

Supporting Information

Spontaneous Formation and Electrogenerated Chemiluminescence of Tris(bipyridine) Ru(II) Derivative Nanobelts

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Experimental Section

Nanobelt Preparation: Ru-LC was prepared by a previously reported method [5]. It is totally insoluble in water, but very soluble in polar organic solvents, such as acetonitrile (MeCN) and acetone. Ru-LC nanobelts were synthesized by a simple reprecipitation method from a 4% w/v solution in MeCN at room temperature. In a typical preparation, 4 μ L of this solution was rapidly injected into 10 mL highly pure Millipore water under ultrasonic stirring at room temperature in an ultrasonic cleaning bath (Branson ultrasonic cleaner, model 2150, USA) for 30 s, followed by aging in a closed vial at room temperature for 24 h. The resulting solution is clear and orangish yellow.

Characterization. UV-vis spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-3 spectrofluorimeter (ISA-Jobin Yvon Horiba, Edison, NJ) using a 1 cm path length quartz cuvette. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer using Cu-K α radiation at a scan rate of 0.05° 2 θ S⁻¹. Scanning electron microscopy (SEM) was performed with a LEO 1450VP microscope at an accelerating voltage of 20 kV and linked with an Oxford Instruments X-ray analysis system. Transmission electron microscopy (TEM) analysis and selected area electron diffraction (SAED) were conducted using a JEOL 2100F microscope at an accelerating voltage of 200 kV. Fluorescence image was observed by an inverted optical microscope (Model TE 300, Nikon) and images of the emission could be taken with a camera (Model 7404-0001, Roper Scientific Inc.) during operation. The ζ potential of Ru-LC nanobelts was measured by Zeta Potential Analyzer (90 Plus/BI-MAS, Brookhaven Instruments Corporate, USA).

ECL experiments: The electrochemical measurements coupled with ECL experiments were performed with an Autolab electrochemical station (Ecochemie) in aqueous solution using 0.1 M phosphate buffer solution (PBS) as supporting electrolyte and 0.1 M tripropylamine (TPrA) as a coreactant. All solutions were prepared with deionized water (Milli-Q, Millipore). The pH value of the aqueous solution was un-adjusted and was 7.2. The working electrode was an inlaid Pt disc (2 mm diameter) [or a Pt ultramicroelectrode (25 μ m diameter) for single nanobelt]; a 2 mm or 25 μ m diameter, J-shaped Pt electrode or ultramicroelectrode was used for ECL intensity measurements. Platinum electrodes were polished with 0.05- μ m alumina to obtain a mirror surface and then were ultrasonicated and thoroughly rinsed with Milli-Q water. The reference electrode was an Ag/AgCl electrode. A platinum wire was used as the auxiliary electrode. The ECL signal was measured with a photomultiplier tube (PMT, Hamamatsu R4220p) installed beside the electrochemical cell. A voltage of 750 V was supplied to the PMT with a high-voltage power supply series 225 (Bertan High Voltage Corp., Hicksville, NY). Current-voltage and light-voltage curves for these devices were taken using an AUTOLAB electrochemical station coupled with an electrometer (Keithley model 6517). All measurements were performed at room temperature (25°C), in ambient atmosphere. To measure the ECL of a single Ru-LC NB, 5 μ L of NB suspension (Conc.: 1 x 10⁻¹⁴ M in NB particles) was dropped on a platinum UME, then dried

in air. We used optical microscopy to determine whether a single Ru-LC NB was deposited on a platinum UME. If a single Ru-LC NB indeed deposited on a platinum UME, then we could measure its ECL signal.

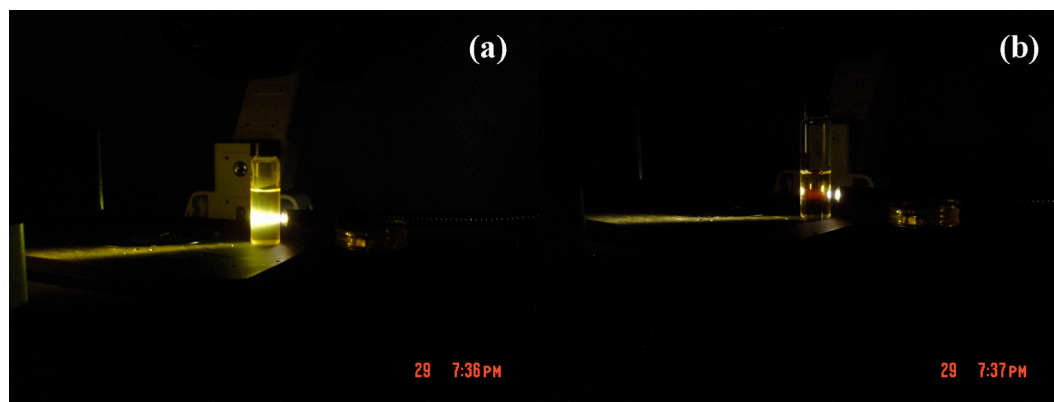


Figure S1. (a) Light scattering of Ru-LC nanobelts dispersion aqueous solution; (b) No light scattering for Ru-LC molecule solution in MeCN

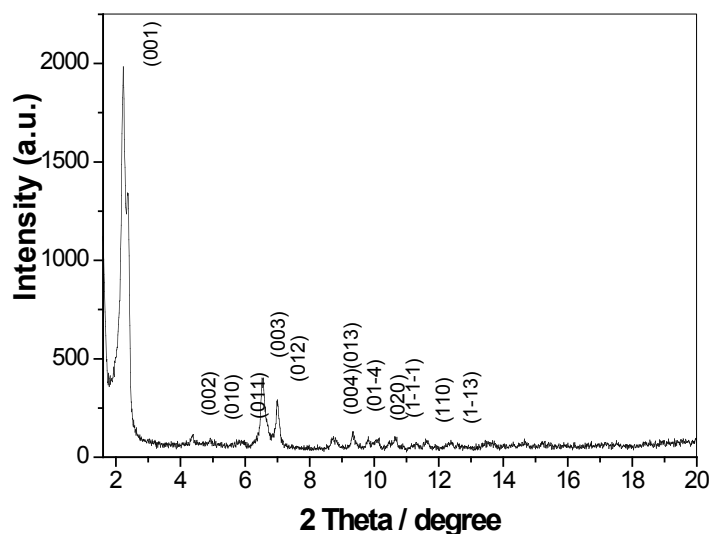


Figure S2. XRD of Ru-LC nanobelt powders

All the peaks in Figure S2 can be readily indexed to a pure triclinic crystalline phase [space group: $P\bar{1}$] of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CH}_3(\text{CH}_2)_{14}\text{COO})_2\text{-bpy})](\text{ClO}_4)_2$ with calculated lattice contents $a = 9.0624 \text{ \AA}$, $b = 18.0713 \text{ \AA}$, $c = 41.0781 \text{ \AA}$, $\alpha = 97.16^\circ$, $\beta = 94.03^\circ$, $\gamma = 97.00^\circ$ and cell volume = 6600.12 \AA^3 , which are in good agreement with the values of single crystal.

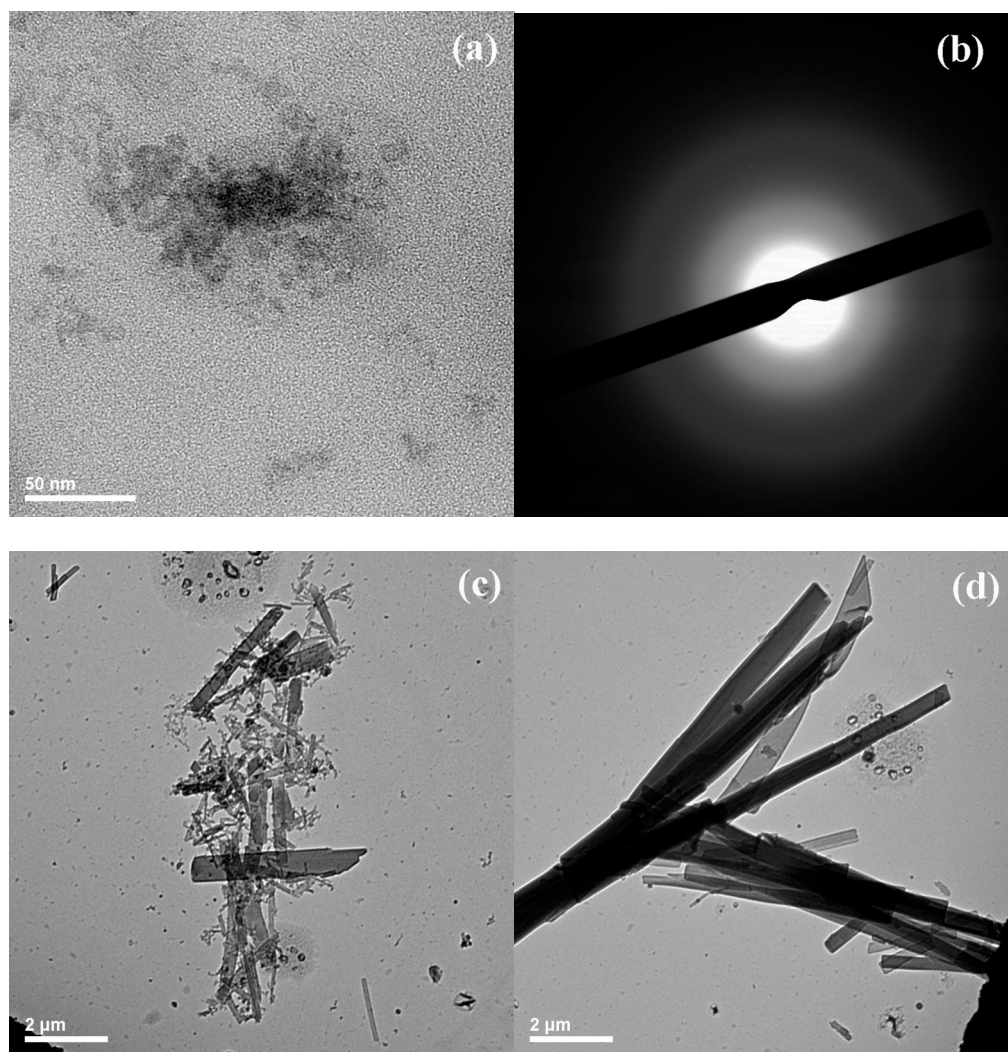


Figure S3. TEM images (**a**, **c** and **d**) and SAED pattern (**b**) of Ru-LC samples obtained at room temperature in early stages. (**a** and **b**) 5 min. (**c**) 30 min. (**d**) 2 h. ($[\text{Ru-LC}] = 1,35 \times 10^{-5} \text{ M}$, pH 7.0).

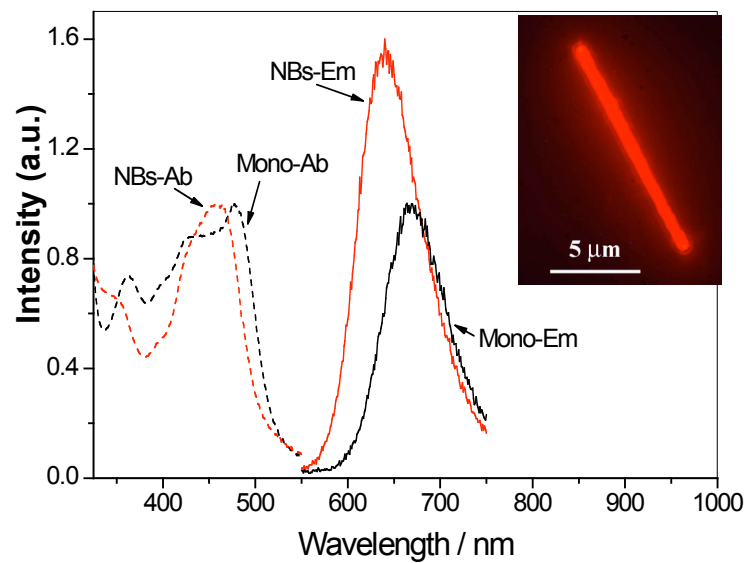
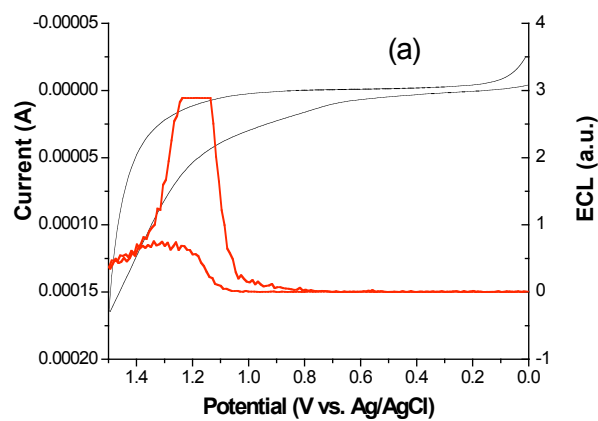


Figure S4. Normalized absorption (dashed) and PL (solid) spectra of Ru-LC nanobelts (red) in water aged for two weeks and Ru-LC monomers (black) in MeCN. Concentrations of Ru-LC monomers and NBs are 6.75×10^{-6} M and 2.25×10^{-14} M, respectively. Inset is fluorescence image of single nanobelt.



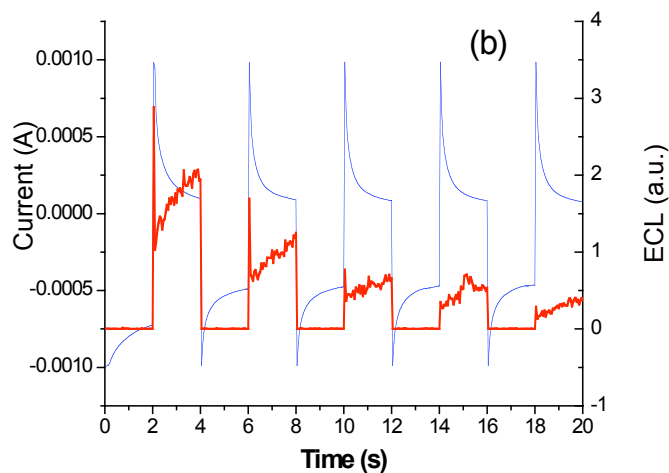


Figure S5. (a) Cyclic voltammogram and ECL curve of Ru-LC nanobelt suspension. (b) Current and ECL for potential steps between -1.25 V and 1.25 V. Step durations are 2, 6, 10, 14 and 18 s at each potential. Supporting electrolyte and coreactant are 0.1 M phosphate buffer solution (pH 7.2) and 0.1 M TPrA, respectively. Concentration of NBs is 2.2×10^{-14} M. Platinum electrode, 1.5 mm, (a) potential scan rate, 0.1 V/s and (b) pulse width, 2 s. The limiting flat portion of the ECL emission in (a) was caused by saturation of the current amplifier used to measure light intensity.