Title: Eu(III)-coupled Graphene oxide as a Luminescent Material

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Experiment section

1.Materials.

Graphene oxide (GO) purchased from Jiansin Scientific and Trading Co., Ltd. Europium chloride ($EuCl_3{\cdot}6H_2O$) was obtained by dissolving Eu_2O_3 (99.99%, Shanghai Yuelong) in hydrochloric acid followed by successive fuming to remove excess acid. 2-Thenoyltrifluoroacetone (Htta, AR), 1,10-phenanthroline (AR), and the other chemicals were all commercially available and used as received.

2.Characterization and test of the materials.

^1H NMR spectra were recorded on a Varian Mercury-300B spectrometer. CHN elemental analyses were measured on an Elementar Vario EL analyzer. The contents of Eu3$^+$ ion were obtained by inductively coupled plasma-atomic emission spectroscopy (ICP) using an IRIS Advantage ER/S spectrophotometer. Fourier transform infrared (FTIR) spectra were conducted within the 4000-400 cm^{-1} wavenumber range using a Nicolet 360 FTIR spectrometer with the KBr pellet technique. Transmission electron microscope images were taken on a TECNAI G2Tf20 transmission electron microscope (PEI American) apparatus. The UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 950 spectrophotometer. The luminescence spectra and the lifetime measurements were measured on an Edinburgh Instruments FSL920 fluorescence spectrometer, with a 450 W Xe arc lamp as the steady-state excitation source or a Nd-pumped OPOlette laser as the excitation source for lifetime measurements; in the experiments of photoluminescent stability, monochromic light (384 nm) separated from the 450 W Xe arc lamp was used as the irradiation source, with a shutter opening after 10 s for 1200 s. Thermogravimetric analysis(TGA) was performed on a Perkin-Elmer thermal analyzer up to 800°C at a heating rate of 10°C /min under N_2 atmosphere.

3. Synthetic procedures

3.1. Preparation of 1,10-Phenanthroline-5, 6-dione (1).

The method used for the synthesis of 1,10-Phenanthroline-5,6-dione was similar to the method used in the literature procedure [1]. 1,10-Phenanthroline monohydrate (5 g, 25.2 mmol) was dissolved in small portions with stirring in 35 mL of concentrated mixture acid of sulfuric acid and nitric acid (v/v=2:1) in a round-bottom flask in ice bath. After stirring 5 minutes, add Sodium bromide (5.19 g, 50.4 mmol) equipped with a reflux condenser, the flask with the mixture was heated slowly to 85 °C and kept at reflux temperature for 4 h. After 4 h, the mixture was dropped into 200ml of cold water while it was hot.

In 200ml of water was dissolved 1 mol of sodium hydroxide, and then it was dropped into the mixture followed by cooled to 0°C. After being neutralized to PH=7, the turbid solution was standing and filtered. In the next step, the solids were washed 4-5 times with water and dichloromethane. The combined aqueous solutions were extracted with several portions of dichloromethane, and evaporated under reduced pressure. The combined crystalline residue was recrystallized from 150 mL of ethanol at 85°C to give the pure product. Yield: 40% (4.6 g). δH (300 MHz, DMSO-d_6): 7.58-7.62 (d, 2H), 8.49-8.52 (d, 2H), 9.11-9.13 (d, 2H). Anal. Calcd for

$(C_{12}H_6N_2O_2)_3(H_2O)$: C, 66.67; H, 3.11; N, 12.96%. Found: C, 67.00; H, 2.99; N, 12.99%.

3.2. Synthesis of 2-(4-nitrophenyl)-2,3-dihydro-1H-imidazo[4,5-f][1,10]phenanth-Roline (2).

The product **2** was synthesized according to a modified literature procedure [2]. 1, 10-Phenanthroline-5,6-dione(1) (1.68 g, 8 mmol), 4-nitrobenzaldehyde(1.25 g, 8.3 mmol), and ammonium acetate (12.32 g, 160 mmol) were dissolved in 53 mL of glacial acetic glacial acetic acid lowed. Then the solution was neutralized with concentrated ammonia to PH=7. The precipitate was filtered off and washed with large portions of water. To obtain the pure yellow product, the crystalline residue was recrystallized from ethanol. Yield: 70% (5.2g).δH (300 MHz, DMSO-d_6): 7.81-7.85 (m, 2H), 8.44-8.46 (d, 2H), 8.50-8.53 (d, 2H), 8.90-8.93 (d, 2H), 8.97-9.03 (d, 2H), 8.03-9.04 (d, 2H). MS (CI): m/z=342(MH^+). Anal. Calcd for $C_{19}H_{11}N_5O_2$: C, 66.86; H, 3.23;N, 20.53%. Found: C, 66.80; H, 3.17; N, 20.44%.

3.3. Synthesis of 4-(2,3-dihydro-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)aniline (3).

The product **2** came from last procedure was dissolved in ethanol, added 10% Pd/C and heated to reflux for 1h. Next, hydrazine hydrate (8 ml) was added and kept reflux for another one hour. After the Pd/C was filtered off and the solvent was evaporated, the product **3** was obtained. δH (300 MHz, DMSO-d_6): 6.73-6.76 (d, 2H), 7.80-7.84 (m, 2H), 7.97-7.80 (d, 2H), 8.89-8.92 (d, 2H), 9.00-9.01 (d, 2H), 5.65 (NH^+). MS (CI): m/z=312 (MH^+). Anal. Calcd for $C_{19}H_{13}N_5$: C, 73.31; H, 4.18;

N, 22.51%. Found: C, 73.27; H, 4.09; N, 22.48%.

3.4. Synthesis of Eu(Ⅲ) complexes (4). **(Scheme 1)**

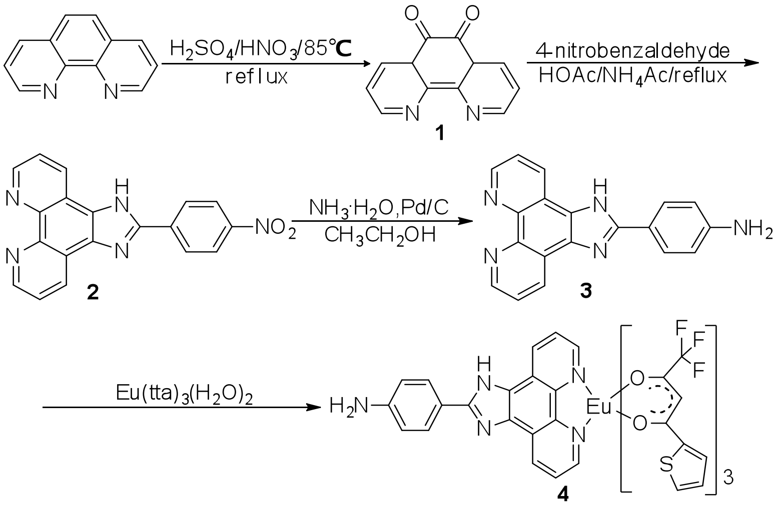
The $Eu(tta)_3(H_2O)_2$ complexes were according to the procedure described by Melby et al [3]. The product **4** was prepared according to the procedure described by Uekawa et al [4]. Production **3** (31.1 mg, 0.10 mmol) was mixed with 25 ml of 95% ethanolic solution with $Eu(tta)_3(H_2O)_2$ (85 mg, 0.10 mmol), and the suspension was sonicated to completely dissolve production **3** and filtered. The filtrate was added 25 ml of water, filtered. The dark yellow solid was washed with ethanol-water (V/V=1:1) and dried in vacuum at room temperature, obtained 43 mg of Eu(Ⅲ) complexes. Elem. Anal. Calcd for $C_{34}H_{28}O_6N_5S_3F_9Eu$: C, 45.68; H, 2.57; N, 6.20; Eu, 17.85%. Found: C,45.61; H, 2.51; N, 6.17; Eu, 17.81%.

3.5. Synthesis of Phen-GO (5).

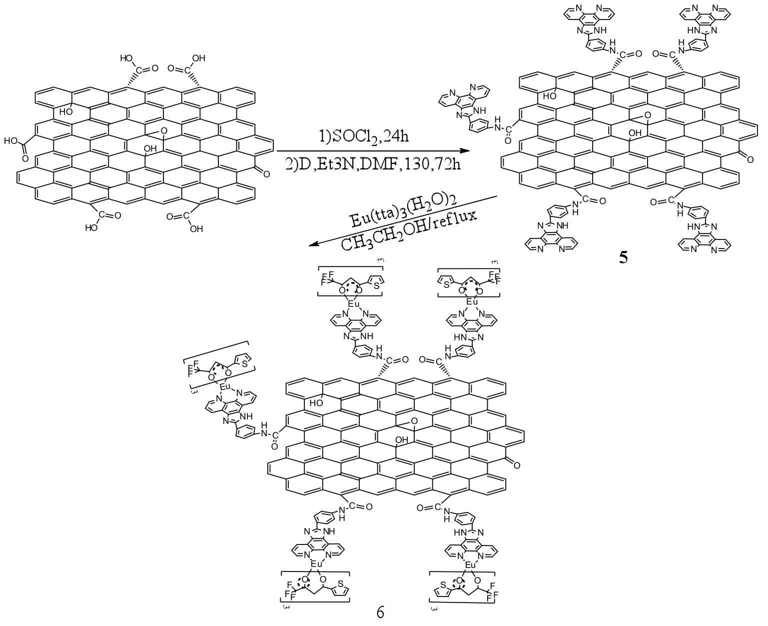
GO (30 mg) was refluxed in $SOCl_2$ (20mL) in the presence of DMF (0.5mL) at 70 °C for 24 h under argon atmosphere. At the end of the reaction, excess $SOCl_2$ and solvent were removed by distillation. In the presence of triethylamine (Et_3N, 0.5mL), the above product was allowed to react with product **3** (30mg) in DMF (10mL) at 130 °C for 72 h under argon. Product **3** has been removed using extensive solvent washing, sonication, and membrane filtration.

3.6. Synthesis of Eu-GO. **(Scheme 2)**

A batch of 8 mg of Phen-GO was refluxed with 10 mg of $Eu(tta)_3(H_2O)_2$ in ethanol. The suspension was collected by centrifugation after 24h, and the excess of unbounded complex was thoroughly washed away with ethanol until no red emission of the washing solution was witnessed under UV.



Scheme1. Synthesis of Eu(Ⅲ) complexes.



Scheme 2. Synthesis of Eu-GO.

Results and discussion

1. Photoluminescent Data.

	A	t1	t2	t1(rel%)	t2(rel%)	B1	B2	X^2
a	1.505	55.93	216.83	46.42	53.58	2453.86	730.62	1.403
b	1.260	92.29	340.57	38.95	61.05	1920.31	815.69	1.439

function of emission curves decay: $Fit=A+B_1*e^{(-t/t1)}+B_1*e^{(-t/t2)}$

Table S1: Photoluminescent Data of Eu(Ⅲ) complexes(a) and Eu-GO(b) in Solids

2.TGA analysis.

The stability of were further studied by the TGA measurement. As the TGA curves show, the initial little weight loss of Eu-GO and GO 150°C is ascribed to the elimination of adsorbed solvent. For GO, about 34.87% weight loss over the temperature range 160 – 310 °C is due to the removal of the oxygen functional groups[5,6]. After covalently modified, the oxygen functional groups of GO would be decreased. As respect, the weight lose of Eu-GO is about 4.93%. Moreover, the Eu-GO start to lose mass only upon heating at 300 °C, which indicates that such functionalized materials are thermally highly stable.

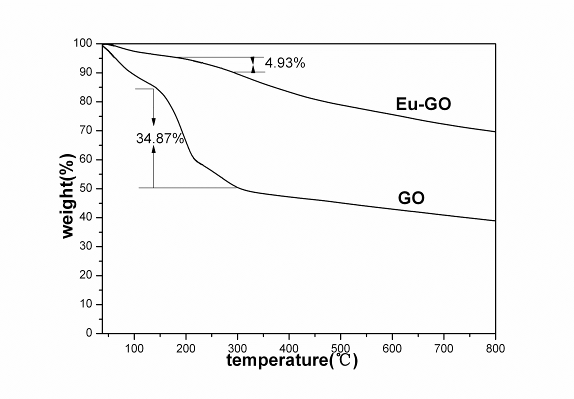


Fig. S1 TGA curves of Eu-GO and GO

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