

Synthesis and Properties of Three Tris(1,10-phenanthroline) ruthenium (II) Derivatives

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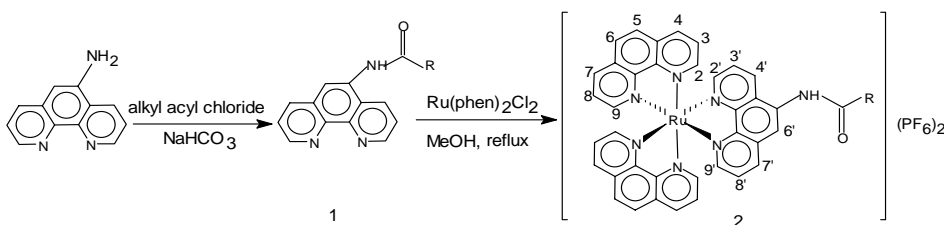
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Abstract: Three new asymmetrical ruthenium (II) complexes: $[\text{Ru}(\text{phen})_2\{\text{phen-NHCO}(\text{CH}_2)_4\text{Br}\}](\text{PF}_6)_2$, $[\text{Ru}(\text{phen})_2\{\text{phen-NHCO}(\text{CH}_2)_5\text{Br}\}](\text{PF}_6)_2$ and $[\text{Ru}(\text{phen})_2\{\text{phen-NHCO}(\text{CH}_2)_{10}\text{Br}\}](\text{PF}_6)_2$ were synthesized, which were confirmed by the technique of FT-IR, ^1H NMR and ESI-MS. The electrochemical and fluorescent properties of three Ru (II) complexes were investigated with cyclic voltammetry and fluorometry.

Keywords: Tris(1,10-phenanthroline)ruthenium(II) complexes, synthesis, electrochemistry, fluorescence.

Ru (II) polypyridine complexes have attracted many researchers because of their excellent properties of photochemistry, photophysics and electrochemistry¹. Recently, Bis (2,2'-bipyridine)[4-methyl-4'-(bromohexyl)-2,2'-bipyridine] ruthenium (II) perchlorate was used as an optode material for ECL sensors to selectively detect oxalic acid². It is known that ECL efficiency of Ru (1,10-phenanthroline)₃²⁺ is higher than that of Ru (2,2'-bipyridine)₃²⁺³. In order to develop more efficient ECL sensor, we designed and synthesized three new asymmetrical tris (1,10-phenanthroline)ruthenium (II) hexafluorophosphate derivatives with a ligand 5-substituted by ω -bromo-alkyl amides shown in **Scheme 1**.

Scheme 1 Synthesis of three new tris (1,10-phenanthroline)ruthenium (II) hexafluorophosphate derivatives^a



^a a $\text{R}=(\text{CH}_2)_4\text{Br}$, b $\text{R}=(\text{CH}_2)_5\text{Br}$, c $\text{R}=(\text{CH}_2)_{10}\text{Br}$

The key materials, 5-amino-1,10-phenanthroline and *cis*-Ru (phen)₂Cl₂, were prepared by the methods of references^{4,5}.

Synthesis of 1a, 1b and 1c

Equimolar amounts of corresponding ω-bromo-alkylacylchloride was added dropwise to a suspension of 5-amino-1,10-phenanthroline and sodium dicarbonate in dry acetonitrile with stirring at room temperature under nitrogen for 4-6 hours. Then the resulting solid was filtered and washed by acetonitrile, 5% sodium bicarbonate aqueous solution and water in turn. After being dried *in vacuo*, yellow microcrystals **1a-c** were obtained.

Synthesis of 2a, 2b and 2c

After equimolar amounts of **1a-c** and *cis*-Ru (phen)₂Cl₂ were refluxed in 4:1 methanol/H₂O for 10 hours under nitrogen, superfluous sodium hexafluorophosphate was added into the cold solution. The orange microcrystals **2a-c** were obtained.

Electrochemistry

The electrochemical properties of the three title compounds were investigated by cyclic voltammetry. **Table 1** shows the cyclic voltammetric data of **2**. They undergo a reversible single-electron oxidation when the potential scans from 1.15 to 1.50 V.

Table 1 Cyclic voltammetric data for tris (1,10-phenanthroline)ruthenium(II) hexafluorophosphate derivatives **2a-c**^a

compound	E^{pa}/V	E^{pc}/V	$E^{1/2}/V$	$\Delta E^p/mV$
2a	1.306	1.238	1.272	68
2b	1.306	1.237	1.272	69
2c	1.305	1.239	1.272	66

^aExperimental conditions: **2** (*ca.* 10⁻³ mol·dm⁻³), supporting electrolyte *n*-Bu₄N⁺PF₆⁻ (*ca.* 0.1 mol dm⁻³) in dry acetonitrile, working electrode Au, counter electrode Pt, reference electrode SCE, scan rate 100 mV s⁻¹ using CHI 660 electrochemical station.

Fluorescence

The fluorescence emission maximal peaks of 0.1 mmol·dm⁻³ **2a-c** in ethanol at room temperature are 595 nm ($\lambda_{\text{excitation}} = 473$ nm), 592 nm ($\lambda_{\text{excitation}} = 465$ nm) and 594 nm ($\lambda_{\text{excitation}} = 472$ nm) respectively. These intense emissions are significant contribution to the excited state from an interaction between the metal *d* orbitals and the ligand π system⁶.

Electrochemiluminescence (ECL)

ECL intensity of **2a** and 0.05 mol dm⁻³ *n*-tripropylamine is positive related to its

concentrations from 10^{-3} to 10^{-8} mol dm⁻³ in 0.01 mol dm⁻³ phosphate buffer aqueous solution (pH=7.5) when a 1.3 V voltage was applied to the Au working electrode, so are **2b** and **2c**.

Conclusion

As expected from these results, all new Ru (II) complexes **2** behave as good materials for optodes, thus further experiments are underway to prepare highly selective and sensitive ECL sensor based on the new Ru (II) complexes.

Acknowledgment

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References and Notes

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- 7 New compounds **1a-c** and **2a-c** have been characterized and presented satisfactory spectra data
For **1a**: light red solid (yield 87%); IR (KBr)/cm⁻¹ 1666 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.95 (m, 2H, CH₂), 2.07 (m, 2H, CH₂), 2.71 (t, 2H, CH₂), 3.74 (t, 2H, CH₂), 7.86 (q, 1H, 8-H), 7.95 (q, 1H, 3-H), 8.30 (s, 1H, 6-H), 8.57 (q, 1H, 7-H), 8.73 (q, 1H, 4-H), 9.15 (q, 1H, 9-H), 9.25 (q, 1H, 2-H), 10.32 (s, 1H, NH); ESI-MS 380.9 ([M+Na]⁺).
For **1b**: yellow solid (yield 63%); IR (KBr)/cm⁻¹ 1663 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.64 (m, 2H, CH₂), 1.86 (m, 2H, CH₂), 1.92 (m, 2H, CH₂), 2.67 (t, 2H, CH₂), 3.70 (t, 2H, CH₂), 7.86 (q, 1H, 8-H), 7.94 (q, 1H, 3-H), 8.57 (d, 1H, 7-H), 8.72 (d, 1H, 4-H), 9.15 (d, 1H, 9-H), 9.24 (d, 1H, 2-H), 10.24 (d, 1H, NH); ESI-MS 395.0 ([M+Na]⁺).
For **1c**: yellow solid (yield 70%); IR (KBr)/cm⁻¹ 1659 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.39 (br, 12H, CH₂ × 6), 1.78 (m, 2H, CH₂), 1.87 (m, 2H, CH₂), 2.69 (t, 2H, CH₂), 3.67 (t, 2H, CH₂), 7.83 (q, 1H, 8-H), 7.95 (q, 1H, 3-H), 8.28 (s, 1H, 6-H), 8.53 (d, 1H, 7-H), 8.70 (d, 1H, 4-H), 9.14 (d, 1H, 9-H), 9.23 (d, 1H, 2-H), 10.22 (s, 1H, NH); ESI-MS 465.3 ([M+Na]⁺).
For **2a**: IR (KBr)/cm⁻¹ 1697 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.96 (m, 4H, CH₂), 2.70 (m, 2H, CH₂), 3.85 (t, 2H, CH₂), 7.85 (m, 6H, 3-H, 8-H, 3'-H and 8'-H), 8.20 (m, 6H, 2-H, 9-H, 2'-H and 9'-H), 8.52 (m, 4H, 5-H and 6-H), 8.91 (m, 7H, 4-H, 7-H, 4'-H, 7'-H and 6'-H), 10.62 (s, 1H, NH); ESI-MS 964.4 ([M-PF₆]⁺), 409.9 ([M-2PF₆]²⁺).
For **2b**: IR (KBr)/cm⁻¹ 1701 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.85 (br,

6H, CH₂×3), 2.73 (t, 2H, CH₂), 3.80 (t, 2H, CH₂), 7.89 (br, 6H, 3-H, 8-H, 3'-H and 8'-H), 8.20 (br, 6H, 2-H, 9-H, 2'-H and 9'-H), 8.52 (d, 4H, 5-H and 6-H), 8.94 (br, 7H, 4-H, 7-H, 4'-H, 7'-H and 6'-H), 10.55 (s, 1H, NH); ESI-MS 978.4 ([M-PF₆]⁺), 416.8 ([M-2PF₆]²⁺).

For **2c**: IR (KBr)/cm⁻¹ 1696 (C=O); ¹H NMR (400 MHz, DMSO-d₆) δ_H: 1.40 (br, 12H, CH₂×6) 1.69 (m, 2H, CH₂), 1.86 (m, 2H, CH₂), 2.69 (t, 2H, CH₂), 3.70 (t, 2H, CH₂), 7.84 (br, 6H, 3-H, 8-H, 3'-H and 8'-H), 8.18 (br, 6H, 2-H, 9-H, 2'-H and 9'-H), 8.57 (d, 4H, 5-H and 6-H), 8.97 (br, 7H, 4-H, 7-H, 4'-H, 7'-H and 6'-H), 10.53 (s, 1H, NH); ESI-MS 1048.6 ([M-PF₆]⁺), 451.8 ([M-2PF₆]²⁺).

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