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Synthesis and Properties of $Ru(phen)_2(phen\text{-}NHCOCH_2Br)(PF_6)_2$

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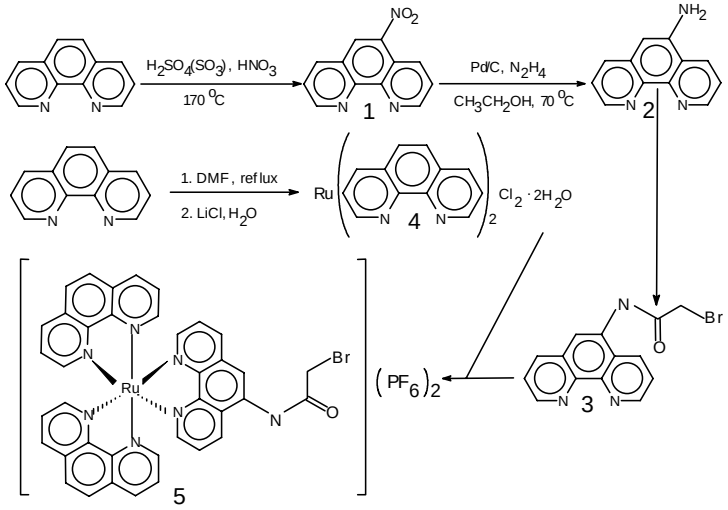
Abstract: A new active material for ECL sensor, $Ru(phen)_2(phen\text{-}NHCH_2Br)(PF_6)_2$, has been designed and synthesized. Its structure was confirmed by means of IR, MS and ^1H NMR. Also, some of its properties such as electrochemistry, fluorescence and ECL are reported.

Keywords: $Ru(phen)_2(phen\text{-}NHCH_2Br)(PF_6)_2$, electrochemistry, fluorescence, ECL.

Recently, an electrochemiluminescent (ECL) Pt electrode coated with a $Ru(bpy)_3^{2+}$ derivative modified chitosan/silica gel membrane developed by Zhao *et al*[1]. has been successfully applied in selective detection of oxalic acid. Yang *et al.*[2]. have discovered that ECL efficiency of $Ru(phen)_3^{2+}$ is much higher than that of $Ru(bpy)_3^{2+}$. Thus, we designed and synthesized a new active material for ECL sensor, $Ru(phen)_2(phen\text{-}NHCH_2Br)(PF_6)_2$, and the synthetic route is shown in **Figure 1**.

Figure 1. Scheme for synthetic route of $Ru(phen)_2(phen\text{-}NHCH_2Br)(PF_6)_2$.



Compounds **1**, **2** (phen') and **4** were synthesized by the methods of Smith *et al*[3]., Lecomte *et al*[4]. and Cook *et al*[5]., respectively. Compound **3** was synthesized by the reaction of **2**, sodium bicarbonate and 2-bromo-acetyl bromide in MeCN. The title compound **5** was obtained from **3** and **4** by refluxing in water-methanol solution.

The orange title compound was confirmed by IR, ESI-MS and ^{1}H NMR. IR (ν/cm^{-1}): 3390 (N-H), 1698 (C=O). ESMS (*m/z*): 922 ([M-PF_6]$^+$). ^{1}H NMR (DMSO, δ_H): 10.98 (s, 1H, N-H), 8.93 (m, 6H, 4-H and 7-H of phen and phen'), 8.76 (s, 1H, 6-H of phen'), 8.51 (s, 4H, 5-H and 6-H of phen), 8.17 (m, 6H, 2-H and 9-H of phen and phen'), 7.88 (m, 6H, 3-H and 8-H of phen and phen'), 4.67 (s, 2H, CH_2).

Figure 2. Cyclic voltammogram of 5.

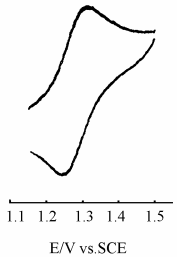


Figure 3. Fluorescence spectrum of 5.

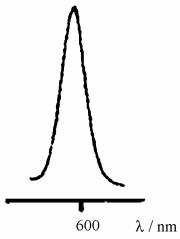


Figure 2 shows a typical cyclic voltammogram of 10^{-4} mol/L compound **5** in MeCN/0.1 mol/L (TBA)ClO_4 at a scan rate of 100 mV/s. The fluorescence spectrum of a saturated aqueous solution of **5** at 25 ℃ is shown in **Figure 3**.

ECL experiments were carried out on self-made ECL instrument with a working electrode of gold with a surface area of 2 cm^2 in aqueous solutions of 0.001 mol/L tri-*n*-propylamine and variable concentrations (10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} mol/L) of **5**, and the corresponding relative ECL intensities are 3123, 311, 31.4 and 3.13 units at pH 7.5, respectively.

Acknowledgments

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