

# **Electrogenerated Upconverted Emission from Doped Organic Nanowires**

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**Electronic Supplementary Information (ESI)**

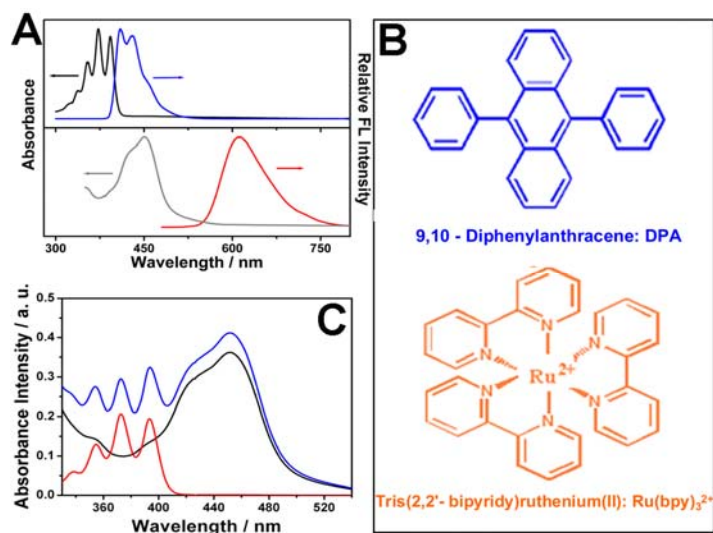
### *Experimental details*

$\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (bpy=2,2'-bipyridine) was synthesized according to the literatures [ J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, 1983, **105**, 5583-5590.] Tripropylamine (TPrA), 9, 10-Diphyanthracene (DPA) and Hexadecyl trimethyl ammonium bromide (CTAB) were purchased from Alfa-Aesar. The 0.20 M stock solutions of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  (Beijing chemical reagent Ltd.) were used for the preparation of phosphate buffer solutions (PBS, pH 8.0). Ethanol, acetone, acetonitrile and tetrahydrofuran were purchased from Beijing chemical reagent Ltd. All chemicals were of analytical grade and without further purification.

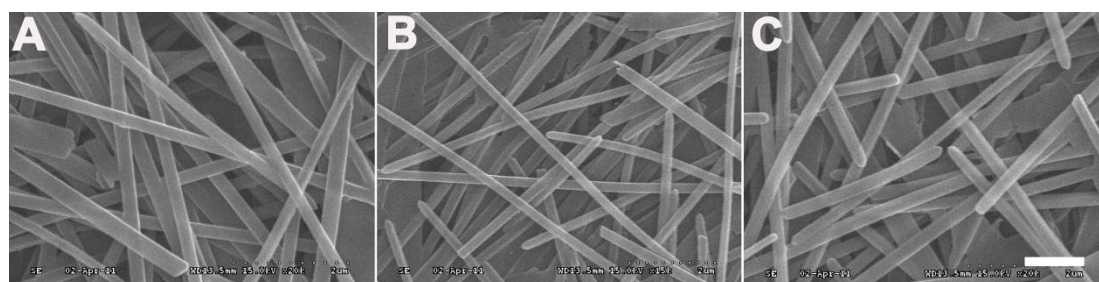
$\text{Ru}(\text{bpy})_3^{2+}$ @DPA doped organic wires were fabricated via a simple reprecipitation method. In a typical preparation, a mixed stock solution of  $\text{Ru}(\text{bpy})_3^{2+}$  and DPA (100  $\mu\text{L}$ ) with different molar ratios dissolved in a good solvent of acetonitrile and tetrahydrofuran (1:1, v/v) were rapidly injected into the poor solvent of water in the presence of CTAB (5 mL,  $C_{\text{CTAB}} = 0.25$  mM) under continuous ultrasonication. After aging for 2 h, the colloidal suspension of doped wires was obtained and treated with three centrifuge-wash circles to remove the surfactant CTAB. The molar ratio of  $\text{Ru}(\text{bpy})_3^{2+}$  to DPA was controlled by fixing the concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  at 50  $\mu\text{M}$  and changing that of DPA in the stock solutions to ensure the comparability. The morphologies and sizes of the doped wires were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 15 kV. To minimize sample charging, a thin layer of Pt was deposited onto the samples before SEM examination. TEM image was obtained using a JEOL JEM-2010 transmission electron microscope with an accelerating voltage of 200 kV. Fluorescence microscopy image of wires was obtained by laser confocal scanning microscope (Olympus, FV1000-IX81), excited with the UV band (330-380 nm) of a mercury lamp.

ECL measurements were performed using a homemade system, consisting of a BPCL Ultra-Weak Chemiluminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China), an electrochemistry workstation (Zahner, Zennium, Germany), an electrochemical cell and a computer control systems. Cyclic voltammetric measurements were carried out with an electrochemistry

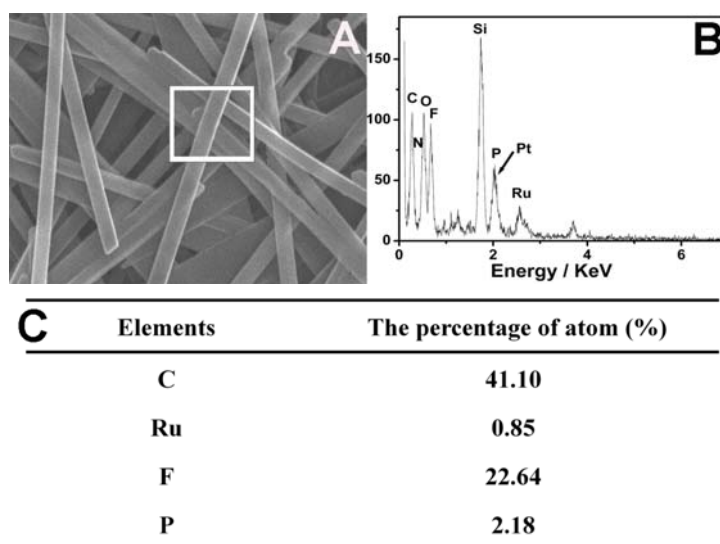
workstation. A conventional three-electrode system was used and a glass carbon electrode (GCE) was used as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode (sat. KCl) as the reference electrode. The working electrode was pretested prior to use by polishing its surface with aqueous slurries of alumina powders (average particle diameters: 1.0  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$   $\alpha$ - $\text{Al}_2\text{O}_3$ ) on a polishing microcloth and rinsed with water, sonicated in acetone for 5 min and dried in air. A commercial 5 mL cylindroid quartz cell was used as electrochemical reaction cell which was the ECL cell. ECL signals were recorded by an Ultra-weak Chemiluminescence Analyzer controlled by a personal computer with 0.1 second of sample interval. While collecting CL signals, the ECL cell was placed directly in front of the photomultiplier (PMT operated at  $\sim 1000$  V). The emitted light is measured with a selected high sensitivity, low noise photo multiplier. The doped organic wires dropped on the clean GCE to test its ECL.



**Figure S1** (A) Normalized absorption and fluorescence emission spectra of DPA (top) and Ru(bpy)<sub>3</sub><sup>2+</sup> (bottom) monomers dissolved in solvent of acetonitrile and tetrahydrofuran (1:1, v/v). DPA was excited with 375 nm, while Ru(bpy)<sub>3</sub><sup>2+</sup> was excited with 510 nm and measured under the air free condition. (B) Chemical structures of DPA (top) and Ru(bpy)<sub>3</sub><sup>2+</sup> (bottom). (C) The absorption spectra of the doped wires (blue), DPA (red) wires dispersed in CTAB solution, and Ru(bpy)<sub>3</sub><sup>2+</sup> (black) monomers dissolved in solvent of acetonitrile and tetrahydrofuran (1:1, v/v). The absorption spectrum of the doped wires has the absorption peaks of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and DPA, which has no considerable difference to that of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and DPA wires. It indicated that there was no interactions between Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and DPA in the ground state.



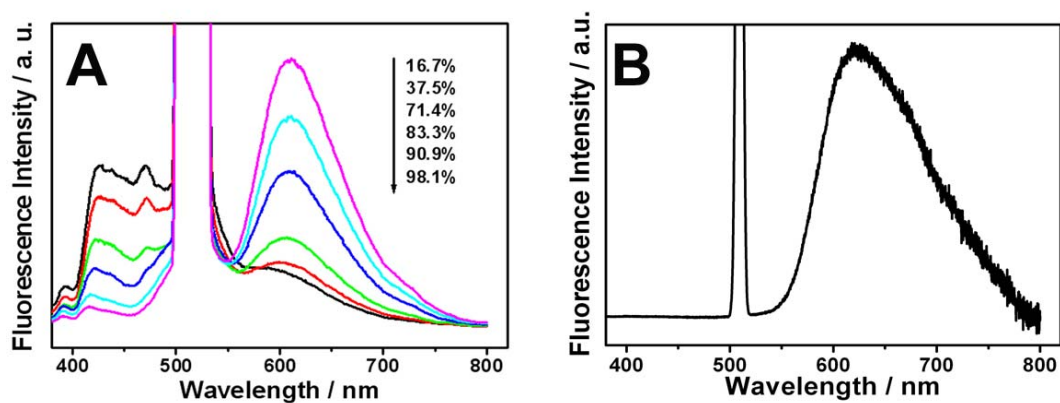
**Figure S2** SEM images of the wires with different molar ratio of  $\text{Ru}(\text{bpy})_3^{2+}/\text{DPA}$ : (A) 1:3, (B) 1:5, and (C) 1:10. All the wires with different molar ratio have well-defined wire-like structures. The molar ratio of  $\text{Ru}(\text{bpy})_3^{2+}/\text{DPA}$  does not have an obvious effect on the morphology and surface topography of the samples. Scale bar is 1  $\mu\text{m}$ .



**Figure S3** EDX spectra of the  $\text{Ru}(\text{bpy})_3^{2+}@\text{DPA}$  wires (B) was taken from the area marked in (A). The Si, O peak is from the silicon wafers and the Pt peak is from the thin layer of Pt deposited onto the samples before SEM examination. There are intense peaks of C, N, P, F and Ru, which proves that the composite wires are composed of  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  and DPA. (C) The exact concentrations of main elements loaded in the wires.

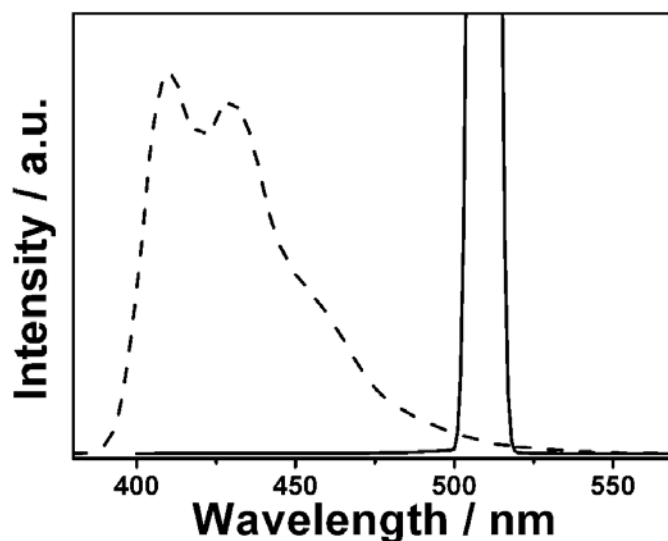
<b>Physicochemical properties</b>	<b>Ru(bpy)<sub>3</sub><sup>2+</sup></b>	<b>DPA</b>
<b>Singlet excited level energy, eV</b>	<b>2.70</b>	<b>3.05</b>
<b>Triplet excited level energy, eV</b>	<b>2.03</b>	<b>1.77</b>
<b>Life time, ns</b>	<b>~1000</b>	<b>8.14</b>

**Table S1** Physicochemical properties of Ru(bpy)<sub>3</sub><sup>2+</sup> and DPA

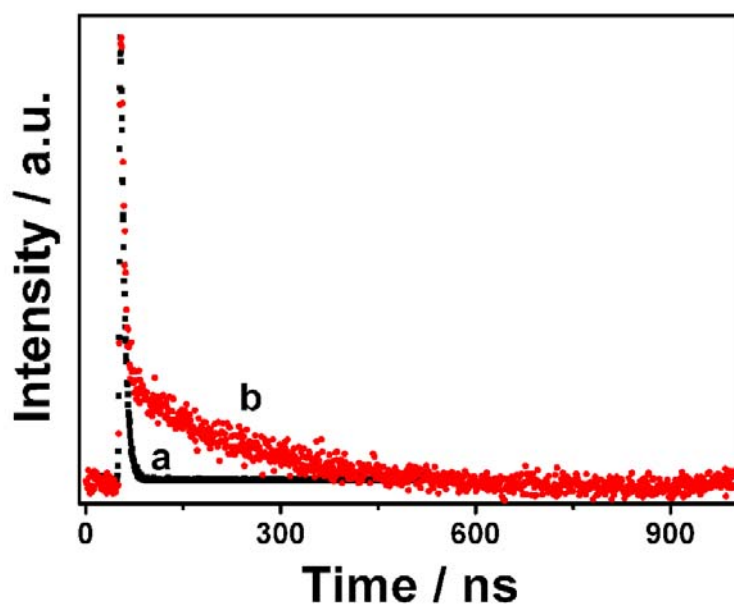


**Figure S4** (A) Fluorescence spectra of the doped wires with different molar ratios of Ru(bpy)<sub>3</sub><sup>2+</sup>/DPA. (B) In the fluorescence spectrum of the pure Ru(bpy)<sub>3</sub><sup>2+</sup>, no peak appears at 450 nm, which indicates that the high energy peak at 450 nm in (A) is related to DPA. The intense peak at 510 nm is from the scattering of the excitation light.

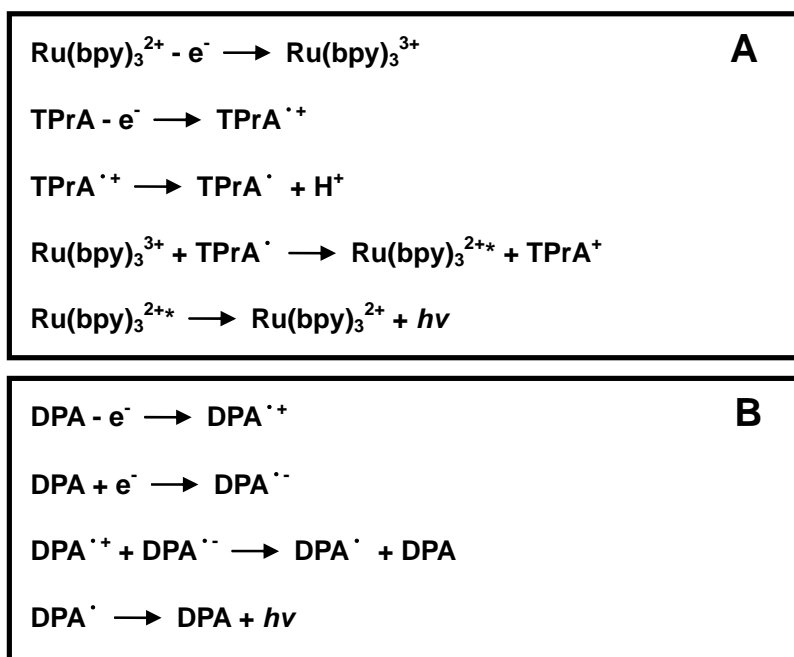




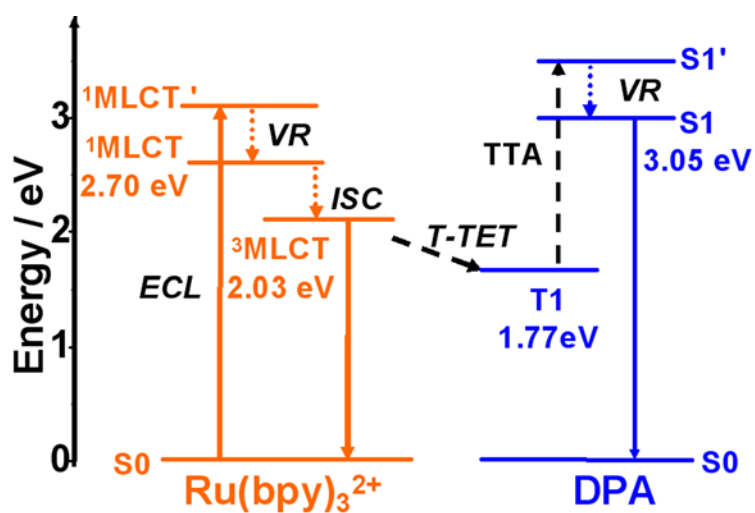
**Figure S5** PL spectra of pure DPA wires (the solid line, excited with 510 nm) and the doped wires (the dashed line, excited with 375 nm) prepared with reprecipitation method. The peak at 510 nm is from the excitation light. The result indicates that DPA itself is not luminescent under green excitation, and the blue PL band in the doped wires are from the triplet-triplet energy transfer between  $\text{Ru}(\text{bpy})_3^{2+}$  and DPA, and the subsequent upconversion based on triplet-triplet annihilation.



**Figure S6** Fluorescence decay profiles of DPA wires (a) and the doped wires (b) monitored at 450 nm. The lifetime of doped wires ( $\sim 300$  ns) is much more elongated than that of pure DPA wires ( $\sim 6$  ns), because it is temporally limited by the  $\text{Ru}(\text{bpy})_3^{2+}$  decay-time and the diffusion. The result confirms the upconversion in the doped wires.



**Scheme S1** The ECL mechanisms of (A)  $\text{Ru(bpy)}_3^{2+}$  and (B) DPA. TPrA was oxidized in the electrode to form excited TPrA before  $\text{Ru(bpy)}_3^{2+}$  was oxidized in the electrode to form  $\text{Ru(bpy)}_3^{3+}$ . Then, the  $\text{TPrA}^{\cdot+}$  radical loses a proton to form the strongly reducing intermediate TPrA radical. TPrA radical can reduce  $\text{Ru(bpy)}_3^{3+}$  into  $\text{Ru(bpy)}_3^{2+*}$  which would produce ECL emission. The ground-state DPA molecules were oxidized and reduced at electrode. Ground- and excited-state molecules were generated as the result of the annihilation reaction between anion and cation radicals, and the excited state emitted blue light.



**Scheme S2** Qualitative energy states involved in a TTA supported upconversion process from Ru(bpy)<sub>3</sub><sup>2+</sup> to DPA by ECL which supplies excitation energy. The dashed pathway represents the energy transfer and upconversion in the system. Acronyms: EC, electrochemical reaction; VR, vibrational relaxation; ISC, intersystem crossing; T-TET, triplet-triplet energy transfer; TTA, triplet-triplet annihilation.