Supporting Information for

A Mild Liquid Reduction Route toward Uniform Blue-Emitting $EuCl_2$ Nanoprisms and Nanorods

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Materials. Oleylamine (OM, >80%, Acros), 1-octadecene (ODE, 90%, Acros), oleic acid (OA, 90%, Sigma-aldrich), trichloroacetic acid (CCl_3COOH, A.R.) and acetamidine hydrochloride (AAM, 97%, Alfa Aesar) were used without further purification. Picolinamidine hydrochloride (PAM),[1] $Eu(CCl_3COO)_3{\cdot}2H_2O$[2] and $Eu(CH_3COO)_3{\cdot}H_2O$[2] were synthesized according to published literatures. Anal. Found for $C_6Cl_9EuO_6{\cdot}2H_2O$: C, 10.59; H, 0.63. Calcd: C, 10.67; H, 0.60. Anal. Found for $C_6H_9EuO_6{\cdot}H_2O$: C, 20.84; H, 3.29. Calcd: C, 20.76; H, 3.19.

Synthesis of $EuCl_2$ nanoprisms: 1.0 mmol of acetamidine hydrochloride (AAM, or picolinamidine hydrochloride (PAM)) and 0.30 mmol of $Eu(CCl_3COO)_3{\cdot}2H_2O$ were mixed in 30 mmol of oleylamine (OM) in a three-necked flask. The mixture was stirred at about 40 ºC for 5-10 min to form a clear, colourless solution. Subsequently, the solution was heated to 300 ºC, when the color of the mixture turned to light brown. The reaction was maintained at 300 ºC for 1 h with stirring and then cooled naturally by removing heat source. After cooling to about 60 ºC, 30 mL ethanol was added to the flask, and gray-white product would precipitate at the bottom. The final product was collected by centrifugation at 7000 rpm for 12 min.

Synthesis of $EuCl_2$ nanorods: $EuCl_2$ nanorods were prepared with the same procedure used for $EuCl_2$ nanoprisms, except that $Eu(CH_3COO)_3{\cdot}H_2O$ replaced $Eu(CCl_3COO)_3{\cdot}2H_2O$ as the precursor.

Instrumentation. Powder X-ray diffraction (XRD) patterns of the nanoparticles were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 1/2 ° at a scanning rate of 4 °/min, with a Cu-K radiation source (λ = 1.5418 Å). The morphology analysis was performed on a JEOL 200CX (Japan) low-resolution transmission electron microscope (TEM) and a Philips FEI Tecnai T20 (Netherlands) high-resolution TEM, operated at 160 kV and 200 kV, respectively. Energy-dispersive X-ray spectroscopy (EDX) characterization was performed on a Philips Tecnai F30 FEG-TEM (Netherlands) operated at 300 kV. Size distributions of the nanoparticles were obtained by counting no less than 100 nanoparticles. Thermogravimetric analysis was carried out on an SDT2960 Simultaneous DTA-TGA (America) with a heating speed of 10 ºC/min. The Fourier Transform Infrared (FT-IR) spectrum of products was measured on Bruker VECTOR 22 FT-IR spectrometer (Germany). X-ray

photoelectron spectroscopy (XPS) characterization was carried out on an ion-pumped chamber (evacuated to 1.3 × 10^{-8} Torr) of Axis Ultra (UK) spectrometer equipped with a focused monochromatised X-ray source (Al Kα, *hv* = 1486.6 eV) at a power of 225 W. The UV–vis absorption spectrum was measured on a Shimadzu UV-3100 spectrometer. The photoluminescence (PL) spectra and lifetime data were collected on an Edinburgh Analytical Instruments FLS920 spectrometer. Luminescence quantum yield (Φ) in *n*-hexane was measured at room temperature with a solution of quinine bisulfate in 0.1 N H_2SO_4 as a standard (Φ = 0.577).[3]

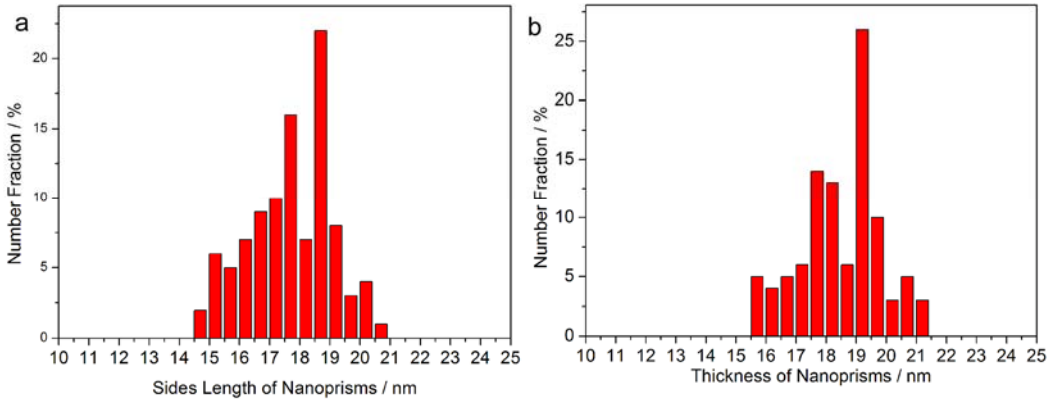

Figure S1. (a) Sides length (17.7 ± 1.7 nm) and (b) thickness (20.5 ± 1.6 nm) distributions of the $EuCl_2$ nanoprisms.

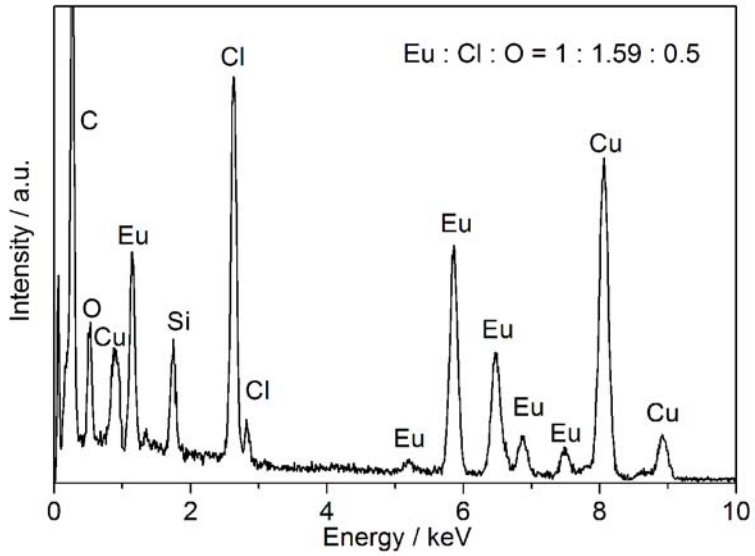

Figure S2. EDX spectrum of the $EuCl_2$ nanoprisms. The atomic ratio of Eu : Cl :O is determined as 1 : 1.59 : 0.5.

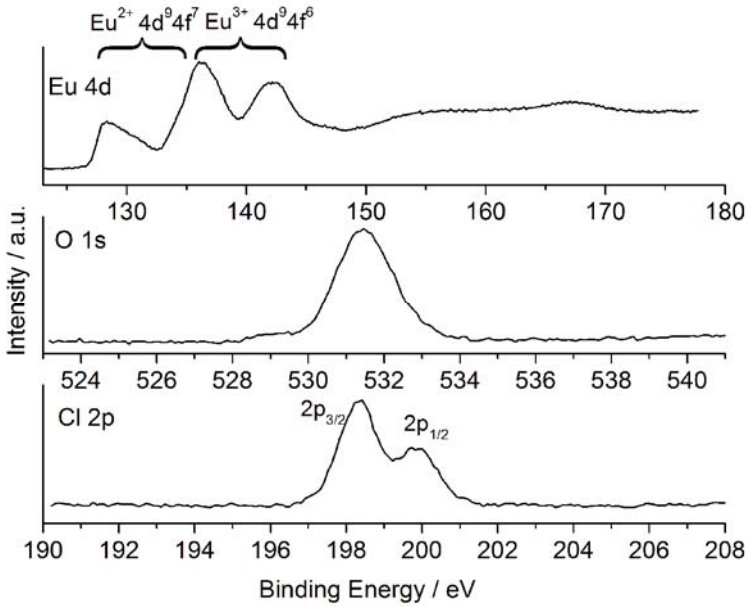

Figure S3. XPS spectra of Eu 4d (Eu^{2+} $4d_{5/2}$: 128.23 eV, $4d_{3/2}$: ~134 eV; Eu^{3+} $4d_{5/2}$: ~136 eV, $4d_{3/2}$: 142.23 eV), O 1s (531.47 eV) and Cl 2p (198.42 eV) for the $EuCl_2$ nanoprisms exposed to air for 1 week. The appearance of the band at around 136.02 eV can be resulted from the overlapping of Eu^{2+} $4d_{3/2}$ and Eu^{3+} $4d_{5/2}$.[4]

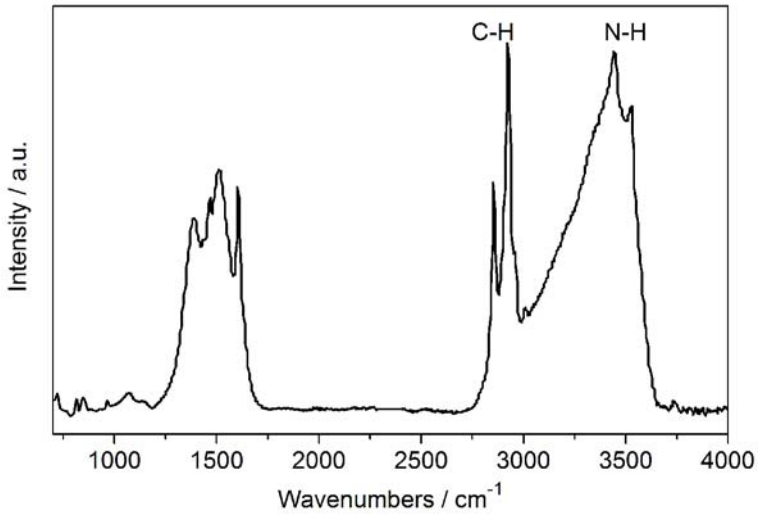

Figure S4. FT-IR spectrum of the $EuCl_2$ nanoprisms. The appearance of very strong narrow peaks around 2900 cm^{-1} (C-H), together with the very strong broad peak at about 3400 cm^{-1} (N-H), proves the existence of OM ligands on the surfaces of the nanoprisms.

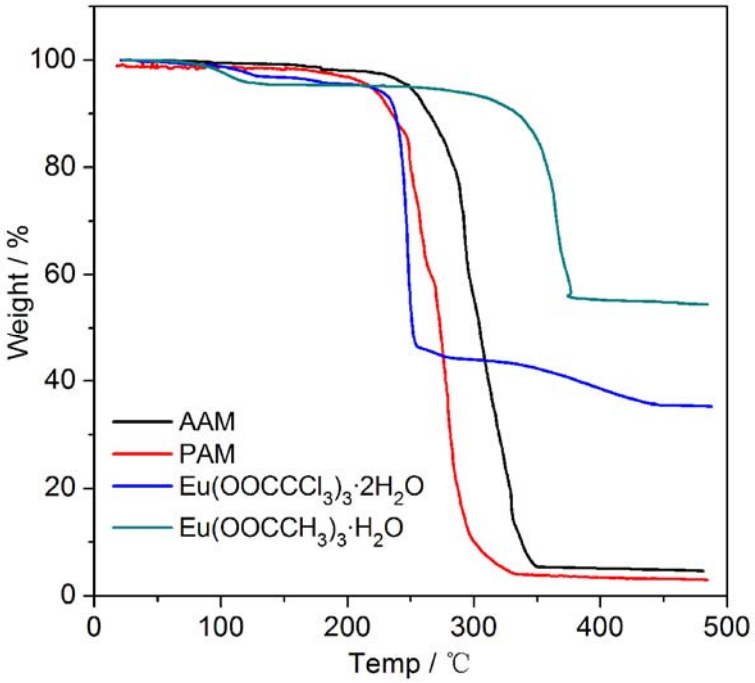

Figure S5. Thermogravimetric analysis of AAM, PAM, $Eu(CCl_3COO)_3 \cdot 2H_2O$, and $Eu(CH_3COO)_3 \cdot H_2O$. Their decomposition temperatures (T_d) are 292 ºC, 280 ºC, 250 ºC, and 374 ºC, respectively.

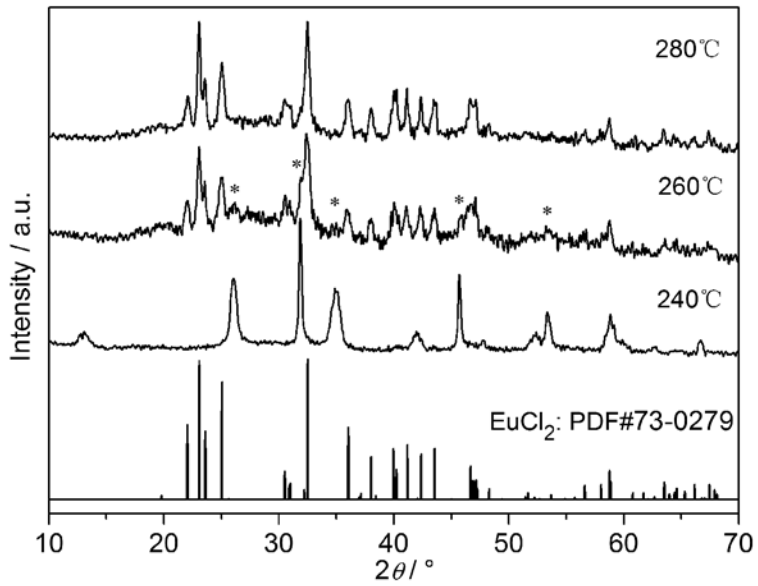

Figure S6. PXRD patterns of the products forming at different reaction temperatures. (Peaks marked with asterisks indicate the formation of EuOCl.) When the reaction was carried out at 280 ºC, pure $EuCl_2$ nanoparticles were still produced because AAM already began to decompose at this temperature. However, for those prepared at 260 ºC, obvious EuOCl peaks (marked with asterisks) were found in addition to $EuCl_2$ because the decomposition of AAM was so slow at this temperature that the amount of released ammonia was insufficient to fully reduce Eu^{III}. When the temperature was lowered further to 240 ºC, pure EuOCl was obtained, implying that no ammonia was released.

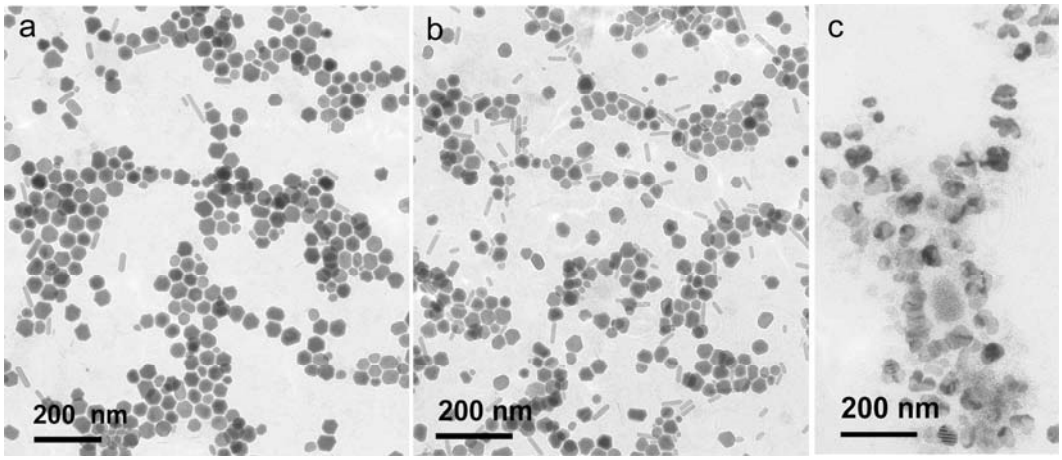

Figure S7. TEM images of the products prepared at different reaction temperatures: (a) 280 ºC, (b) 260 ºC and (c) 240 ºC.

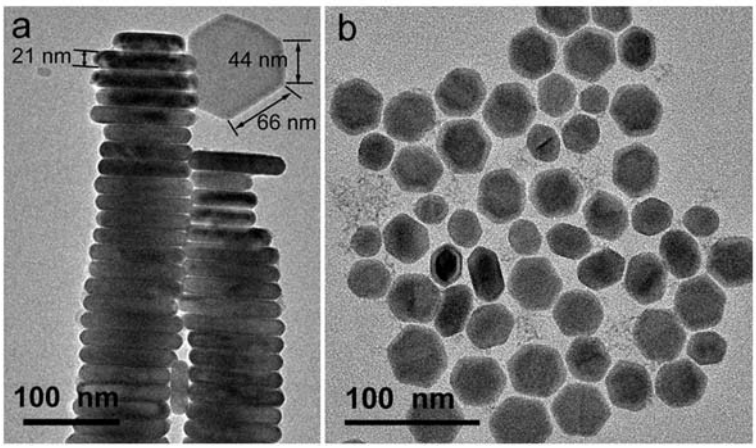

Figure S8. TEM images of $EuCl_2$ nanoprisms prepared (a) in OM under a flow of N_2 and (b) in OM/ODE (1:1) under air.

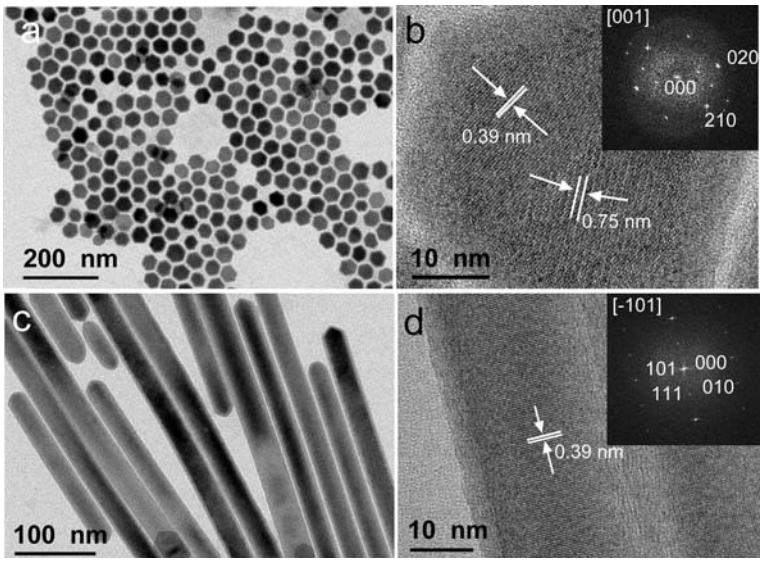

Figure S9. TEM (a) and HRTEM (b) images of the $EuCl_2$ nanoprisms synthesized from PAM and $Eu(CCl_3COO)_3{\cdot}2H_2O$; TEM (c) and HRTEM (d) images of the $EuCl_2$ nanorods synthesized from PAM and $Eu(CH_3COO)_3{\cdot}H_2O$.

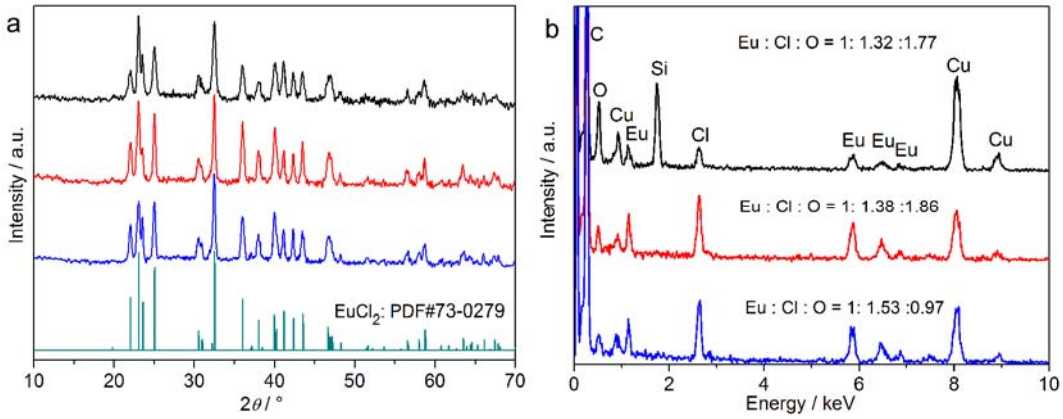

Figure S10. (a) PXRD patterns and (b) EDX spectra of three as-synthesized products (black: $EuCl_2$ nanoprisms synthesized from PAM and $Eu(CCl_3COO)_3{\cdot}2H_2O$; red: $EuCl_2$ nanorods synthesized from AAM and $Eu(CH_3COO)_3{\cdot}H_2O$; blue: $EuCl_2$ nanorods synthesized from PAM and $Eu(CH_3COO)_3{\cdot}H_2O$).

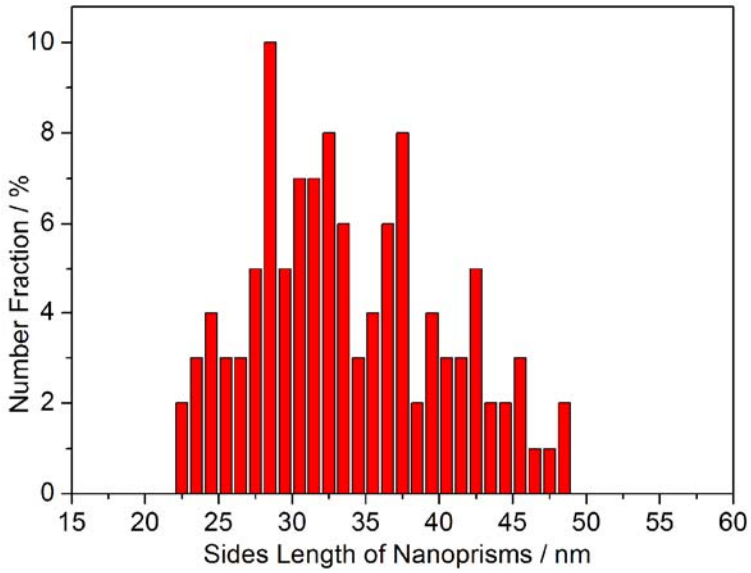

Figure S11. Width distribution (34.4 ± 7.5 nm)of the $EuCl_2$ nanorods.

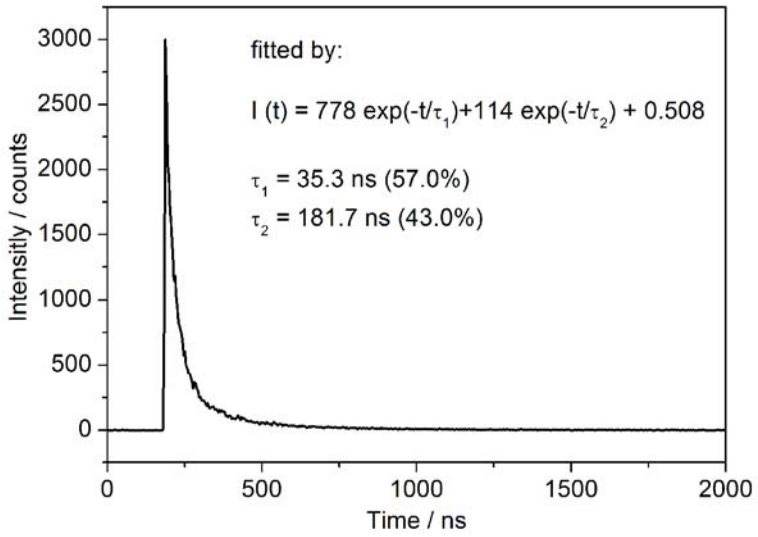

Figure S12. Luminescence decay curve for the 404 nm emission of the $EuCl_2$ nanoprisms in *n*-hexane at room temperature.

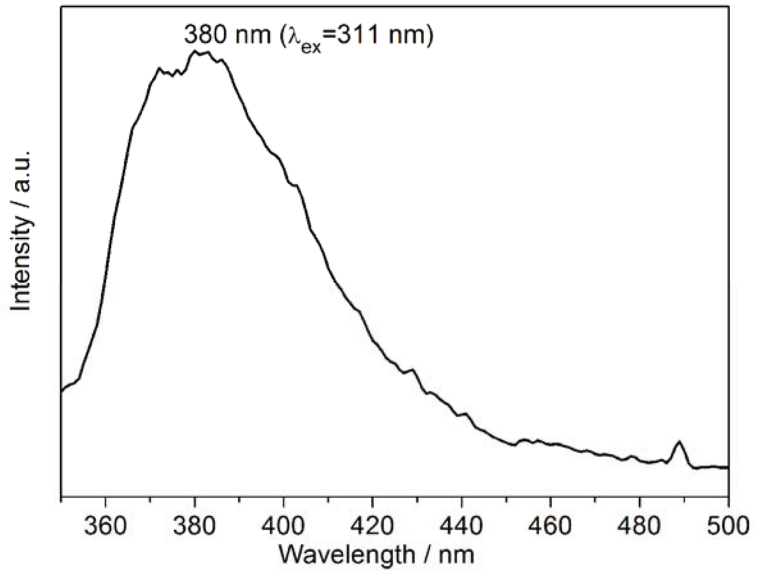

Figure S13. Emission spectrum (λ_{ex} = 311 nm) of the $EuCl_2$ nanorods dispersed in *n*-hexane.

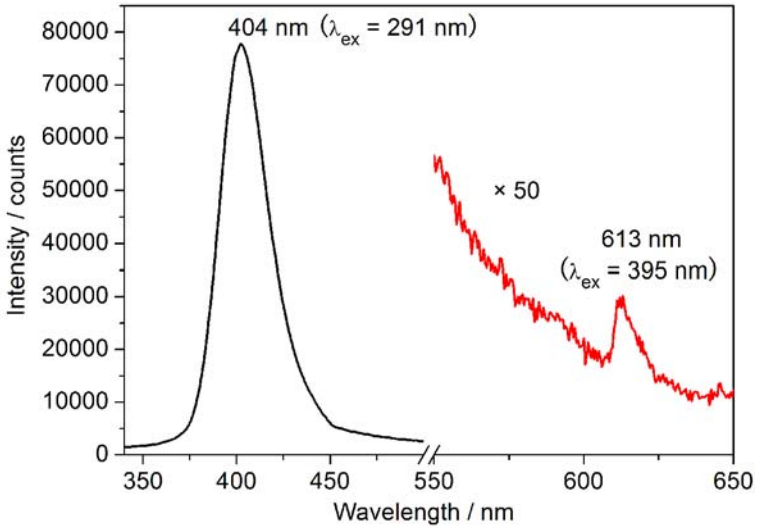

Figure S14. Emission spectra of the $EuCl_2$ nanoprisms after stored in air for three months. The excitation wavelength for 613 nm is 395 nm, a characteristic absorption ($^7F_0 \rightarrow {}^5L_6$) of Eu^{3+}. The emission spectrum excited at 395 nm is multiplied by a factor of 50.

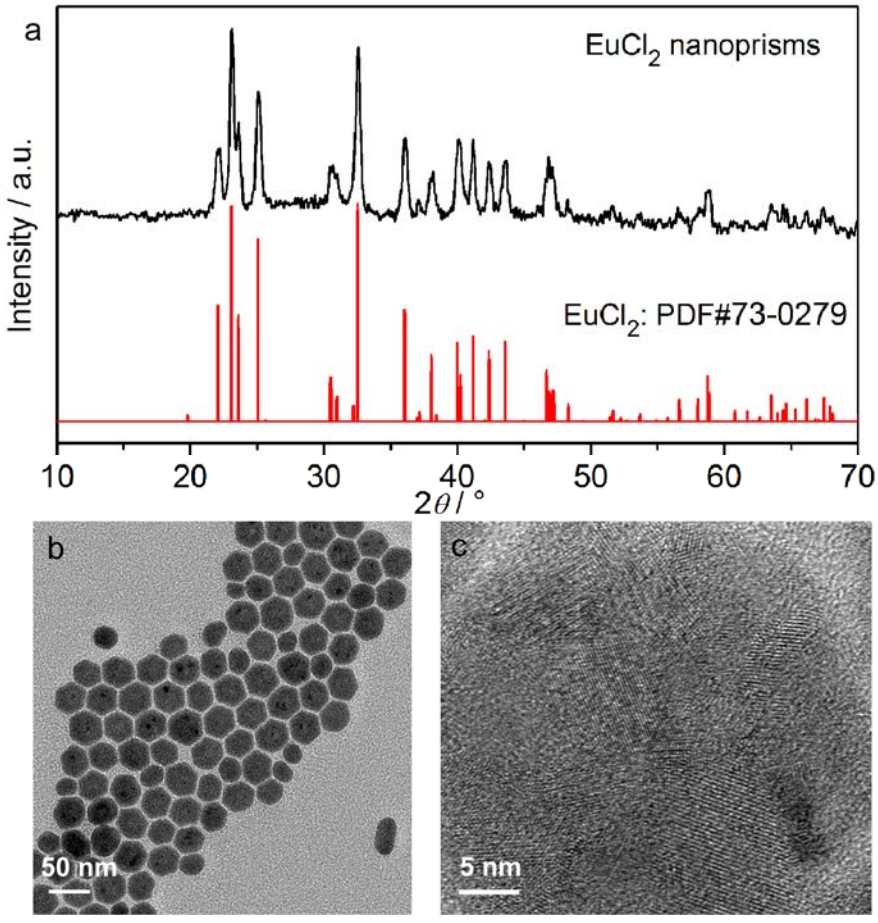

Figure S15. (a) PXRD pattern of the $EuCl_2$ nanoprisms exposed to air for six months (top) and the JCPDS card file for $EuCl_2$ (bottom); (b) TEM and (c) HRTEM images of the $EuCl_2$ nanoprisms stored in air for six months.

References:

(1) Medwid, J. B.; Paul, R.; Baker, J. S.; Brockman, J. A.; Du, M. T.; Hallett, W. A.; Hanifin, J. W.; Hardy, R. A.; Tarrant, M. E.; Torley, L. W.; Wrenn, S., *J. Med. Chem.* **1990,** *33*, 1230.

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(3) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishic, S.; Tobita, S., *Phys. Chem. Chem. Phys.* **2009,** *11*, 9850.

(4) Lu, D. Y.; Sugano, M.; Sun, X. Y.; Su, W. H., *Appl. Surf. Sci.* **2005,** *242*, 318.