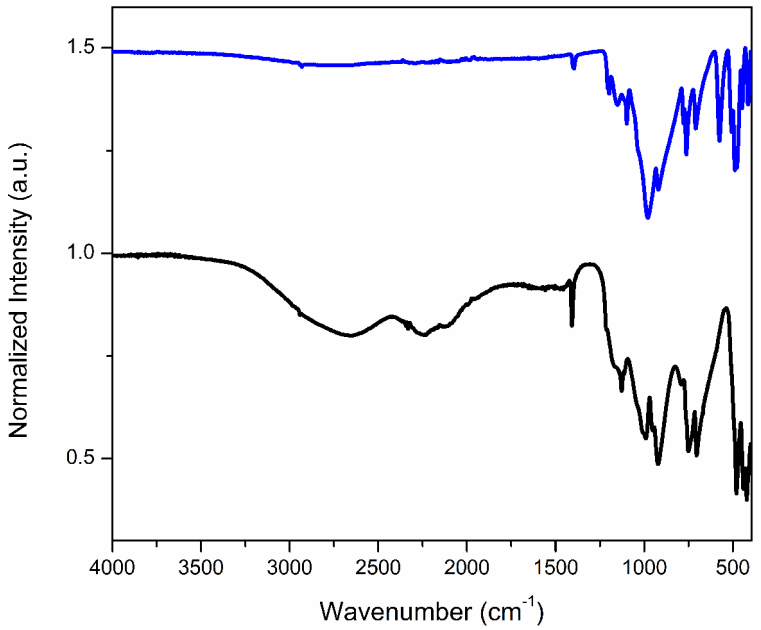

Figure S14. FT-IR spectra of TJU-12 and free EPA ligand.

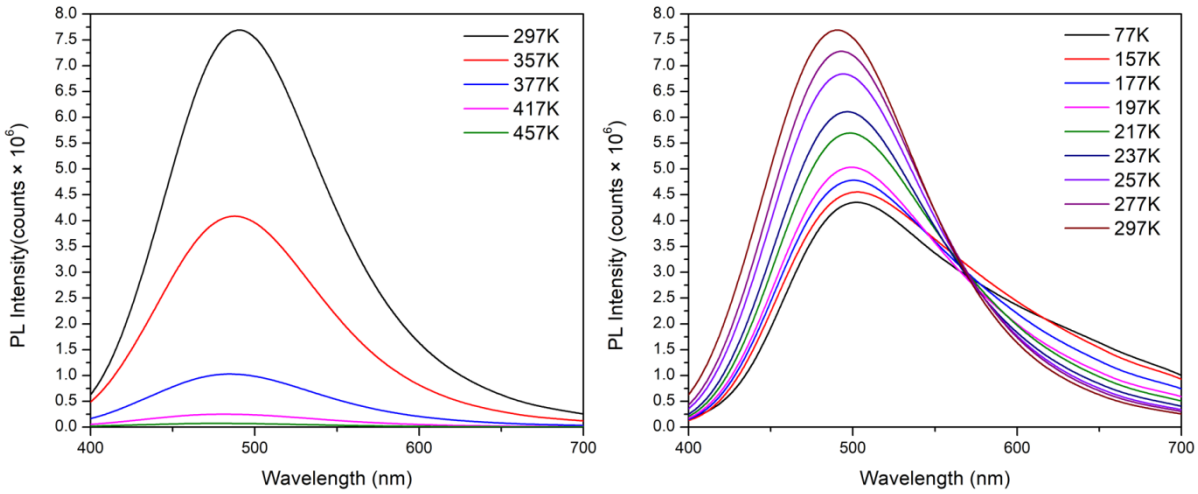

Figure S15. Left: Temperature-dependent photoemission spectra of TJU-12 from 297 K to 457 K upon 247 nm excitation. The photoemission intensity gradually decrease with increasing temperature. Right: Temperature-dependent photoemission spectra of TJU-12 from 77 K to 297 K upon 247 nm excitation. The photoemission intensity gradually increase with increasing temperature.

Table S2. Crystal data and structure refinement for TJU-12.

Identification code	TJU-12
Empirical formula	$C_2H_5O_6P_2Sb$
Formula weight	308.74
Temperature/K	297.0
Crystal system	triclinic
Space group	P-1
a/ Å	4.6992(11)
b/ Å	4.9757(12)
c/ Å	15.625(4)
α/°	83.397(8)
β/°	83.782(8)
γ/°	68.108(7)
Volume/ $Å^3$	335.90(14)
Z	2
ρcalcg/cm^3	3.043
μ/mm^{-1}	4.561
F(000)	290.0
Crystal size/mm^3	0.18 × 0.16 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.896 to 55.174
Index ranges	-6 ≤ h ≤ 5, -6 ≤ k ≤ 6, -20 ≤ l ≤ 20
Reflections collected	4694
Independent reflections	1545 [Rint = 0.0292, Rsigma = 0.0323]
Data/restraints/parameters	1545/0/100
Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	R1 = 0.0199, wR2 = 0.0475
Final R indexes [all data]	R1 = 0.0218, wR2 = 0.0484
Largest diff. peak/hole / e $Å^{-3}$	0.81/-0.99

$R_1=\Sigma(||Fo|-|Fc||) / \Sigma|Fo|$; $wR_2=\{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)]^2\}^{1/2}$