

Supporting information

Hyperbranched Microspheres Formed by EDTA-based Coordination

Polymer with Ternary Architectures Assembled by Ultrathin

Nanoribbons and Their Tricolor Luminescent Properties

Ming Yang,^a Tiehong Chen,^c Zhongqing Wei,^d Min Li,^d Huichao Bi,^a Qingdao Zeng,^{*b}
Zhurui Shen^{*a} and Yongtao Shen^{*a}

^a Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University & School of material Science and Engineering, Tianjin University, Tianjin 300072, PR China.

E-mail: shenzhurui@tju.edu.cn; shenyt@tju.edu.cn

^b National Center for Nanoscience and Technology, 11 Zhongguancun Beiyitiao, Beijing 100190, People's Republic of China.

E-mail: zengqd@nanoctr.cn.

^c Key Laboratory of Energy-Material Chemistry and Engineering Research Center of Energy Storage & Conversion (MOE), College of Chemistry, Nankai University, Tianjin 300071, PR China.

^d Institute of High Energy Physics, the Chinese Academy of Sciences, CAS Key Lab for Biomedical Effects of Nanomaterials and Nanosafety, Beijing 100049, People's Republic of China.

Experimental Section

Synthesis. All chemical reagents are commercially available and were used as received. In a typical synthesis, 4 mmol disodium EDTA was dissolved in 24 ml H₂O at 45°C. 8 mmol rare earth salt (La(NO₃)₃•6H₂O, Ce(NO₃)₃•6H₂O, etc.) was added in the disodium EDTA solution above-mentioned under stirring, and several minutes later, some white precipitates were produced. Then the suspension obtained was transferred into 30 ml autoclave, sealed and heated under 160 °C for 24 hours. The as-prepared lanthanide coordination polymers (CPs) were washed by deionized water and absolute ethanol and dried in air under 60 °C.

Characterizations. The thermogravimetry and differential thermal analysis (TG-DTA) of the sample were performed on a Rigaku TG-DTA thermal analyzer. XRD patterns were recorded with a Rigaku D/max-2500 diffractometer. SEM was measured on Shimadzu SS-550 and Hitachi Model S-4800 instruments. TEM was measured by Philips Tecnai G² F20 instrument. AFM was measured by Veeco Metrology Nanoscope IIIa. XPS spectra were obtained with a Kratos Axis Ultra DLD spectrometer. Element analysis data were obtained with an Elementar Vario-EL instrument. FTIR spectra were carried out on KBr pellets in a BRUKER VECTOR 22 spectrometer.

	Without Hydrothermal Treatment	Hydrothermal Treatment 6h	Hydrothermal Treatment 12h
C	25.95	22.85	20.32
H	3.65	3.11	3.44
N	6.31	6.41	6.11

Table S1 EA analysis data of La-EDTA CPs obtained by (column a) without hydrothermal treatment and after 6 h (column b), 12 h reaction (column c) at 160 °C with the molar ratio of EDTA-2Na: La³⁺=4: 8, and the La³⁺ is 8 mmol.

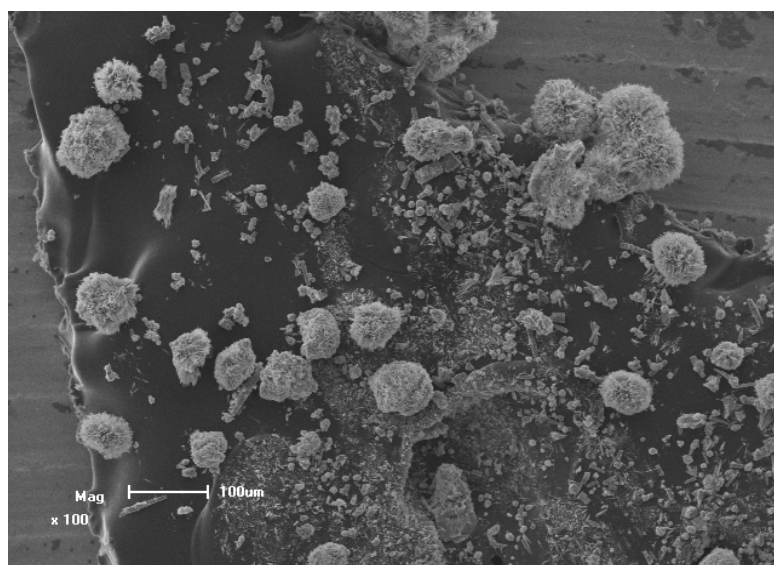


Fig. S1 Low resolution SEM image of Ce-EDTA hyperbranched microspheres assembled by ultrathin nanoribbons.

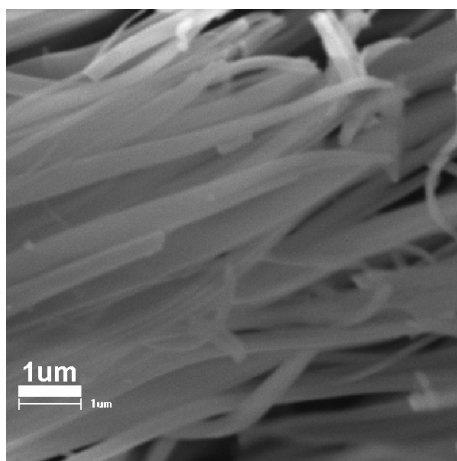


Fig. S2 The high resolution SEM image of nanoribbons of Ce-EDTA coordination polymers (CPs).

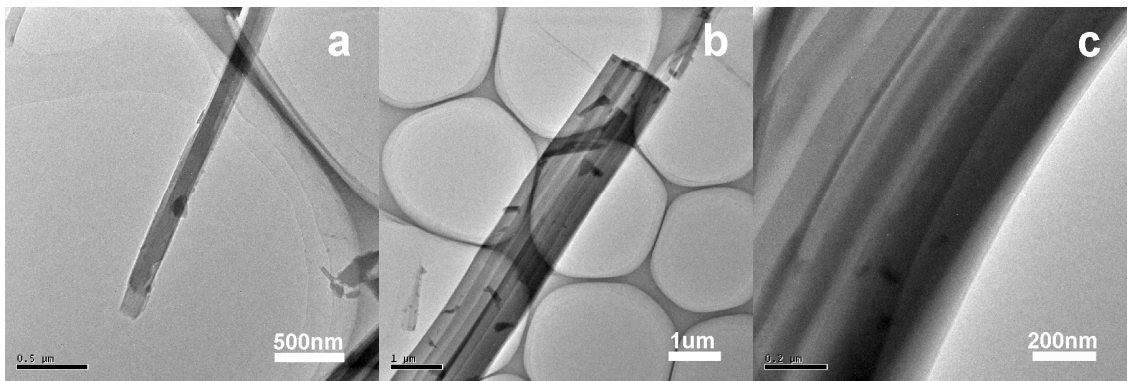


Fig. S3 TEM images of multi-layer nanoribbons of La-EDTA CPs.

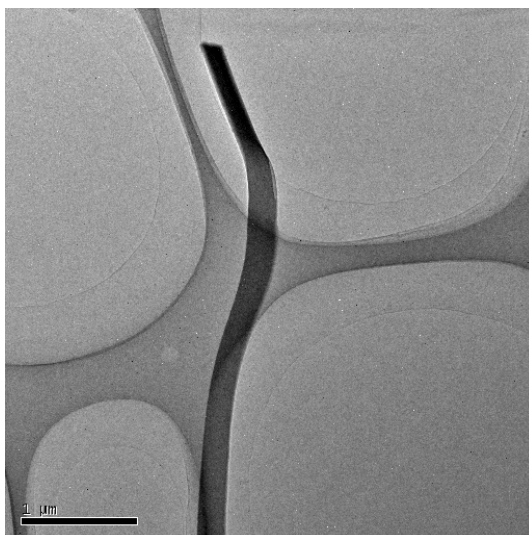


Fig. S4 TEM image of ultrathin nanoribbon of La-EDTA CPs in Figure 1d after radiation of electrons for several seconds.

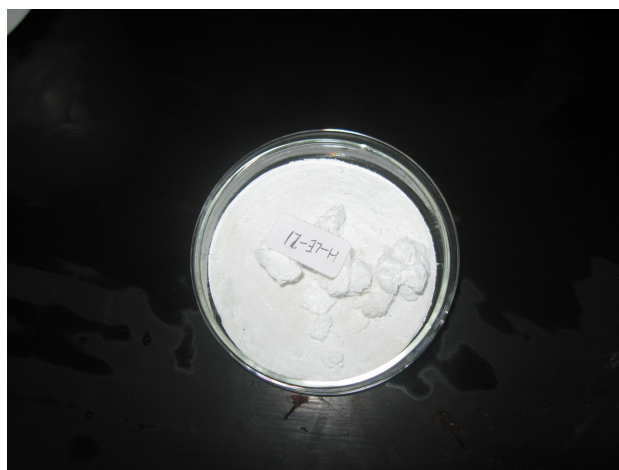


Fig. S5 An optical photo of La-EDTA CPs as-prepared products.

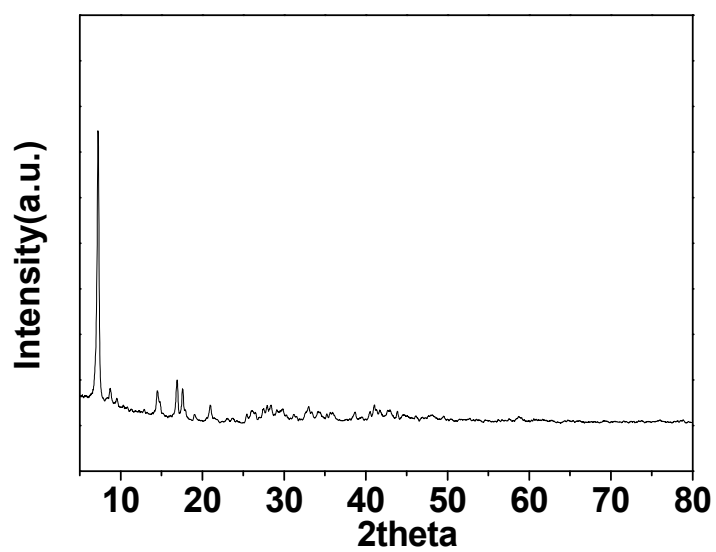


Fig. S6 The XRD pattern of La-EDTA CPs products obtained after 24 h reaction at 160 °C, with the molar ratio of EDTA-2Na: La³⁺=4: 8, and the La³⁺ is 8 mmol.

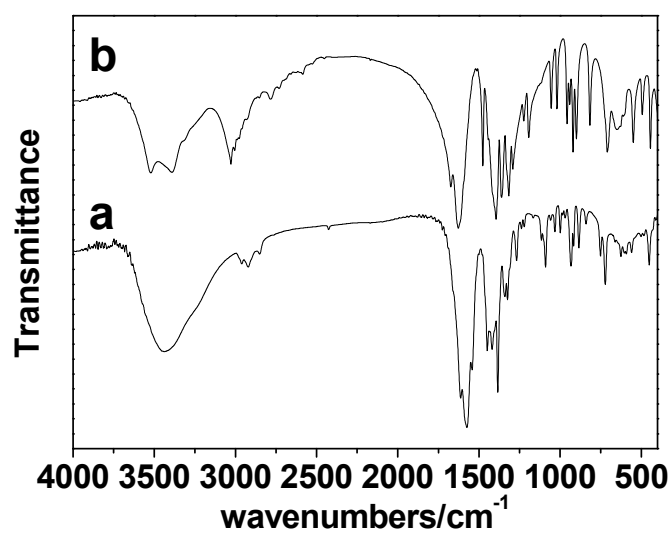


Fig. S7 The FTIR spectra of (a) La-EDTA coordination polymers obtained after 24 h reaction at 160 °C with the molar ratio of EDTA-2Na: La³⁺=4: 8, and the La³⁺ is 8 mmol; (b) Pure EDTA-2Na ligands (C₁₀H₁₄N₂O₈Na₂·2H₂O).

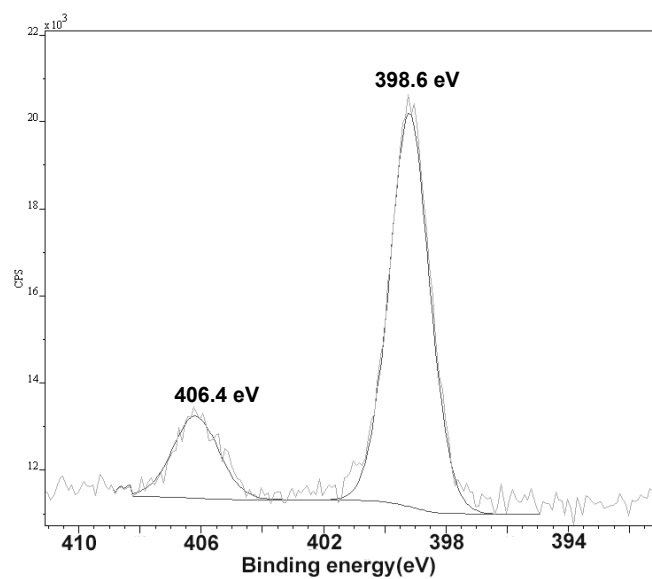


Fig. S8 The XPS spectrum of La-EDTA CPs obtained after 24 h reaction at 160 °C with the molar ratio of EDTA-2Na: La^{3+} =4: 8, and the La^{3+} is 8 mmol.

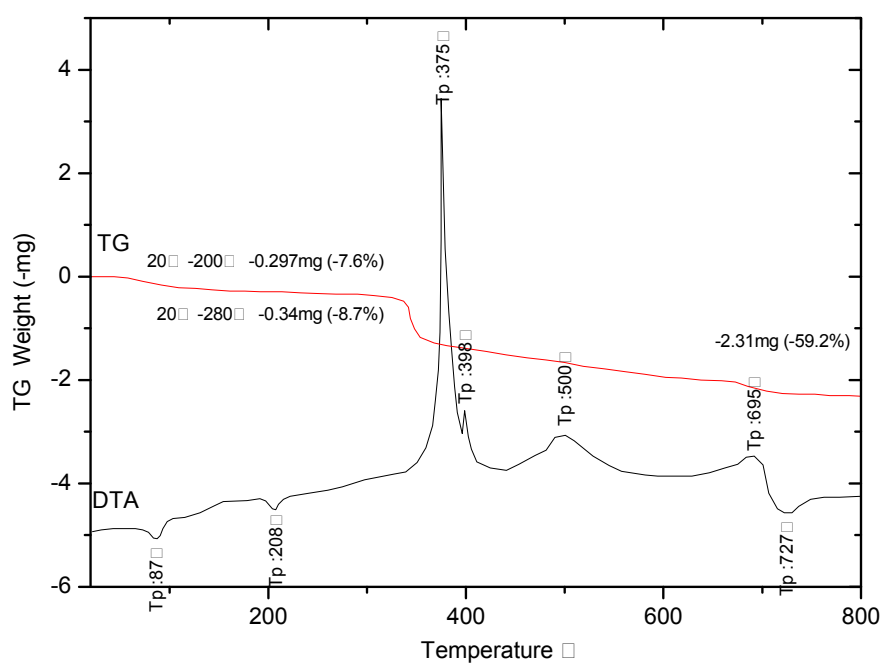


Fig. S9 The TGA curve of La-EDTA CPs obtained after 24 h reaction at 160 °C with the molar ratio of EDTA-2Na: La³⁺=4: 8, and the La³⁺ is 8 mmol.

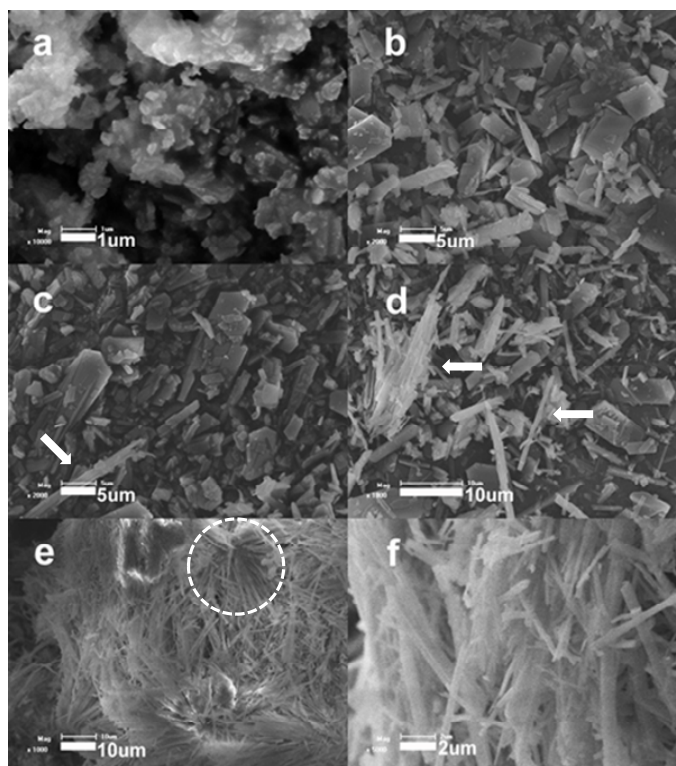


Fig. S10 SEM images of La-EDTA CPs obtained (a) without hydrothermal treatment. After 2 h(b), 6 h(c), 8 h(d) and 12 h(e, f) reaction at 160 °C with the molar ratio of EDTA-2Na: La^{3+} =4: 8, and the La^{3+} is 8 mmol.

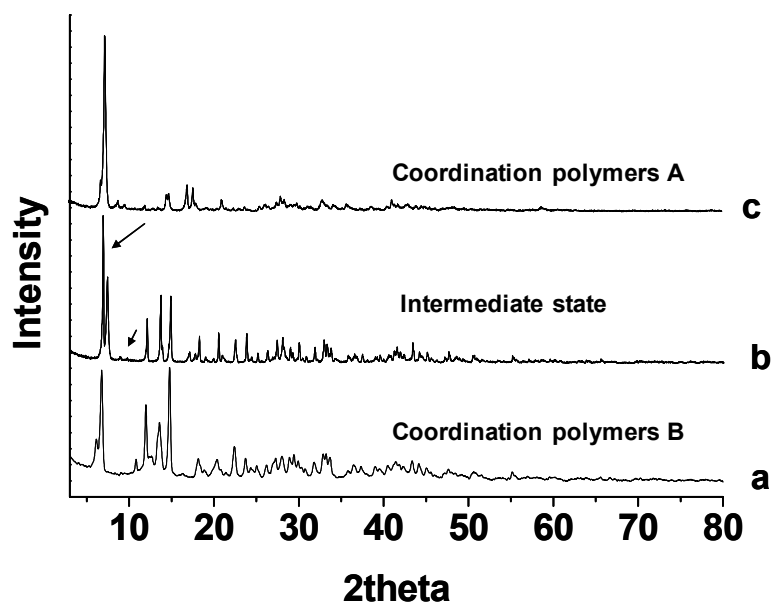


Fig. S11 The XRD patterns of La-EDTA CPs obtained (a) without hydrothermal treatment. (b) After 6 h. The arrows pointed out the “coordination polymers A” in intermediate state. (c) After 2 h reaction at 160 °C with the molar ratio of EDTA-2Na: La^{3+} = 4: 8, and the La^{3+} is 8 mmol.