Electronic Supplementary Information

Room-temperature and ultra-fast Eu^{3+} ion doping for highly luminescent and extremely small $CaMoO_4$ nanocrystals

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Experimental Section

Chemicals

Calcium nitrate (99%) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 99%) were purchased from Beijing Chemical works. Butyric acid (A.R.), butyl amine (A.R.) and ethanol (A.R.), europium nitrate hexahydrate ($Eu(NO_3)_3\cdot 6H_2O$, 99.99%) were supplied by Aladdin Inc. Methanol (A.R.) and chloroform (A.R.) were bought by Chengdu Kelong Chemicals Ltd. All the initial chemicals in this work were used without further purification.

Room-temperature preparation of undoped $CaMoO_4$ nanoparticles

The synthesis of $CaMoO_4$ nanoparticles is as follows: 10.0 mmol of $Ca(NO_3)_2$, 120 ml of ethanol and 15 ml of butyric acid were added into a 250 ml of beaker. Next, under magnetic stirring, 10 ml of butylamine was slowly dropped into the beaker, forming a homogeneous and clear solution. Subsequently, 10 mmol of ammonium molybdate was dissolved into 40 ml of methanol and 10 ml of butylamine by ultrasound, forming a transparent solution. The two solutions are then mixed together at room temperature under magnetic stirring to form copious white precipitate. The white precipitate was collected by centrifugation and washed several times with ethanol. Finally, $CaMoO_4$ nanoparticles was dissolved in 100 ml of chloroform.

Room-temperature cation exhange for synthesis of Eu-doped $CaMoO_4$ nanoparticles

For the synthesis of Eu-doped $CaMoO_4$ nanoparticles with an Eu/Ca feeding ratio of 1:1, 1.0 mmol of $Eu(NO_3)_3$, 1.0 ml of butyric acid and 1.0 ml of butylamne were added into a glass vial. The mixture was magnetically stirred on a hotplate at 100°C until all the solid was dissolved. The solution was cooled to the room temperature, and 3 ml of chloroform was added into the vial. Next, the $Eu(NO_3)_3$ chloroform solution is swiftly injected into 10 ml of $CaMoO_4$ nanoparticle chloroform solution to form Eu-doped $CaMoO_4$ luminescent nanoparticles. During the cation exchange process, PL spectra and integrated PL intensity were *in-situ* recorded by using Ocean Optics USB2000+ spectrometer with a Y-type fiber optic probe and a 280 nm deep UV-LED as the excitation source. Finally, Eu-doped $CaMoO_4$ nanoparticles were precipitated by using methanol and redispered in chloroform.

2.3 Characterizations

The XRD patterns were measured by BRUKER AXS GMBH with Cu-Kα target. The morphology and size of the samples were observed by transmission electron microscopy (TEM, FEI TECNAI G2 F30) at accelerating voltage of 300 kV. Photoluminescence (PL) spectra, photoluminescence excitation (PLE) spectra, PL lifetime and absolute photoluminescence quantum yields (PLQYs) were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer and Edinburgh FLS-1000 spectrofluorometer. Thermogravimetric curve was measured on a TGA/DSC 1 STARE of Mettler-Toledo in air. I-V-L curves of LED were synchronously measured by Minolta LS-150 luminance meter and Keithley 2400 source meter. Fourier transform infrared spectroscopy (FT-IR) curve was obtained on a Bruker Vertex 70 FT-IR spectrophotometer. The valence states of elements were measured by X-ray photoelectron spectroscopy (XPS, Thermo-Fisher Scientific ESCALAB 250Xi). The chemical compositions were detected by BRUKER X-ray fluorescence spectrometer (S8 TIGER).

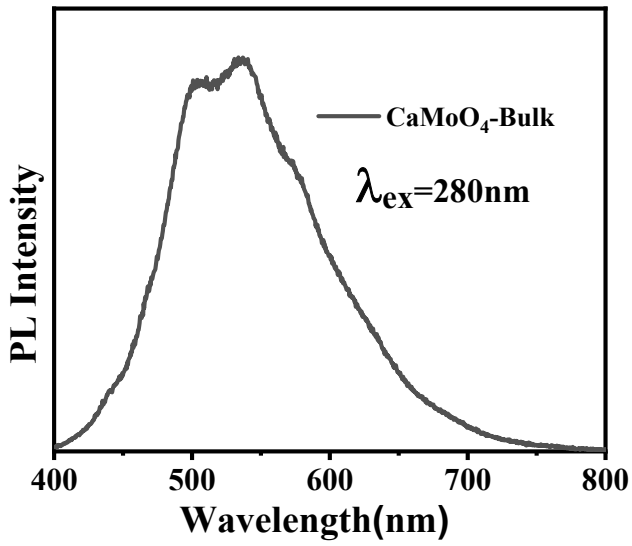

Figure S1. Defect emission spectrum of undoped bulk $CaMoO_4$ powder.

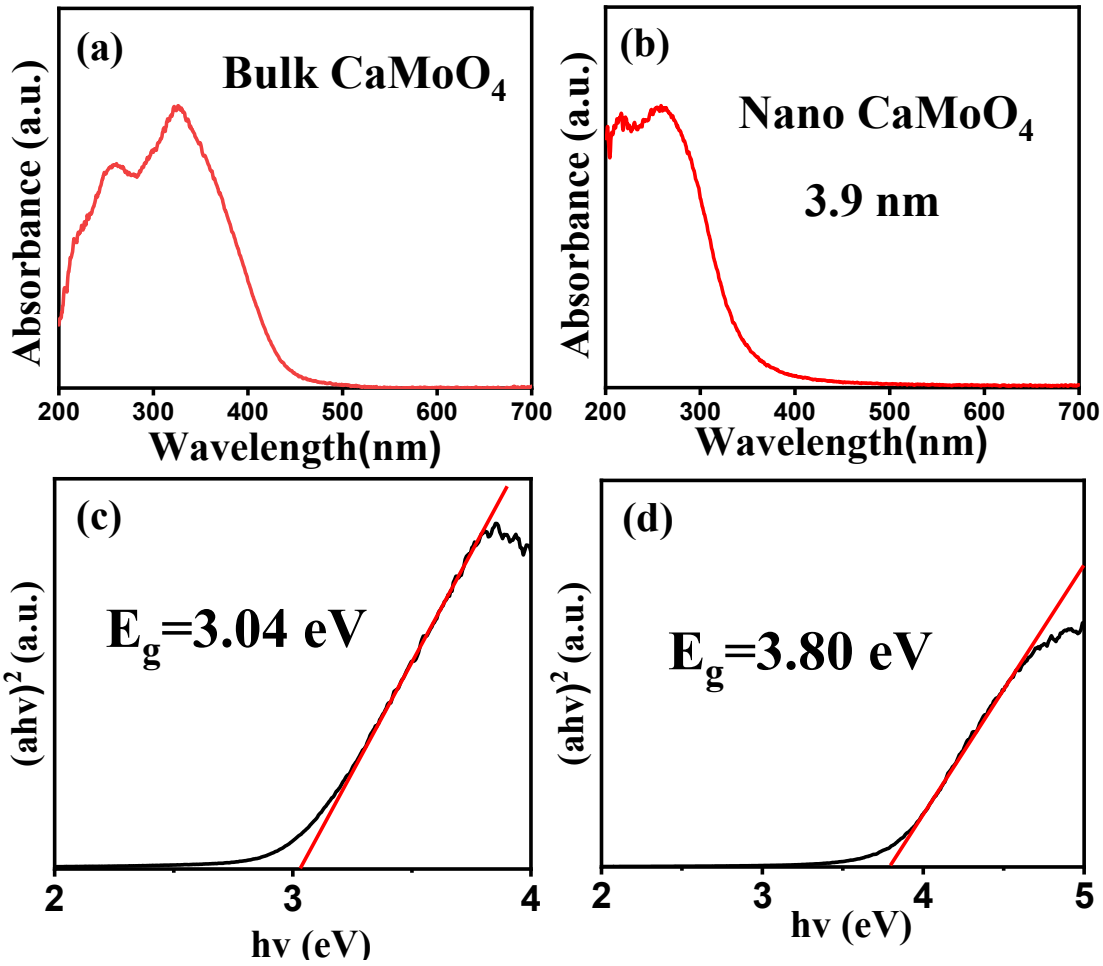

Figure S2. UV-vis diffuse reflectance spectra (a, b) and the optical band gaps (c, d) of bulk $CaMoO_4$ powder (a, c) and the corresponding $CaMoO_4$ nanocrystals (b, d).

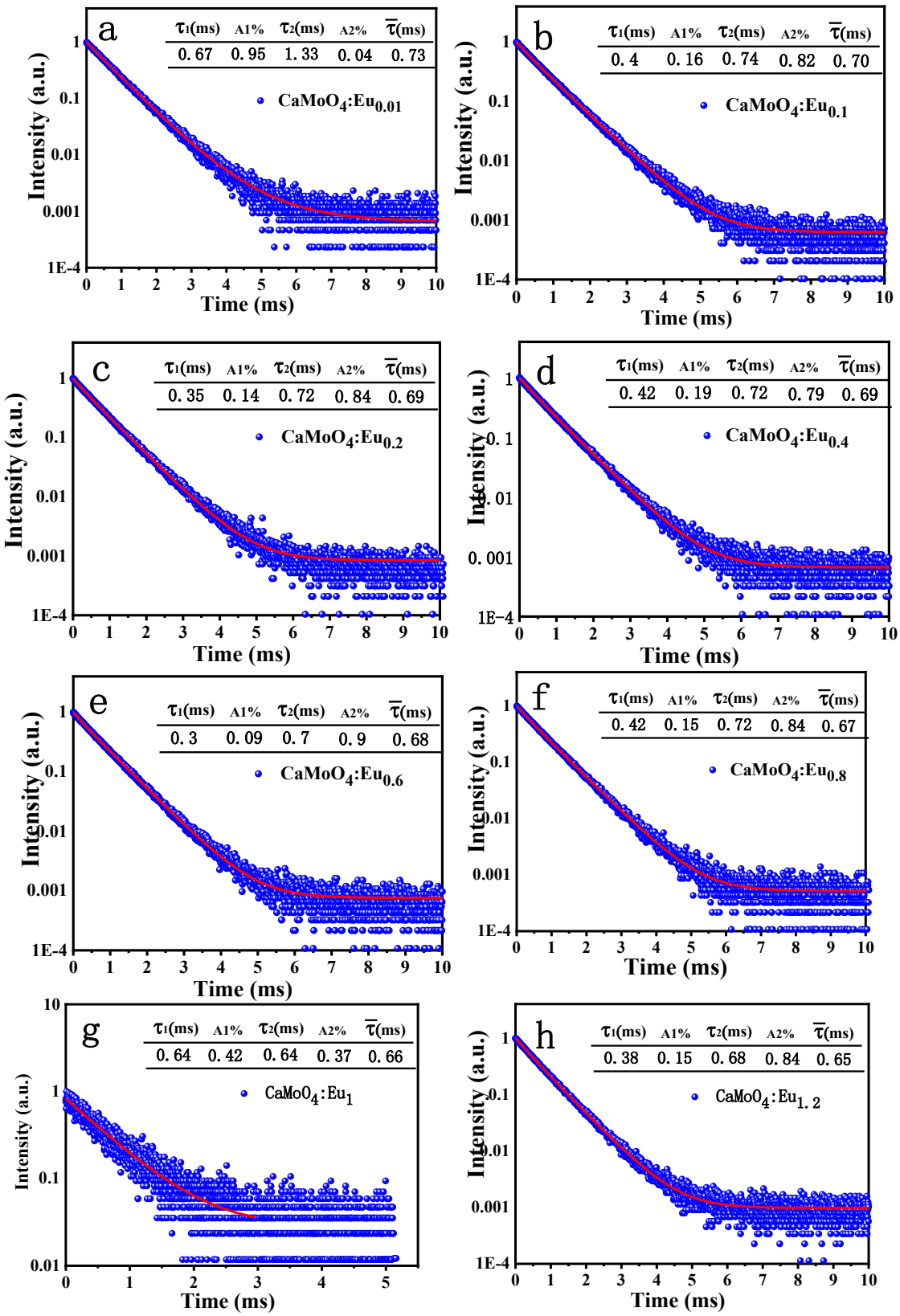

Figure S3 PL decay curves of Eu-doped $CaMoO_4$ nanoparticles with different Eu^{3+} feeding ratios (x=Eu/Ca=0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.2).

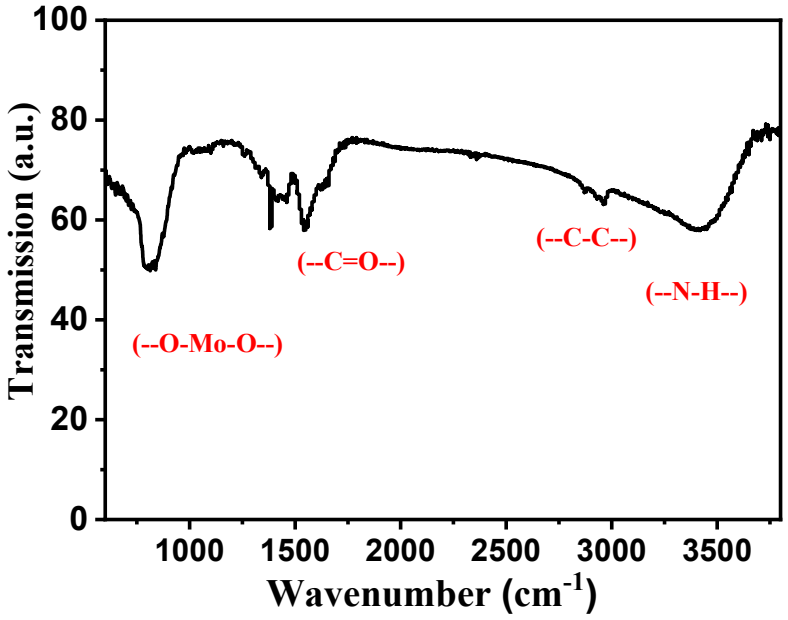

Figure S4 FT-IR spectrum of butyric acid/butylamine-capped Eu-doped $CaMoO_4$ nanocrystals with Eu/Ca feeding ratio of 1:1.

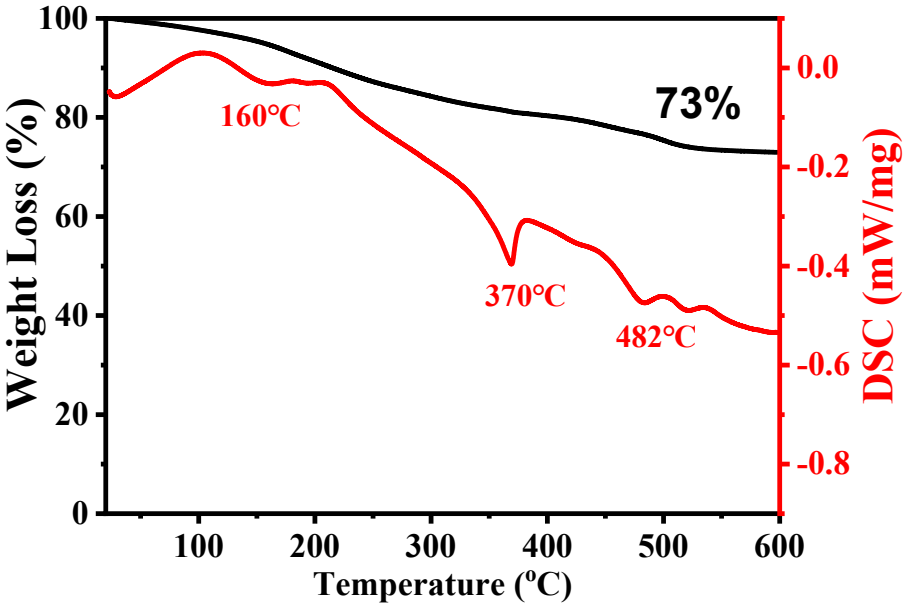

Figure S5 TGA-DSC curves of butyric acid/butylamine-capped Eu-doped $CaMoO_4$ nanocrystals with Eu/Ca feeding ratio of 1:1.

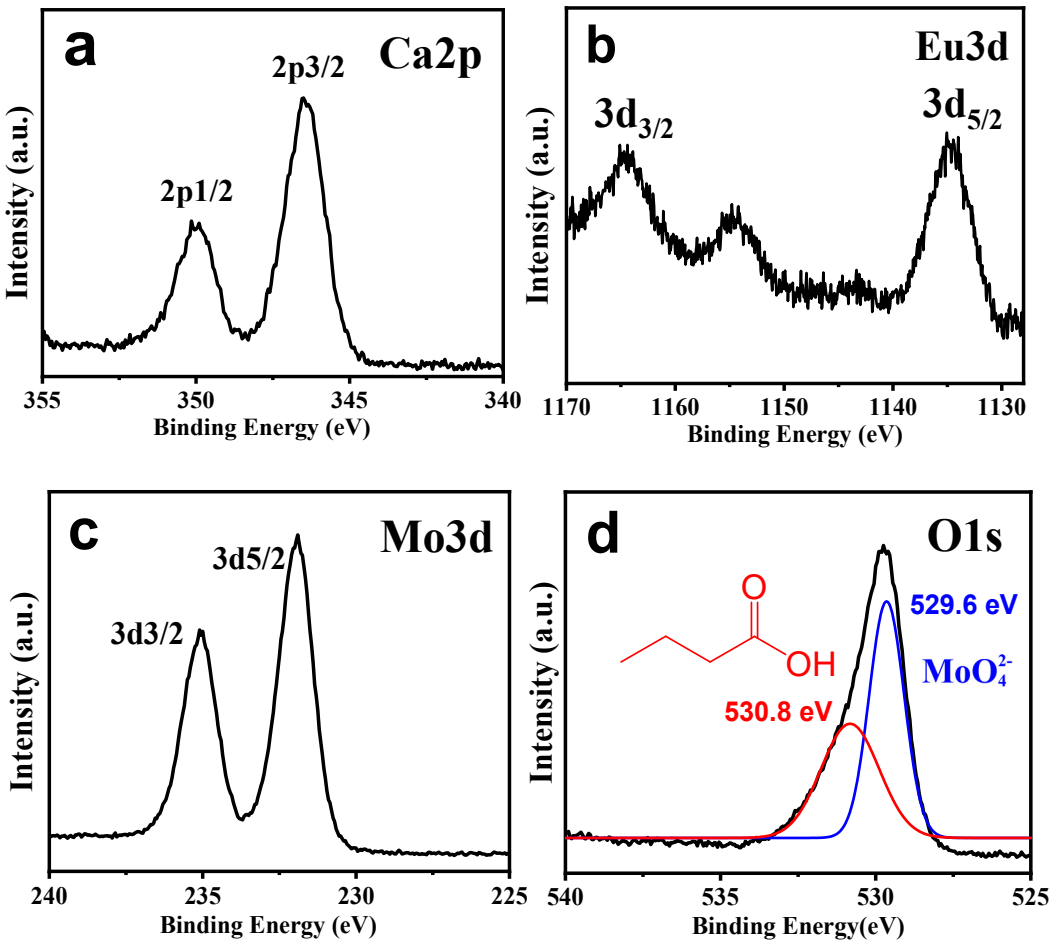

Figure S6 XPS spectra of Eu-doped $CaMoO_4$ nanocrystals with Eu/Ca feeding ratio of 1:1. (a) Ca2p; (b) Eu3d; (c) Mo3d; (d) O1s.

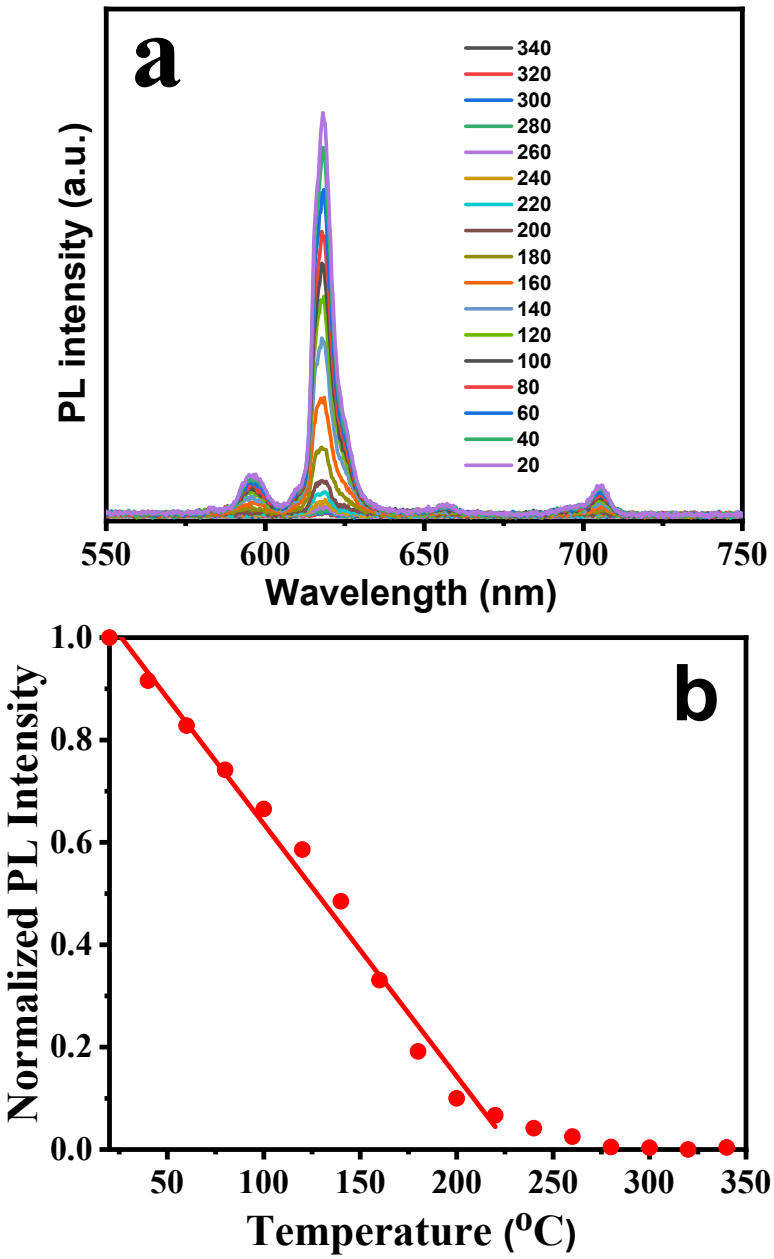

Figure S7 (a) Temperature-dependent PL spectra of Eu-doped $CaMoO_4$ nanocrystals with Eu/Ca feeding ratio of 1:1. (b) the plot of PL intensity *vs* temperature for Eu-doped $CaMoO_4$ nanocrystals with Eu/Ca feeding ratio of 1:1.