Supporting Information

Enhanced electrochemiluminescence efficiency of Ru(Ⅱ) derivative covalently linked carbon nanotubes hybrid

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Experimental Section

Materials and Reagents

4,4'-dicarboxy-2,2'-bipyridine was from Chemzam Pharmtech Co.Ltd. CNTs were obtained from Shenzhen Nanotech Port Co. Ltd (China). 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-Hydroxysuccinimide (NHS) were obtained from Aldrich (USA). Tri-*n*-propylamine (TPA, 98%) and Nafion perfluorinated ion-exchange resin (5 wt % solution in a mixture of lower aliphatic alcohols and 15-20% water) were purchased from Sigma. Other chemicals were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with deionized water (18.2 MΩ, PureLab Classic Corp., USA).

Apparatus

^{1}H NMR spectra were conducted on a Bruker AVANCE DRX-500 spectrometer at room temperature. Chemical shifts reported relative to tetramethylsilane were given in ppm. Electrospray mass spectrum (ESI-MS) was collected on a LCQTM MS^n mass spectrometer (Finnigan, USA). UV-vis absorption spectra were recorded on a UV3600 spectrophotometer (Shimadzu, Japan). FT-IR spectrum were carried out on a Tensor 27 (Bruker Inc., Germany) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Pure KBr was used as a nonabsorbing reference powder. Element Analysis was obtained from CHN-O-Rapid instrument (Heraeus, Germany). Cyclic voltammetry (CV) was performed with the CHI 1140A electrochemical workstation. The three-electrode system was consisted of modified GC electrodes as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The ECL signals were measured with an MPI-A multifunctional electrochemiluminescent analytical system (Xi'an Remex Analyse Instrument Co. Ltd.). A voltage of 600 V was supplied to the photomultiplier tube (PMT).

Synthesis of Ligand (4,4'-Aminomethyl-2,2'-bipyridine)

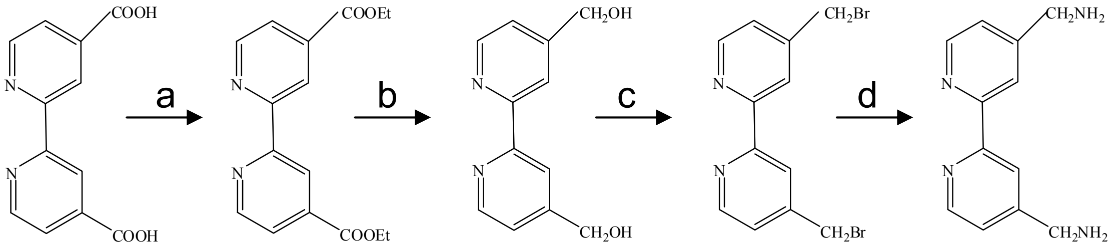

Figure S1. Preparation of Ligand 4,4'-$(CH_2NH_2)_2$bpy, a: EtOH-H_2SO_4, reflux, 92%; b: $NaBH_4$-EtOH, reflux, 98%; c: HBr-H_2SO_4, reflux, 66%; d: potassium phthalimide, N_2H_4, heat, 99%

Figure S1 illustrates the synthesis procedure of 4,4'-Aminomethyl-2,2'-bipyridine. Steps a, b and c were carried out according to literature and

4,4'-bromomethyl-2,2'-bipyridine was obtained. In step d, a mixture of 4,4'-bromomethyl-2,2'-bipyridine (157 mg, 0.7 mmol) and potassium phthalimide (846 mg) in DMF (20 mL) was heated at 50 ^{o}C under nitrogen atmosphere. After 15 h, excess water was added to the mixture, and the resulting precipitate was filtered and dried. A mixture of resultant solid above (120 mg) and hydrazine monohydrate (250 μL) in EtOH (10 mL) was heated at 100 ^{o}C for 18 h. Saturated aqueous NaCl solution (35 mL) was added to the mixture. The mixture was adjusted to pH 13 with 50% NaOH solution. The organic layer was extracted with CH_2Cl_2 (100 mL × 4), dried over anhydrous Na_2SO_4, and evaporated to dryness, yielding 69.75 mg of 4,4'-Aminomethyl-2,2'-bipyridine (71% yield) as a white powder.

Products of each step were characterized by ^{1}H NMR spectral analysis and the results were in good agreement with those reported in the literatures previously. The resultant solid was used for the next step without further purification.

Sythesis of Ru(bpy)$_2$(4,4'-(CH$_2$NH$_2$)$_2$bpy)Cl$_2$

Ru(bpy)$_2$Cl$_2$ was prepared according to a modified procedure from commercial $RuCl_3·3H_2O$ and bipyridine (B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.* **1978**, 17, 3334).

Ru(bpy)$_2$(4,4'-(CH$_2$NH$_2$)$_2$bpy)Cl$_2$ (Ru(II)) was prepared using a modified literature method[7] for ruthenium(II) bipyridyl complexes with phosphonic acid functional groups. A solution of 4,4'-Aminomethyl-2,2'-bipyridine (0.187 mmol) and [Ru(bpy)$_2$Cl$_2$] (0.187mmol) in a 20 mL mixture of EtOH/H_2O (9:1, v:v) was heated at reflux under a nitrogen atmosphere for 12 h. The solvents were removed by rotary evaporation and a red-orange solid was resulted. ^{1}H NMR (500MHz,CD_3OD) δppm 8.74(m, 6H), 8.15(s, 4H), 7.85(s, 4H), 7.73(d, 2H, *J*=5.4 Hz), 7.50(s, 6H), 4.08(s, 4H); ESI-MS: m/z 314.17(see Figure S2). The Ru(bpy)$_2$(4,4'-(CH$_2$NH$_2$)$_2$bpy)Cl$_2$ showed remarkable stability, and it could be stored in aqueous solutions for months.

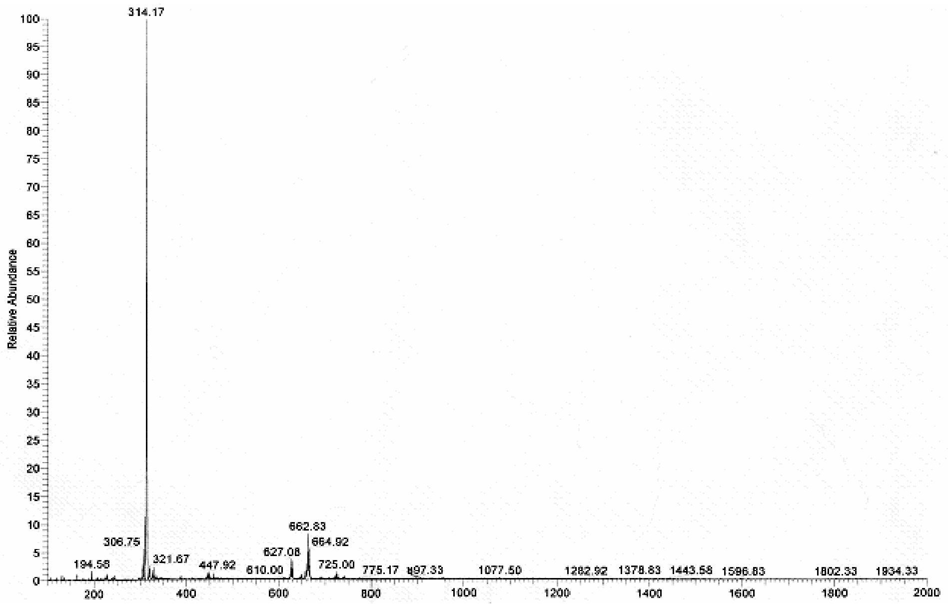

Figure S2. Electrospray Mass Spectrum(ESI-MS) of

Ru(bpy)$_2$(4,4'-(CH$_2$NH$_2$)$_2$bpy)Cl$_2$ in H$_2$O

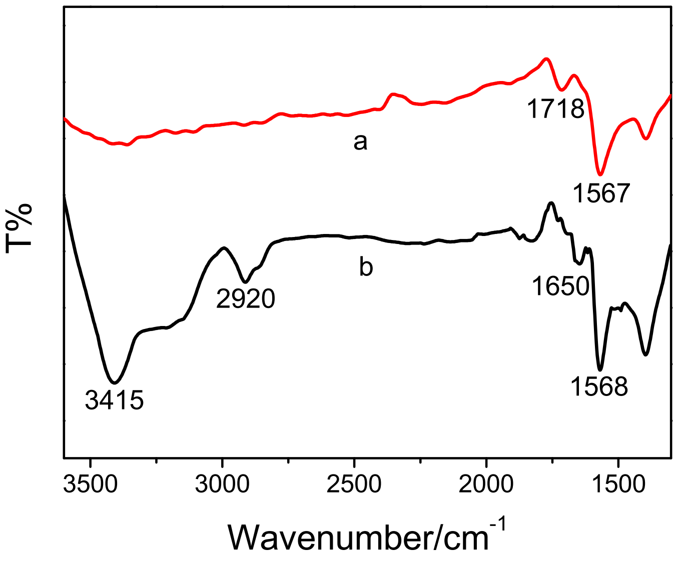

Figure S3. FT-IR spectra of oxidized CNTs (a) and Ru-CNTs (b)

Preparation of the ECL sensor

To a suspension of 2 mg oxidized CNTs in a mixture (1 mL) of EDC (5 mg/mL) and NHS (5 mg/mL) was added 1 mL of 4 mM Ru(II) complex. The resulting suspension was stirred overnight, then centrifuged, washed with deionized water and evaporated to dryness. The desired solid was then dispersed in deionized water to a concentration of 1 mg/mL. Otherwise, Ru-CNTs was more difficultly soluble in deionized water than oxidized CNTs due to the reaction between –COOH from oxidized CNTs and -NH_2 from Ru(II) complex. Before modification, a glassy carbon electrode (GCE) was polished successively. A 5 μL of aforesaid suspension was dropped on the surface of the pretreated electrode and the solvents were allowed to evaporate at room temperature in the air. The CNTs/GCE and Ru-CNTs/GCE electrodes were then coated by hand with a 5 μL 1.0 % Nafion solution. The modified GCEs were then placed in an electrolytic cell containing 2 mL 100mM PBS (pH 7.4) and 50 mM NaCl to perform electrochemical and ECL measurements.