Rapid Synthesis of New Emitting Ir(III) Polypyridine Complexes

Naokazu Yoshikawa,Yoshitaka Masuda, and Takeko Matsumura-Inoue*
Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528

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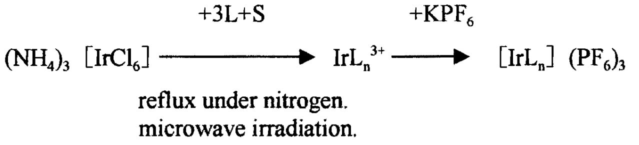
A microwave-assisted synthesis of photosensitive iridium(III) polypyridine complexes has been developed. The spectroscopic and electrochemical properties of the newly prepared complexes were studied. These complexes were characterized by intense phosphorescence emission from 505 nm to 630 nm.

Transition metal complexes with polypyridine ligands have attracted much attention for their photoinitiated energy transfer and redox properties.[1–3] In particular, iridium polypyridine complexes have been the subject of recent studies.[3–5] However, the synthesis of iridium polypyridine complexes is time consuming and laborious for purification and thus the yield is very low. Here, we report a rapid synthesis of Ir(III) complexes by microwave irradiation and the spectroscopic and electrochemical properties of the newly prepared complexes. The synthetic procedures are given in Scheme 1.



$$(NH_4)_3\,[IrCl_6] \xrightarrow[\text{reflux under nitrogen. microwave irradiation.}]{+3L+S} IrL_n^{3+} \xrightarrow{+KPF_6} [IrL_n]\,(PF_6)_3$$

Scheme 1. Reaction scheme of the synthesis of the polypyridine complexes. L represents a bipyridine ligand. S refers to ethylene glycol.

A typical procedure of the preparation of polypyridine complexes is as follows. The precursor $(NH_4)_3[IrCl_6]\cdot H_2O$ (0.238 g, 0.5 mmol) and 2,2'-bipyridine (0.234 g, 1.5 mmol) were suspended in ethylene glycol (15 mL). Under purging nitrogen atmosphere, the suspension was subjected to reflux for 15 min in the microwave oven[6] (RR-12AF, 500 W, Mitsubisi Denki co. Ltd) with a frequency of 2450 MHz activates the OH group of ethylene glycol, and then cooled to room temperature. The saturated aqueous solution of KPF_6 (20 mL) was added for precipitation. The precipitate was filtrated and recrystallized from acetonitrile / diethyl ether to afford $[Ir(bpy)_3](PF_6)_3$ in a yield of 84%. The other complexes were also prepared by the procedures similar to those for $[Ir(bpy)_3](PF_6)_3$.[7] The abbreviations of these complexes and ligands are as follows: $[Ir(bpy)_3](PF_6)_3$: (1A), 2,2'-bipyridine: bpy, $[Ir(dmbpy)_3](PF_6)_3$: (2A), 4,4'-dimetyl-2,2'-bipyridine: dmbpy, $[Ir(dpbpy)_3](PF_6)_3$: (3A), 4,4'-diphenyl-2,2'-bipyridine: dpbpy, $[Ir(phen)_3](PF_6)_3$: (4A), 1,10-phenanthroline: phen, $[Ir\ (dpphen)_3](PF_6)_3$: (5A), 4,7-diphenyl-1,10-phenanthroline: dpphen, $[Ir(bqn)_3](PF_6)_3$:

Table 1. Yields, absorption, luminescence, and electrochemical properties of the complexes

	Complexes	Yields %	Absorption (298 K)			Luminescence[a] (298 K)		Electrochemistry V vs. Ag/AgCl		
			λ max /nm (ε $10^3 M^{-1}cm^{-1}$)		E_{ab} eV	λ max/nm (ε $10^7 M^{-1}cm^{-1}$)	E_{em} eV	Red1st	Ox	ΔE
1A	$[Ir(bpy)_3]$	84	284(41.9)	379(8.1)	3.27	528(3.58)	2.35	-1.09,	2.07	3.16
1B	$[Ir(bpy)_2Cl_2]$	75	283(26.8)	381(3.8)	3.25	535(3.31)	2.32	-1.07,	2.07	3.14
2A	$[Ir(dmbpy)_3]$	62	273(50.4)	378(8.4)	3.28	525(2.00)	2.36	-1.18,	1.97	3.15
2B	$[Ir(dmbpy)_2Cl_2]$	72	270(58.3)	378(7.0)	3.28	532(2.49)	2.33	-1.16,	1.95	3.11
3A	$[Ir(dpbpy)_3]$	45	282(104)	398(13.8)	3.12	506(163)	2.45	-1.02,	1.98	3.00
3B	$[Ir(dpbpy)_2Cl_2]$	55	282(62.1)	398(6.93)	3.12	505(111)	2.46	-1.02,	1.99	3.01
4A	$[Ir(phen)_3]$	72	265(67.2)	397(4.1)	3.12	529(4.38)	2.34	-1.07,	2.05	3.12
4B	$[Ir(phen)_2Cl_2]$	60	267(50.0)	403(5.7)	3.07	529(5.51)	2.34	-1.09,	2.04	3.13
5A	$[Ir(dpphen)_3]$	91	282(112)	402(16.4)	3.08	539(18.1)	2.30	-1.04,	1.99	3.03
5B	$[Ir(dpphen)_2Cl_2]$	80	281(64.8)	405(8.4)	3.06	543(12.7)	2.28	-1.04,	1.97	3.01
6A	$[Ir(bqn)_3]$	43	269(103)	465(5.9)	2.67	630(22.4)[b]	1.97	-0.51,	2.03	2.54
6B	$[Ir(bqn)_2Cl_2]$	64	270(65.3)	465(7.0)	2.67	622(13.8)[b]	1.99	-0.50,	2.03	2.53
7A	$[Ru(bpy)_3]$					600(0.98)	2.07	-1.26		

Acetonitrile solution was used unless otherwise noted. Electrochemical data are from differential pulse voltammograms.
ΔE represents the potential difference between the first reduction and oxidation peaks.

[a] λex=318 nm. [b] λex=383 nm.

(6A), 2,2'-biquinoline: bqn.

The spectroscopic and electrochemical properties of the newly synthesized complexes are summarized in Table 1. The absorption spectra in acetonitrile give the intensive absorption bands below 300 nm (ε in the range 10^4–10^5 $M^{-1}cm^{-1}$), which are assigned to π–π^* transition of polypyridine ligands in the complexes, and the shoulder at 378–465 nm, which corresponds to a mixed π–π^* and metal-to-ligand charge transfer transition (MLCT).[8, 9]

The complexes exhibit an intense luminescence (excitation at 318 nm) around 505–630 nm in acetonitrile solution at room temperature, which can be assigned to a triplet π–π^* emission (Table 1).[10] In particular, the emission intensity of $Ir(dpbpy)_3{}^{3+}$ is more than one hundred times as large as that for $Ru(bpy)_3{}^{2+}$ (excitation at 318 nm). The range of π–π^* absorption band energy is 2.67 eV to 3.28 eV, while that of emission band energy is 1.97 eV to 2.36 eV. The complex $Ir(bqn)_3{}^{3+}$ with electron-withdrawing ligands shows a phosphorescence emission and a large red-shift to 630 nm. It is noticed that Ir polypyridine complex shows intense emission with various colors, such as yellow for $Ir(dpphen)_3{}^{3+}$, red for $Ir(bqn)_3{}^{3+}$, which can be applied to photosensitizers.

Cyclic voltammograms of these complexes show three or four reduction waves corresponding to the reduction of polypyridine ligands in the complexes from 0 to –2.0 V. The reduction and oxidation potentials of iridium(III) bis-bipyridine complexes are nearly equal to those of iridium(III) tris-bipyridine complexes. Thus, these trends are different from those of Ru polypyridine complexes.[11]

The reduction and oxidation potentials are changed by the electronic donor or acceptor properties of ligands.[12] $Ir(dmbpy)_3{}^{3+}$, a complex with an electron-donating ligand, give smost negative reduction potential among the complexes listed in Table 1. On the other hand, $Ir(bqn)_3{}^{3+}$, a complex with an electron-withdrawing ligand exhibits most positive reduction potentials. The oxidation waves of $Ir(phen)_3{}^{3+}$, $Ir(dpphen)_3{}^{3+}$, and $Ir(bqn)_3{}^{3+}$ at 2.05 V, 1.99 V and 2.03 V respectively, are nearly equal to those of the free ligands, and thus the oxidation process corresponds to the removal of an electron from the lumo π orbital of ligands in the complexes. The oxidation-potentials of $Ir(bpy)_3{}^{3+}$ and $Ir(dmbpy)_3{}^{3+}$ are more negative (+0.2 V) than those of the free ligands, which suggests the weak contribution to ligand π orbitals. It is confirmed that an electron is removed from the π orbital of ligand in the oxidation process, while in the reduction process three or four electrons are added one by one to π^* orbitals of the ligand.

The correlation between π–π^* absorption band energy (E_{ab}) and redox potentials (ΔE) shows a linear relationship with a slope of unity (Figure 1), which indicates that the potential difference between the first reduction and the oxidation peaks is consistent with the absorption band energy.

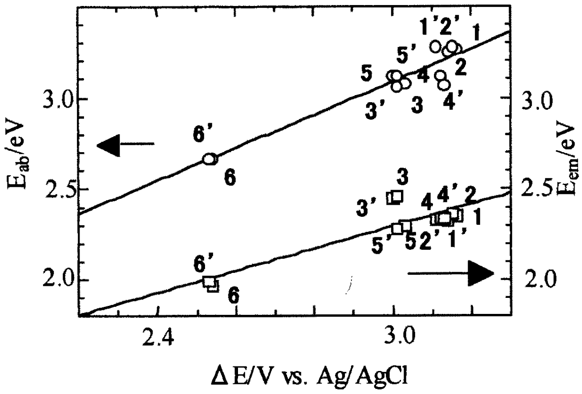


Figure 1. Relationships between the emission and absorption energy versus ΔE. The entry is the same as in Table 1. ○ : Plot of E_{ab} vs. ΔE. □ : Plot of E_{em} vs. ΔE. 1～6 correspond to tris-bipyridine complexes. 1'～6' correspond to bis-bipyridine complexes.

References and Notes

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7 Anal. Found: C, 53.08; H, 3.07; N, 5.55%. Calcd for $C_{72}H_{48}N_6IrP_3F_{18}$: C, 53.23; H, 2.96; N, 5.17%. Found: C, 48.96; H, 3.46; N, 5.14%. Calcd for $C_{66}H_{48}N_6IrP_3F_{18}$: C, 51.06; H, 3.09; N, 5.42%. Found: C, 37.09; H, 3.13; N, 7.17%. Calcd for $C_{36}H_{36}N_6IrP_3F_{18}$: C, 36.27; H, 3.02; N, 7.05%. Found: C, 44.57; H, 2.56; N, 5.75%. Calcd for $C_{54}H_{36}N_6IrP_3F_{18}$: C, 46.44; H, 2.58; N, 6.02%.

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