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A New Series of Ru(II) Polypyridine Surfactants: Synthesis, 2D NMR, Fluorescence, Electrochemistry and Electrochemiluminescence

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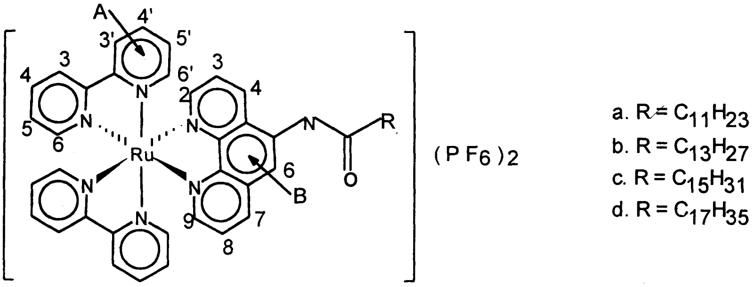
A new series of Ru(II) polypyridine surfactants, $Ru(bpy)_2[phenNH CO(CH_2)_nCH_3](PF_6)_2$, where n is 10, 12, 14 or 16, has been prepared and characterized. The ^1H-NMR spectra of these new Ru(II) complexes were attributed and discussed by the ^1H-^1H COSY method. The comparative analysis of IR spectra of these complexes and their responding free ligands has shown that there are intensive $d \rightarrow \pi^*$ feedback interactions between central Ru(II) and their ligands. Their fluorescent, electrochemical and electrochemiluminescent behaviours are also reported.

INTRODUCTION

The modified electrodes by the immobilized molecular monolayers can be achieved by both the self-assembly or Langmuir-Blodgett (LB) techniques, by which it is possible to immobilize a wide range of compounds.[1] The past few years have seen a significant increase in the number of reports describing the synthesis, structure, photochemistry and photophysics of Ru(II) polypyridine complexes.[2] Electrochemiluminescent (ECL) organized Langmuir monolayers of a $Ru(bpy)^{2+}$-based surfactant on different electrodes have been reported.[3, 4] In the previous work, our group has synthesized a series of $Ru(phen)_3^{2+}$-based complexes with different long hydrocarbon tails and prepared ECL monolayers based on them.[5, 6] We report herein the synthesis and physical characterization of a new series of Ru(II) polypyridine surfactants: $\{Ru(bpy)_2[phen\ NHCO(CH_2)_nCH_3]$ $(PF_6)_2$ shown in Scheme 1, where bpy is 2,2′-bipyridine, phen is 1,10-phenanthroline, and *n* is 10, 12, 14 or 16.



Scheme 1. Chemical structure of new Ru(II) polypyridine surfactants

EXPERIMENTAL

Sodium hexafluorophosphate and tetra-*n*-butylammonium hexafluorophosphate were purchased from Aldrich Corporation and used without further purification. Acetonitrile were dried by CaH_2 and distilled before use, and other reagents are all analytical grade. The key starting materials, *cis*-bis(2,2′-bipyridine)ruthenium chloride and four 1,10-phenanthroline derivatives 5-substituted by long chain alkyl amide, were synthesized according to the reported methods[5, 7].

IR spectra were recorded in KBr pellets on Bio-RAD FTS-7 infrared spectrometer. ^1H NMR spectra were carried out at room temperature on a Varian 400 spectrometer, and samples were dissolved in DMSO-d_6 and chemical shifts were expressed in ppm using TMS as the internal standard. Mass spectra were performed on a LDI-1700 mass spectrometer using DHB as the matrix. Fluorescence spectra were taken on a Shimadzu RF-5000 fluorescence spectrometer at 20°C. Voltammetric recordings were obtained by using a CHI 660 electrochemical station. A Au disk, a wire of Pt and a saturated calomel electrode (SCE) were used as the working, auxiliary and reference electrodes, respectively. All voltammetric measurements were made under nitrogen atmosphere at 18°C, and all potentials are given with respect to SCE.

Synthesis

0.4844 g (1 mmol) *cis*-$Ru(bpy)_2Cl_2$ and 0.3772 g (1 mmol) 5-lauroyl amide-1,10-phenanthroline were stirred in refluxing 25 mL methanol and 5 mL water for 12 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 g sodium hexaflurophosphate in 20 mL water. The resulting solution was cooled in an ice bath for 6 h. The resulting precipitate of orange microcrystal was collected by filtration. The further purification was performed on silica gel column chromatography with acetonitrile and dichloromethane as eluent. IR/cm^{-1}: 1698 (C=O); ^1H NMR δ_H: 10.50 (s, 1H, N-H), 9.02 (d, 1H, B4-H), 8.99 (d, 2H, A3-H), 8.95 (d, 2H, A3′ -H), 8.86 (d, 1H, B7-H), 8.78 (d, 1H, B6-H), 8.33 (t, 2H, A4-H), 8.27 (d, 1H, B2-H)), 8.23 (t, 2H, A4′-H), 8.14 (d, 1H, B9-H), 8.03 (q, 1H, B3-H), 7.94 (m, 3H, B8-H and A6-H), 7.69 (m, 4H, A5-H and A6-H), 7.47 (t, 2H, A5′-H), 2.70 (t, 2H, CH_2), 1.81 (m, 2H, CH_2,), 1.45 (m, 16H, CH × 8), 0.95 (t, 3H, CH_3); MS: 936 ($[M-PF_6]^+$).

Syntheses of **b**, **c** and **d** are almost the same as that of **a**.

Selected data for **b**: IR/cm^{-1}: 1701 (C=O); ^1H NMR δ_H: 10.51 (s, 1H, N-H), 9.03 (d, 1H, B4-H), 8.99 (d, 2H, A3-H), 8.95 (d, 2H, A3′-H), 8.86 (d, 1H, B7-H), 8.77 (d, 1H, B6-H), 8.35 (t, 2H, A4-H), 8.27 (d, 1H, B2-H)), 8.22 (t, 2H, A4′-H), 8.14 (d, 1H, B9-H), 8.03 (q, 1H, B3-H), 7.95 (m, B8-H and A6-H), 7.70 (m, 4H, A5-H and 6-H), 7.48 (t, 2H, A5′-H), 2.71 (t, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.45 (m, 16H, $CH_2 \times 10$), 0.96 (t, 3H, CH_3); MS: 964 ($[M-PF_6]^+$.

Selected data for **c**: IR/cm^{-1}: 1702 (C=O); ^1H NMR δ_H: 10.53 (s, 1H, N-H), 9.02 (d, 1H, B4-H), 8.99 (d, 2H, A3-H), 8.94 (d, 2H, A3′-H), 8.86 (d, 1H, B7-H), 8.78 (d, 1H, B6-H), 8.33(t, 2H, A4-H), 8.27 (d, 1H, B2-H)), 8.23 (t, 2H, A4′-H), 8.14 (d, 1H, B9-H), 8.03 (q, 1H, B3-H), 7.94 (m, 3H, B8-H and A6-H), 7.69 (m, 4H, A5-H and A6-H), 7.47 (t, 2H, A5'-H), 2.70 (t, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.45 (m, 16H, $CH_2 \times 12$), 0.96 (t, 3H, CH_3); MS: 992 $[M-PF_6]^+$.

Selected data for **d**: IR/cm^{-1}: 1702 (C=O); ^1H NMR δ_H: 10.50 (s, 1H, N-H), 9.02 (d, 1H, B4-H), 8.99 (d, 2H, A3-H), 8.95 (d, 2H, A3′-H), 8.86 (d, 1H, B7-H), 8.78 (d, 1H, B6-H), 833 (t, 2Hm A4-H), 827 (d, 1H, B2-H)), 8.23 (t, 2H, A4′-H), 8.14 (d, 1H, B9-H), 8.03 (q, 1H, B3-H), 7.94 (m, 3H, B8-H and A6-H), 7.69 (m, 4H, A5-H and A6-H), 7.47 (t, 2H, A5′-H), 2.70 (t, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.45 (m, 16H, $CH_2 \times 14$), 0.95 (t, 3H, CH_3); MS: 1020 $[M-PF_6]^+$.

RESULTS AND DISCUSSION

Infrared spectroscopy

The IR adsorption peaks (—CONH—) of the title compounds (a, b, c and d) appear at wavelengths of about 1701 cm^{-1}, which are abnormally blue-shifted 43 cm^{-1} compared with those of the corresponding 5-alkyl amide-1,10-phenanthroline.[8] Thus, we suggest that these may be an important contribution of d-π feedback effect from metal Ru to ligands. The phenomenon suggests the thermal stability of these compounds which has been proved by the thermogravimetric analysis in our experiments.

Proton nuclear magnetic resonance spectroscopy

^1H NMR spectrum and ^1H-^1H COSY spectrum at low field of **a** are shown in Fig. 1 and Fig. 2, respectively, and the whole attributions of proton nuclear magnetic resonance spectroscopy of the title compounds are in virtue of the ^1H-^1H COSY technique. A3-H and A3′-H, A6-H, A6′-H, B2-H and B9-H occur at higher field due to a local shielding effect from the special adjacent ligands.

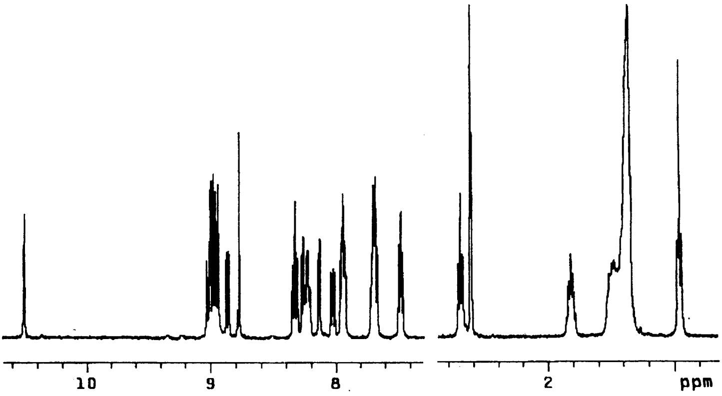


Fig. 1. ^1H NMR spectrum of **a**.

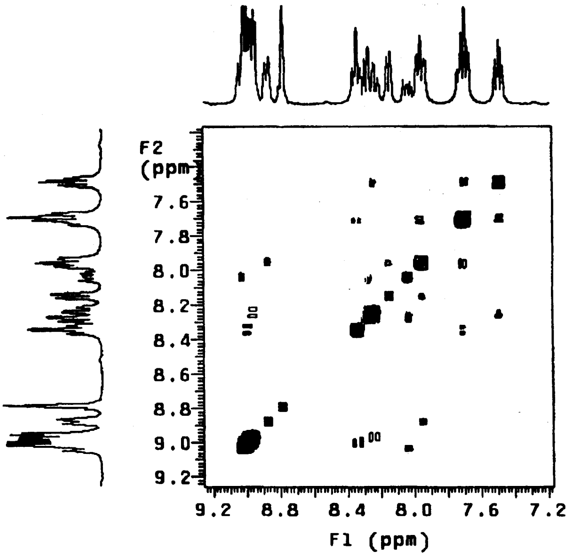
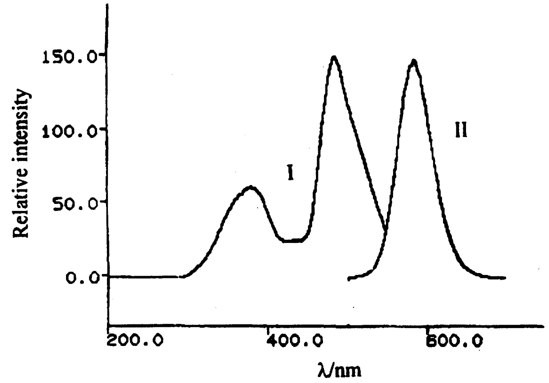


Fig. 2. ^1H-^1H COSY spectrum of **a**.

Fluorescence adsorption and emission

Fig. 3 shows fluorescence spectrum of 10^{-3} mol/L compound **a** in ethanol at room temperature, and almost similar results were obtained for **b-d**. Fluorescence adsorption and emission data of 10^{-3} mmol/L **a-d** are shown in Table 1. These intense adsorption bands are due to the MLCT transition where an electron is promoted from the metal centered t_{2g} orbital into a ligand centered π* orbital. This intense emission occurs at lower energy than does the ligand centered π* → π phosphorescence; here there is a significant contribution to the excited state from an interaction between the metal *d* orbitals and the ligand π system.[9]



I. adsorption spectrum; II. emission spectrum.

Fig. 3. Fluorescence spectrum of **a**.

TABLE-1
DATA OF FLUORESCENCE SPECTRA FOR NEW Ru(II) POLYPYRIDINE HEXAFLUOROPHOSPHATE SURFACTANTS **a-d**.

Compound	$\lambda_{adsorption}$/nm	$\lambda_{excitation}$/nm
a	380, 485	585
b	379, 490	587
c	380, 488	584
d	365, 504	586

Etectrochemistry

The electrochemical properties of the title compounds were investigated by cyclic voltammetry. All new Ru(II) polypyridine hexafluorophosphate surfactants **a-d** undergo a reversible single-electron oxidation when the potential scans from 1.05 to 1.50 V, *e.g.*, Fig. 4, shows the cyclic voltammogram of compound **a** recorded at 100 mV/s, and very similar results were obtained for **b**, **c** and **d**. Table-2 shows cyclic voltammetric data for **a**, **b**, **c** and **d**.

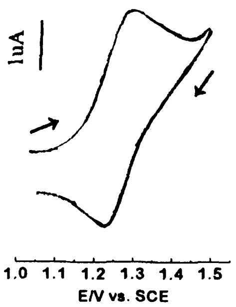


Fig. 4. Cyclic voltammograms of **a**

TABLE-2
CYCLIC VOLTAMMETRIC DATA FOR NEW Ru(II) POLYPYRIDINE HEXAFLUOROPHOSPHATE SURFACTANTS **a–d** [1]

Compound	EP^a/V	EP^c/V	$E^{1/2}$/V	ΔEP/mV
a	1.295	1.228	1.262	67
b	1.294	1.229	1.261	65
c	1.294	1.229	1.261	65
d	1.293	1.230	1.261	63

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[1] Experimental conditions: **a-d** (*ca.* 10^{-3} mol/L), supporting electrolyte *n*-Bu_4 NPF_6 (*ca.* 0.1 mol/L) in dry acetonitrile.

Electrochemiluminescence

ECL intensity of **a** and 0.05 mol dm^{-3} *n*-tripropyl-amine is positively relative to its concentrations from 10^{-5} to 10^{-7} mol/L in 0.01 mol/L phosphate buffer aqueous solution (pH = 7.5) when a 1.25 V voltage *vs.* an Ag quasi-reference electrode was applied to the Au woking electrode; so is each of **b**, **c** and **d.**

Conclusion

As expected from these results, all new Ru(II) complexes **a**, **b**, **c** and **d** behave as good materials for electrochemiluminescent LB monolayer films, and thus further experiments are under way to prepare and investigate LB membrane based on the novel Ru(II) complexes.

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