Asian Journal of Chemistry Vol. 11, No. 4 (1999), 1514–1516

NOTE

Four Novel Screw-like Tris(1,10-phenanthroline) Ruthenium(II) Bishexafluorophosphate Derivatives

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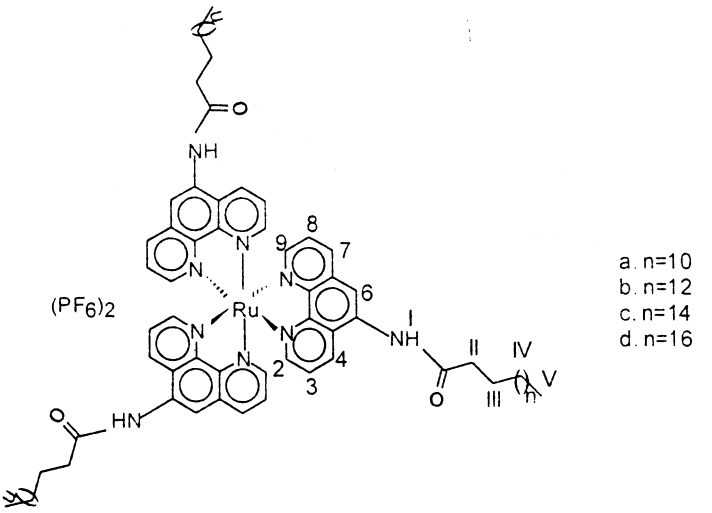
Four novel screw-like Ru(II) complexes, tris(5-lauramide-1,10-phenanthroline)Ru(II) bishexafluorophosphate, tris(5-myristamide-1,10-phenanthroline)Ru(II) bishexafluorophosphate, tris(5-palmi tamide-1, 10-phenanthroline)Ru(II) bishexafluorophosphate and tris (5-stearamide-1,10-phenanthroline)Ru(II) bishexafluorophosphate have been efficiently synthesized. They are confirmed by the techniques of IR, ^{1}H NMR, ^{1}H-^{1}H COSY and ES-MS. Also, their electrochemistry, fluorescence and electrochemiluminescence are reported.

Electrochemiluminescence (ECL) has been a highly sensitive and selective detection technique and attracted many scholars in recent years.[1–3] A sensor of immobilized tris(2,2′-bipyridine)ruthenium(II) in Nafion was used in a flow injection system for ECL quantitation of oxalate, alkyl amines and NADH, but its widespread use is limited by the instability of the sensor in the long term.[4] Leakage of tris(2,2′-bipyridine)ruthenium(II) from matrix to aqueous solution is the key reason for the instability. We think improving the hydrophobicity of active materials for the sensor may solve this problem. It is known that ECL efficiency of tris(1,10-phenanthroline)ruthenium(II) is higher than that of tris(2,2′-bipyridine)ruthenium(II).[5] Thus, four novel screw-like tris(1,10-phenanthroline) ruthenium(II) bishexafluorophosphate derivatives shown in Scheme-1 have been designed and synthesized in order to fabricate new type ECL sensor.

The key starting materials were synthesized according to the method of reference.[6] The title compounds were synthesized as follows. One molar mount of ruthenium chloride and three molar mounts of 1,10-phenanthroline derivatives were refluxed in DMF for 6 h, then the reaction was cooled and filtered. The filtrate was evaporated to be dry by rotary evaporator, and methanol and water were added to the residue. After filtration, the filtrate was added to superfluous sodium hexafluorophosphate, and the solution was kept in refrigerator for 24 h. Orange microcrystals were obtained in 78–82% yield. The title compounds were



Scheme-1. Chemical structure of screw like trist(1,10-phenanthroline)Ru(II)derivatives

confirmed by IR, ^{1}H NMR,^{1}H-^{1}H COSY and ES-MS. All data of proton nuclear magnetic spectra and selected data of IR and ES-MS are shown in Table-1.

TABLE-1
DATA FOR ^{1}H NMR, IR AND ES-MS OF TITLE COMPOUNDS

Com-plex	δ_H/ppm												IR/cm^{-1}	ES-MS
	H_2	H_3	H_4	H_6	H_7	H_8	H_9	H_I	H_{II}	H_{III}	H_{IV}	H_V	ν(C=O)	[M-PF_6]$^+$
a	8.23	7.91	9.01	8.78	8.83	7.82	8.08	10.53	2.71	1.82	1.38	0.95	1700	1377.7
b	8.23	7.91	9.01	8.78	8.83	7.82	8.07	10.51	2.70	1.82	1.37	0.95	1699	1461.5
c	8.24	7.91	9.00	8.78	8.83	7.82	8.06	10.50	2.70	1.81	1.36	0.95	1701	1545.4
d	8.23	7.91	9.00	8.78	8.84	7.82	8.07	10.50	2.70	1.81	1.37	0.97	1700	1629.6

Cyclic voltammetry experiments of 1 mmol/L title compounds in acetonitrile with 0.1 mol/L (TBA)PF_6 as supporting electrolyte were taken on a CHI 660 electrochemical station. The working electrode was an Au disk and all potentials were measured relative to a SCE electrode. The counter electrode was a Pt wire and the scan rate 100 mV/s. Fluorescence spectra of 0.1 mmol/L title compounds in ethanol were taken on a Shimadzu RF-5000 fluorescence spectrometer at 20°C. Data of electrochemistry and fluorescence are shown in Table-2. Our

experiments have shown that these four novel compounds all have good ECL properties.

The further experiments are under way to prepare highly selective and sensitive ECL sensors based on these novel Ru(II) complexes.

TABLE-2
DATA FOR CYCLIC VOLTAMMETRY FLUORESCENCE OF TITLE COMPOUNDS

Complex	Cyclic voltammetry				Fluorescence	
	E^{pa}/V	E^{pc}/V	$E^{1/2}$/V	ΔE^{p}/mV	$\lambda_{adsorption}$/nm	$\lambda_{emission}$/nm
a	1.316	1.248	1.282	68	369, 486	581
b	1.314	1.250	1.282	64	369, 485	582
c	1.314	1.251	1.282	65	370, 485	580
d	1.313	1.251	1.282	62	371, 484	582

ACKNOWLEDGEMENT

The authors would like to thank the Department of Science and Technology of China for the financial support of this key project (Grant No. 96-A23-03-01).

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(Received: 27 January 1999; Accepted: 31 July 1999) AJC– 1825