

Synthesis, Electrochemistry, Fluorescence and ECL of Ru (phen)₂ (dcbpy) (PF₆)₂

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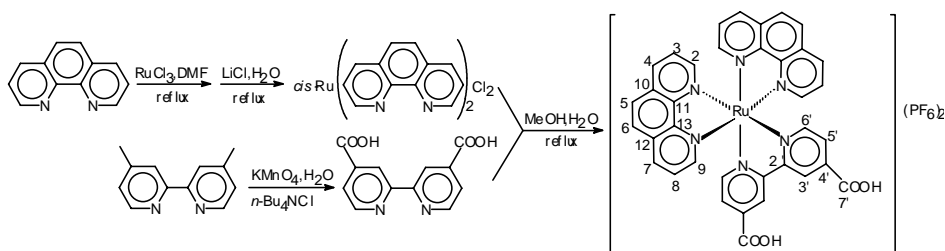
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Abstract: A new ECL-active species, Ru (phen)₂ (dcbpy) (PF₆)₂, has been designed and synthesized. Its structure was confirmed by means of IR, ESI-MS and 2D NMR. Also, its properties of electrochemistry, fluorescence and ECL are reported, which have suggested a good hope of being used in electrochemiluminescent immunoassay and nucleic acid hybridization.

Keywords: Ru (phen)₂ (dcbpy) (PF₆)₂, electrochemistry, fluorescence, electrochemiluminescence.

Highly luminescent Ru (II), Os (II) and Re (I) metal complexes are a promising class of electrochemiluminescent (ECL) materials¹. We have designed and synthesized Ru (phen)₂ (dcbpy) (PF₆)₂.

The synthetic route is shown as follows, 4, 4'-dicarboxylic acid-2, 2'-bipyridine (dcbpy) was synthesized by the method put forward by Sprintschnik *et al.*², except for using *n*-Bu₄NCl as phase transfer catalyst to further improve the product. The synthesis



of *cis*-Ru (1,10-phenanthroline)Cl₂ (phen=1,10-phenanthroline) is the modification to that of *cis*-Ru (2,2'-bipyridine)Cl₂³. The title compound was obtained with *cis*-Ru (phen)₂Cl₂ and dcbpy refluxed in water-methanol solution.

The orange title compound is confirmed by IR, ESI-MS and 2D NMR. IR (ν_{\max} / cm⁻¹): 1726 (C=O). ESI-MS (m/z): 1011 (M⁺), 866 ([M-PF₆]⁺), 721 ([M-2PF₆]⁺). ¹H NMR (DMSO, δ_{H}): 9.34 (2H, s, 3'-H), 8.76 (2H, d, 4-H), 8.87 (2H, d, 7-H), 8.53 (2H, d, 5-H), 8.49 (2H, d, 6-H), 8.38 (2H, d, 2-H), 8.03 (4H, m, 3-H and 9-H), 7.97 (2H, d, 6-H), 7.84 (4H, m, 5'-H and 8-H). ¹³C NMR (DMSO, δ_{C}): 165.16 (7'-C), 157.61 (2'-C), 153.00

(2-C), 152.65 (6'-C), 152.38 (9-C), 147.06 (11-C), 146.73 (13-C), 140.85 (4'-C), 137.28 (4-C), 137.18 (7-C), 130.63 (10-C), 130.55 (12-C), 128.18 (5-C), 128.14 (6-C), 126.75 (5'-C), 126.53 (3-C), 126.49 (8-C), 123.77 (3'-C).

Figure 1 shows typical cyclic voltammogram for 10^{-3} mol/L title compound in MeCN/0.05 mol/L (TBA)ClO₄ at a scan rate of 100 mV/s. The fluorescence spectrum of Ru (phen)₂ (dcbpy) (PF₆)₂ saturated aqueous solution at 25 °C is shown in **Figure 2**.

Figure 1. Cyclic voltammogram

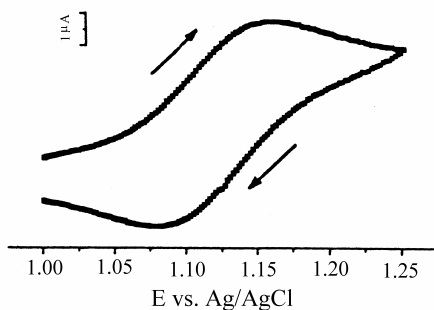
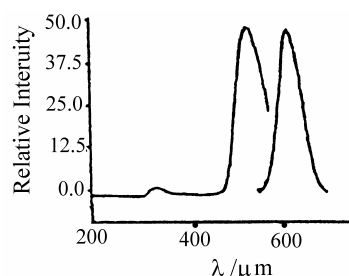


Figure 2. Fluorescence spectrum.



Many studies⁴ have indicated that the ECL spectrum of each Ru (II) complex is very similar to its fluorescence spectrum, so we only report the fluorescence spectrum of Ru (phen)₂ (dcbpy) (PF₆)₂ here. ECL experiments were taken on self-made ECL instrument with a working electrode of gold whose area is 2 cm² in aqueous solutions of 0.1 mol/L tri-*n*-propylamine and variable concentrations of Ru (phen)₂ (dcbpy) (PF₆)₂, and the ECL intensity data are shown in **Table 1**.

Table 1. ECL intensity of different Ru (phen)₂ (dcbpy) (PF₆)₂ concentrations.

Concentration (10 ⁻⁶ mol/L)	0	50	100	150	200	400	800	1000
ECL Intensity (Arbitrary Unit)	4	60	114	167	226	452	896	1114

The studies of using Ru (phen)₂ (dcbpy) (PF₆)₂ as probe in electrochemiluminescent immunoassay assay and nucleic hybridization are presently in progress.

Acknowledgment

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