Synthesis, 2D NMR, Electrochemistry and Luminescence of Ruthenium(II) Complexes with 2,2′-Bipyridine and 5-(ω-Bromoalkylamido)-1,10-phenanthroline

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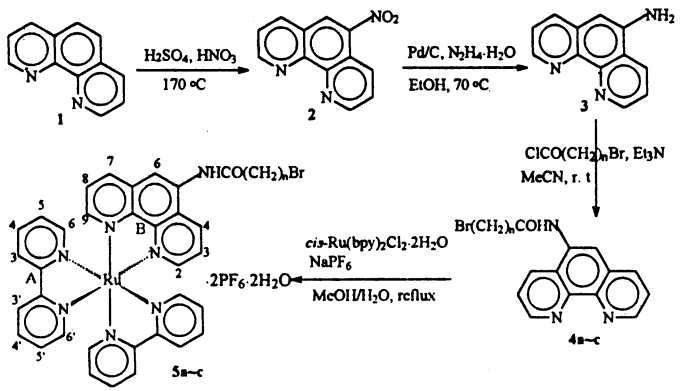
The efficient synthesis of 5-(5-bromovaleramido)-1,10-phenanthroline, 5-(6-bromohexanamido)-1,10-phenanthroline, and 5-(11-bromoundecanamido)-1,10-phenanthroline are described, which reacted with *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and sodium hexafluorophosphate to form $Ru(bpy)_2[phen\text{-}NHCO(CH_2)_nBr](PF_6)_2$ (n = 4, 5 or 10; phen = 1,10-phenanthroline). The intricate ^1H NMR spectra at low field of these complexes were completely assigned in virtue of ^1H-^1H COSY technique. Cyclic voltammetry was used to study electrochemical behaviours of these complexes, and their luminescent properties were investigated with fluorescent spectra.

INTRODUCTION

The design and preparation of ruthenium(II) complexes with new polypyridine ligands have been of great interest in the last decades because of their wide use in the study of photosplitting of water[1], solar energy cell[2], electrochemical catalysis[3], fluorescence[4], chemiluminescence[5], electrochemiluminescence[6] and electroluminescence[7]. To our knowledge, 2-chloroacetamido-1,10-phenanthroline[8], 5-bromoacetamido-1,10-phenanthroline[9], 5-iodoacetamido-1,10-phenanthroline[8, 10] and 5-(ω-bromohexanamido)-1,10-phenanthroline[11] have been synthesized by some groups. Zhao *et al.*[12] have used $Ru(bpy)_2[Me\text{-}bpy\text{-}(CH_2)_6Br](ClO_4)_2$ as active material to prepare electrochemiluminescent sensor for selective detection of oxalic acid, where bpy is 2,2′-bipyridine. Recently, our interest is to fabricate organically modified electrochemiluminescent sensors without leakage by sol-gel method, and the syntheses of polypyridine ruthenium(II) complexes with a kind of ω-bromo-substituted ligands are in need, by which these complexes can be attched to 3-aminopropyltriethoxysilane, then a polycondensation reaction will be catalyzed by hydrogen chloride to form ruthenium(II) complexes modified silicate. The synthetic route of $Ru(bpy)_2[phen\text{-}$

$NHCO(CH_2)_nBr](PF_6)_2$ (**4a–c**) is shown in Scheme 1, where phen is 1,10-phenanthroline and n is 4, 5 or 10.



Scheme 1. Synthetic route for $Ru(bpy)_2[phen\text{-}NHCO(CH_2)_nBr](PF_6)_2$

EXPERIMENTAL

IR spectra were recorded in KBr pellets on a Bio-RAD FTS-135 infrared spectrophotometer. NMR spectra were carried out at room temperature on a Varian 400 spectrophotometer, and samples were dissolved in DMSO-d_6 and chemical shifts were expressed in ppm using TMS as the internal standard. Elemental analysis experiments were performed on a GmbH VarioEl elemental analysis system. Cyclic voltammetry experiments were measured on CHI 660 electrochemical workstation. The electrochemic cell was conventional with an Au disk working electrode and a Pt wire auxiliary electrode, and all potentials were measured referred to a SCE electrode. Solutions were deaerated by nitrogen bubbling prior to the experiments and the elctrochemical cell was kept under nitrogen atmosphere throughout the experiments. Fluorescence excitation and emission spectra were taken on a Shimadzu RF-5000 fluorescence spectrometer at 20°C.

5-Nitro-1,10-phenanthroline was synthesized by the nitration of 1,10-phenanthroline with nitric acid and sulfuric acid at 170°C according to the reference method[13], which was then reduced to 5-amino-1,10-phenanthroline by hydrazine hydrate with 5% Pd/C as catalyst[14], except that the product wasn't purified with HPLC and it was rather pure. *cis*-$Ru(bpy)_2Cl_2·2H_2O$ was prepared with Liu's method[14]. All ω-bromoalkyl chlorides were prepared by the reaction of the corresponding ω-bromoalkyl acids and $SOCl_2$. Acetonitrile was dried with calcium hydride and then distilled. Other reagents are all analytical grade.

Synthesis of 5-(5-bromovaleramido)-1,10-phenanthroline (4a)

To a solution of 5 mmol 5-amino-1,10-phenanthroline and 6 mmol triethylamine in 50 mL MeCN. 5.5 mmol 5-bromovaleryl chloride in 20 mL MeCN was

added with stirring at room temperature. After 2 h, the reaction was quenched with water. The resulting solution was filtered, and the filtrate was washed by MeCN, 5% sodium bicarbonate aqueous solution, and water in turn. After drying in *vacuo*, a light yellow solid was obtained at the yield of 65%. IR ν_{max}/cm^{-1} : 3275 (N—H), 1666 (C=O). ^1H NMR δ_H: 1.92 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 2.71 (t, 2H, J = 6.8 Hz, CH_2), 3.74 (t, 2H, J = 6.4 Hz, CH_2), 7.86 (q, 1H, J = 4.0 Hz, 3-H), 7.95 (q, 1H, J = 4.0 Hz, 8-H), 8.00 (s, 1H, 6-H), 8.57 (dd, 1H, J = 8.0 Hz, 4-H), 8.72 (dd, 1H, J = 8.0 Hz, 7-H), 9.15 (dd, 1H, J = 4.0 Hz, 2-H), 9.24 (dd, 1H, J = 4.0 Hz, 9-H), 10.25 (s, 1H, NH). Anal. Calcd. for $C_{17}H_{16}BrN_3O$: C, 57.00, H, 4.50, N, 11.73. Found: C, 57.05, H, 4.52, N, 11.69.

Synthesis of 5-(6-bromohexanamido)-1,10-phenanthroline (4b)

5-(6-Bromohexanamido)-1,10-phenanthroline was synthesized not by the method of Francois's group[11], but by the method for **4a**, and the yield could increase from 55% to 67%. IR ν_{max}/cm^{-1}: 3273 (N—H), 1663 (C=O). ^1H NMR δ_H: 1.64 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 1.92 (m, 2H, CH_2), 2.67 (t, 2H, J = 6.8 Hz, CH_2), 3.71 (t, 2H, J = 6.4 Hz, CH_2), 7.86 (q, 1H, J = 4.0 Hz, 3-H), 7.95 (q, 1H, J = 4.0 Hz, 8-H), 8.29 (s, 1H, 6-H), 8.57 (dd, 1H, J = 8.0 Hz, 4-H), 8.74 (dd, 1H, J = 8.0 Hz, 7-H), 9.15 (dd, 1H, J = 4.0 Hz, 2-H), 9.25 (dd, 1H, J = 4.0 Hz, 9-H), 10.24 (s, 1H, NH). Anal. Calcd. for $C_{18}H_{18}BrN_3O$: C, 58.08, H, 4.87, N, 11.29. Found: C, 57.09, H, 4.89, N, 11.25.

Synthesis of 5-(11-bromoundecanamido)-1,10-phenanthroline (4c)

5-(11-Bromoundecanamido)-1,10-phenanthroline was also synthesized according to the method for **4a**, except that 5.0 mmol 11-bromoundecanoyl chloride was used, and the more MeCN was used to wash the filtrate and the yield was about 60%. IR ν_{max}/cm^{-1}: 3250 (N—H), 1659 (C=O). ^1H NMR δ_H: 1.40 (br, 12H, $CH_2 \times 6$), 1.84 (m, 2H, $CH_2 \times 2$), 2.68 (t, 2H, J = 6.8 Hz, CH_2), 3.63 (t, 2H, J = 6.4 Hz, CH_2), 8.05 (q, 1H, J = 4.0 Hz, 3-H), 8.09 (q, 1H, J = 4.0 Hz, 8-H), 8.46 (s, 1H, 6-H), 8.84 (dd, 1H, J = 8.0 Hz, 4-H), 8.91 (dd, 1H, J = 8.0 Hz, 7-H), 9.21 (dd, 1H, J = 4.0 Hz, 2-H), 9.32 (dd, 1H, J = 4.0 Hz, 9-H), 10.36 (s, 1H, NH). Anal. Calcd. for $C_{23}H_{28}BrN_3O$: C, 62.44, H, 6.38, N, 9.50. Found: C, 62.49, H, 6.39, N, 9.46.

Synthesis of $Ru(bpy)_2(4a)(PF_6)_2 \cdot 2H_2O$ (5a)

1 mmol *cis*-$Ru(bpy)_2Cl_2 \cdot 2H_2O$ and 1 mmol **4a** were stirred in refluxing 20 mL methanol and 5 mL water for 9 h. The resulting solution was separated by filtration and washed with 8 mL methanol. The combined filtrate and wash solution were treated with a solution of 5.0 g sodium hexafluorophosphate in 25 mL water, and the obtained solution was cooled in an ice bath for 3 h. The resulting precipitate of orange microcrystals was collected by filtration, and the yield was 79% after being dried *in vacuo*. IR/cm^{-1}: 3248 (N—H), 1701 (C=O), 842 (P—F). ^1H NMR δ_H: 1.92 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 2.71 (t, 2H, J = 6.8 Hz, CH_2), 3.74 (t, 2H, J = 6.4 Hz, CH_2), 7.48 (t, 2H, J = 6.4 Hz, A5-H), 7.69 (m, 4H,

A5′-H and A6-H), 7.94 (m, 3H, B3-H and A6′-H), 8.02 (q, 1H, J = 4.0 Hz, B8-H), 8.14 (d, 1H, J = 4.0 Hz, B2-H), 8.23 (t, 2H, J = 7.6 Hz, A4-H), 8.27 (d, 1H, J = 4.4 Hz, B9-H), 8.32 (t, 2H, J = 7.6 Hz, A4′-H), 8.76 (s, 1H, B6-H), 8.86 (d, 1H, J = 8.0 Hz, B4-H), 8.95 (d, 2H, J = 8.4 Hz, A3-H), 8.98 (d, 2H, J = 8.0 Hz, A3′-H), 9.02 (d, 1H, J = 7.6 Hz, B7-H), 10.52 (s, 1H, NH), Anal. Calcd. for $C_{37}H_{36}BrF_{12}N_7O_3P_2Ru$: C, 40.49, H, 3.31, N, 8.93. Found: C, 40.52, H, 3.32, N, 8.95.

Synthesis of Ru(bpy)$_2$(4b)(PF$_6$)$_2$·2H$_2$O (5b)

Ru(bpy)$_2$(**4b**)(PF$_6$)$_2$·2H$_2$O was synthesized by the method for **5a**. Yield: 81%. IR/cm^{-1}: 3250 (N—H), 1691 (C=O), 839 (P—F). ^{1}H NMR δ_H: 1.65 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.93 (m, 2H, CH_2), 2.67 (t, 2H, J = 6.8 Hz, CH_2), 3.72 (t, 2H, J = 6.4 Hz, CH_2), 7.47 (t, 2H, J = 6.4 Hz, A5-H), 7.70 (m, 4H, A5′-H and A6-H), 7.93 (m, 3H, B3-H and A6′-H), 8.01 (q, 1H, J = 4.0 Hz, B8-H), 8.15 (d, 1H, J = 4.0 Hz, B2-H), 8.23 (t, 2H, J = 7.6 Hz, A4-H), 8.28 (d, 1H, J = 4.0 Hz, B9-H), 8.35 (t, 2H, J = 7.6 Hz, A4′-H), 8.77 (s, 1H, B6-H), 8.86 (d, 1H, J = 8.0 Hz, B4-H), 8.94 (d, 2H, J = 8.0 Hz, A3-H), 8.98 (d, 2H, J = 8.0 Hz, A3′-H), 9.03 (d, 1H, J = 7.6 Hz, B7-H), 10.54 (s, 1H, NH), Anal. Calcd. for $C_{38}H_{38}BrF_{12}N_7O_3P_2Ru$: C, 41.06, H, 3.45, N, 8.82. Found: C, 41.10, H, 3.48, N, 8.80.

Synthesis of Ru(bpy)$_2$(4a)(PF$_6$)$_2$·2H$_2$O (5c)

Ru(bpy)$_2$(**4c**)(PF$_6$)$_2$2H$_2$O was synthesized by the method for **5a.** Yield: 76%. IR/cm^{-1}: 3248 (N—H), 1701 (C=O), 840 (P- -F). ^{1}H NMR δ_H: 1.42 (br, 12H, $CH_2 \times 6$), 1.81 (m, 4H, $CH_2 \times 2$), 2.71 (t, 2H, J = 7.6 Hz, CH_2), 3.63 (t, 2H, J = 6.8 Hz, CH_2), 7.48 (t, 2H, J = 6.4 Hz, A5-H), 7.69 (m, 4H, A5′-H and A6-H), 7.94 (m, 3H, B3-H and A6′-H), 8.02 (q, 1H, J = 4.0 Hz, B8-H), 8.14 (d, 1H, J = 4.4 Hz, B2-H), 8.23 (t, 2H, J = 7.6 Hz, A4-H), 8.27 (d, 1H, J = 5.2 Hz, B9-H), 8.33 (t, 2H, J = 7.6 Hz, A4′-H), 8.77 (s, 1H, B6-H), 8.86 (d, 1H, J = 7.6 Hz, B4-H), 8.95 (d, 2H, J = 8.0 Hz, A3-H), 8.99 (d, 2H, J = 8.0 Hz, A3′-H), 9.02 (d, 1H, J = 7.6 Hz, B7-H), 10.51 (s, 1H, NH). Anal. Calcd. for $C_{43}H_{48}BrF_{12}N_7O_3P_2Ru$: C, 43.70, H, 4.09, N, 8.30. Found: C, 43.76, H, 4.08, N, 8.31.

RESULTS AND DISCUSSION

Synthesis

The synthesis of ω-bromoalkyl amide must be performed at room temperature or below, and the byproduct of ω-hydroxyalkyl amide could form at higher reaction temperature. Moreover, 2 h were sufficient for complete amidation.

2d NMR characterization of 5a–c

The ^{1}H NMR study yields some important characteristics of **5a–c**, and the complete assignments of the different peaks were based on ^{1}H-^{1}H COSY spectra. ^{1}H-^{1}H COSY spectrum of aromatic ring of **5c** is presented in Fig. 1. In addition,

five main factors were considered in order to assign resonance peaks of aromatic ring: 1. the electron donating character of groups —$NHCO(CH_2)_nBr$ and the electron drawing character of aromatic ring nitrogen; 2. the shielding effect on aromatic ring hydrogen from the spatial adjacent ligands, especially on A6-H, A6′-H, B2-H, and B9-H; 3. The coupling constants; 4. the effect of ruthenium(II) on aromatic rings; 5. the deshielding effect because of the congesting arrangement of A3-H and A3′-H.

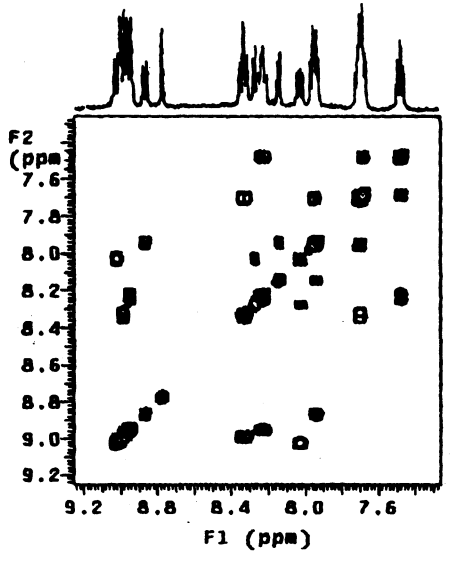


Fig. 1. ^1H–^1H COSY spectrum of aromatic ring of **5c**

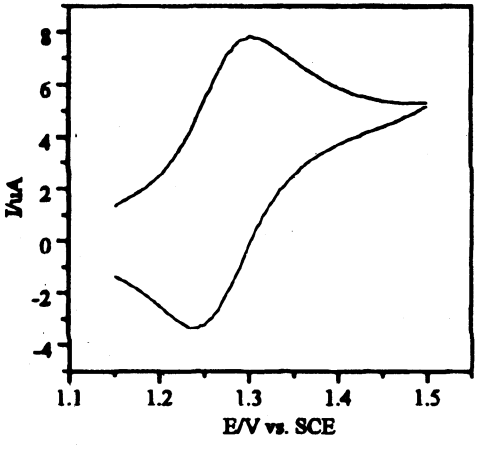


Fig. 2. Cyclic voltammogram of 1 mmol/L **5a** in MeCN with n-Bu_4NPF_6 (scan rate: 1000 mV/s)

Electrochemical Properties of 5a–c

Fig. 2 shows the cyclic voltammogram of 1 mmol/L **5a** in dried MeCN with n-Bu_4NPF_6. Reversible redox wave with $E_{1/2}$ at 1.270 V *vs.* SCE was observed. The i_{pa}/i_{pc} and ΔE values were respectively 1.05 and 62 mV, which suggested a single-electron redox process of Ru(III)/Ru(II). The CV data of **5a–c** are presented in Table 1.

TABLE-1
DATA FROM CYCLIC VOLTAMMOGRAMS OF **5a–c** (scan rate: 100mV/s)

Complexes	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	i_{pa}/i_{pc}	ΔE/mV
5a	1.301	12.39	1.270	1.05	62
5b	1.303	1.240	1.272	1.10	67
5c	1.300	1.242	1.271	1.02	58

Luminescent behaviours of 5a–c

Fig. 3 shows fluorescence excitation and emission spectra of 0.5 mmol/L **5b** in ethanol at room temperature. Emission spectra 1, 2 and 3 all centred at 584 nm were respectively obtained at the excitation wavelengths of 323 nm, 384 nm

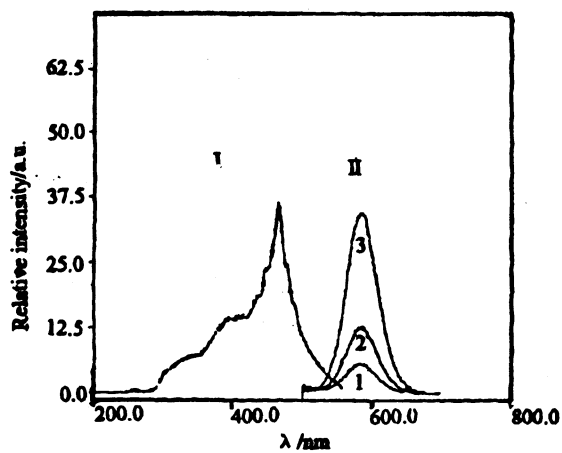


Fig. 3. Fluorescence excitation and emission spectra of 0.5 mmol/L **5b** in ethanol

and 464 nm. The intense excitation band at 464 nm was due to the MLCT transition where an electron was promoted from the metal centred t_{2g} orbital into one ligand centred π^* orbital, and the intense emission occured at lower energy than did the ligand centred $\pi^* \rightarrow \pi$ phosphorescence; hence there was a significant contribution to the excited state from an interaction between the metal d orbitals and the ligand π system. Complexes **5b** and **5c** had almost the same luminescent behaviors as that of **5a**, and the data from fluorescence spectra of **5a–c** are shown in Table-2.

TABLE-2
THE DATA FROM FLUORESCENCE SPECTRA OF 5a–c

Complexes	$\lambda_{excitation}$/nm	$\lambda_{emission}$/nm
5a	322, 386, 467	584
5b	323, 384, 464	584
5c	326, 379, 465	586

Further work using these new complexes to fabricate sol-gel electrochemiluminescent sensors is in progress.

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