Synthesis, Electrochemistry, and Fluorescence of Two $Ru(phen)_3^{2+}$-based Surfactants

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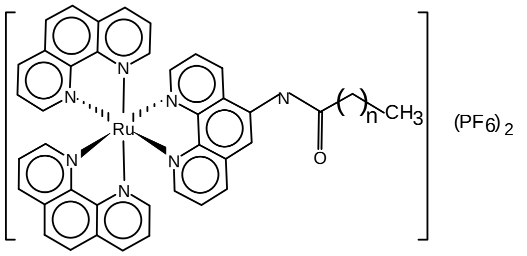
Abstract: Two new $Ru(phen)_3^{2+}$-based surfactants, $Ru(phen)_2(phenNHCO\text{-}C_{11})(PF_6)_2$ and $Ru(phen)_2(phenNHCO\text{-}C_{17})(PF_6)_2$, have been designed and synthesized, whose chemical structures were characterized by means of IR, ^1H NMR and MS. Also, electrochemistry and fluorescence of them are reported.

Keywords: $Ru(phen)_3$-based surfactant, synthesis, electrochemistry, fluorescence.

In 1988, Zhang and Bard[1] first observed the electrochemiluminescence (ECL) from a monomolecular organized assembly layer of a $Ru(bpy)_3^{2+}$-based surfactant confined to the surface of a solid electrode by the Langmuir-Blodgett method. Subsequently, their group[2] further studied this kind of monolayer membrane by the technique of ECL photography. Zhao *et al*.[3] have found ECL efficiency of $Ru(phen)_3^{2+}$, where phen is 1,10-phennanthroline, is much higher than that of $Ru(bpy)_3^{2+}$. In order to develop high efficiently ECL devices, we designed and synthesized two new $Ru(phen)_3^{2+}$ surfactants,



1. n =10; 2. n =16

cis-$Ru(phen)_2Cl_2$, 5-nitro-1,10-phenanthroline, lauroyl chloride and stearoyl chloride were synthesized according to the references[4-6]. 5-amino-1,10-phenanthroline was synthesized from 5-nitro-phenanthroline by the method proposed by Lecomte *et al*.[7] 5-Lauramide-1,10-phenanthroline or 5-stearamide-1,10-phenanthroline was synthesized by the reaction of sodium bicarbonate, 5-amine-1,10-phenanthroline , and lauroyl chloride or stearoyl chloride at room temperature in MeCN, respectively. **1** and **2** were synthesized by refluxing *cis*-Ru(phen)$_2$Cl$_2$ and the corresponding phennanthroline derivatives with 10 or 16 carbon long chains in ethanol for 15 hours, then precipitated by sodium hexafluorophosphate.

The two Ru(phen)$_3^{2+}$-based surfactants are both orange powders, and their chemical structures were confirmed by IR, ^{1}H NMR and ESI-MS. **1**. IR (ν/cm^{-1}): 1696 (C=O); ^{1}H NMR (DMSO-d$_6$, $_H$): 10.54 (s, 1H), 9.05-8.79 (m, 7H), 8.52 (s, 4H), 8.19-8.08 (m, 6H), 7.72-7.96 (m, 6H), 2.72 (t, 2H), 1.79 (m, 2H), 1.39-1.30 (m, 18H), 0.94 (t, 3H); ESMS (*m/z*): 883 ([M-145]$^+$). **2**. IR (ν_{max}/cm^{-1}): 1699 (C=O); ^{1}H NMR (DMSO-d$_6$, $_H$): 10.51 (s, 1H), 8.89 (m, 7H), 8.50 (s, 2H), 8.20 (m, 6H), 7.89 (m, 6H), 2.70 (t, 2H), 1.80 (m, 2H), 1.33 (m, 28H), ESMS (*m/z*): 969 ([M-PF$_6$]$^+$).

The $E_{1/2}$ obtained from cyclic voltammograms of 1 mmol/L **1** or **2** in MeCN with (TBA)ClO$_4$ as supported electrolyte is 1.266 or 1.264 mV referenced to saturated calomel electrode (SCE), respectively. The maximal fluorescence emission of 0.1 mmol/L 1 or 2 in ethanol is 580 or 584 nm, respectively.

Further work will employ these two Ru(phen)$_3^{2+}$-based surfactants as active materials of ECL membrane and hopefully develop ECL devices.

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