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Deuteration isotope effect on nonradiative transition of *fac*-tris (2-phenylpyridinato) iridium (III) complexes

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ABSTRACT

Deuterated 2-phenylpyridine and coordinated iridium(III) complexes $Ir(ppy-h_8)_n(ppy-d_8)_{3-n}$ (n = 0, 1, 2, 3) have been prepared. Both the relative and absolute phosphorescent quantum yields and the emission decay times of dilute solutions have been studied around room temperature. Phosphorescent quantum yields of fully deuterated $Ir(ppy-d_8)_3$ have ranged from 0.80 to 0.93 in several solvents, which are higher than that of normal complex $Ir(ppy-h_8)_3$. Ligand deuteration increases the quantum yield. On the other hand solvent deuteration has almost no effect. Nonradiative rate constants show little temperature dependence for the both complexes ($k_{nr} = 1.4 \pm 0.3 \times 10^5 \text{ s}^{-1}$ and $0.95 \pm 0.2 \times 10^5 \text{ s}^{-1}$) at 273–308 K.

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1. Introduction

Cyclometallated iridium(III) complexes have been widely studied for decades because of their intriguing photophysical properties and the good prospects they offer for developing a new field of applications in organic light-emitting diodes (OLEDs) [1–6]. Ir(ppy-*h*₈)₃ (ppyH-*h*₉: 2-phenylpyridine) is a well-known complex because of its prominent features, which include a relatively shortlived excited state, a high luminescence quantum yield and clear green luminescence. This complex can be used as a phosphorescent emitter in OLEDs and its emission mechanism has also been studied theoretically [6-13]. To investigate the excited state properties and relaxation processes, the deuteration of organic molecules and transition metal complexes have been studied [14-20]. The deuteration of polypyridyl ruthenium(II) and rare earth complexes pushes up their luminescent quantum yield (Φ) and excited state lifetime (τ) [21,22]. The ligand deuteration of a complex [Ru(bpy- $(d_8)_3]^{2+}$ (bpy = 2,2'-bipyridine) results in an approximately 20% increase in its τ , in addition solvent deuteration doubles [15]. Yanagida et al. have realized an enhanced Φ with polymer doped neodymium(III) complexes by eliminating C-H vibrational oscillators [23]. A reduction in the number of C-H oscillators by the deuteration and/or fluorination of Nd(HFA- h_1)₃ in PMMA [HFA- h_2 : hexafluoroacetylacetone and PMMA: poly(methylmethacrylate)] greatly increases to $\Phi = 0.7$ for Nd(HFA- d_1)₃/P-FiPMA [P-FiPMA: poly(hexafluoroisopropylmethacrylate)] from $\Phi < 0.01$ for Nd-(HFA- h_1)₃/PMMA. These enhancements of Φ and τ are caused by the diminished nonradiative processes that result from reducing

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the probability of vibronic coupling between the electronically excited complex and vibrational modes [22]. Although the deuteration effect on phosphorescent metal complexes seem to be poorer than that of fluorescent molecules [22], investigations on the candidate materials in OLEDs will afford further information for better understanding [20].

Photophysical study of deuterated iridium(III) complex $IrCl_2(bpy-d_8)_2^+$ was first reported from Watts et al. [24]. The excited state lifetime, which showed temperature dependence from 77 to 354 K, was increased by deuteration of the ligands. Deuteration seems to contribute in the decay kinetics that is a dual emission from the thermally equilibrated charge transfer and ligand field excited states to the ground state. Although cyclometallated iridium(III) complexes have drawn attention for their phosphorescent character, there have been few reports on the isotope effect of them. Therefore, in this study we measured luminescence spectra and decay times to examine the nature of the radiative and nonradiative processes of $Ir(ppy-h_8)_3$ and $Ir(ppy-d_8)_3$. Both the ligand and solvent deuteration isotope effects of a dilute solution are discussed (see Fig. 1).

2. Experiments

General: UV–vis absorption spectra were measured by Hewlett–Packard 8453 diode array spectrometer. The luminescence spectra were recorded with a spectrometer (HORIBA JOBIN YVON-SPEX Fluorolog-3) to determine the relative luminescence quantum yield of Ir(ppy)₃. The excitation wavelength was set at 370 nm for every measurement. ESI-MS measurements were carried out on a Thermo Quest FINNIGAN AQA. ¹H NMR spectra were measured by a Bruker Avance 400 spectrometer (external standard



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Fig. 1. Structure of $Ir(ppy-h_8)_n(ppy-d_8)_{3-n}$ (*n* = 0, 1, 2, 3).

TMS = 0.00 ppm). Emission lifetimes were evaluated by the least square method on a PC for luminescence time courses recorded after a laser pulse (Nd:YAG laser 355 nm, 1 mJ/pulse). The detection system consisted of a photomultiplier H3186 (Hamamatsu, rise time 2 ns) directly coupled to a monochromator HR320 (Iobin-Yvon 1200 g/mm). The signal from the PM was directly analyzed by an oscilloscope TDS310 (Tektronix) working in average mode. Absolute luminescence quantum yields were measured by a Hamamatsu photonics k.k. C9920-02 system. Relative phosphorescence quantum yields were determined with using ethanol solution of rhodamine6G (Φ_{FL} = 0.95 at 298 K) as an external standard [25]. All solutions for luminescence measurements were prepared using the optical dilute method $(1.0 \times 10^{-6} \text{ to } 1.0 \times 10^{-6})$ 10^{-7} mol/l) and degassed by the freeze-pump-thaw method [26]. A microwave apparatus CEM Discover (2.45 GHz frequency, CEM Corporation, NC, USA) and WMO1000S (TOKYO RIKAKIKAI CO, LTD) were used for small (within 3 mL) and large scale syntheses, respectively.

Materials: Deuterium oxide (99.9 atom%) was purchased from ISOTECTM. Other reagents were purchased from commercial suppliers and used without further purification. $Ir(ppy-h_8)_3$ was prepared by a microwave assisted method according to a literature procedure [27].

2-Phenylpyridine- d_9 : A mixture of D₂O 40 g (2 mol), ppyH- h_9 5.0 g (32 mmol), 200 mg of Pt/C (5 wt.%, 0.25 mol%) and 200 mg of Al powder (200 mesh, 7.4 mmol) were set in a stainless reactor which was sealed and then heated with stirring at 180 °C for 24 h. After cooling to room temperature, the suspension was filtered and washed by acetone. The filtrate was extracted by dichloromethane and the solvents of collected organic phase were evaporated. Resulting liquid was reacted again with the same procedure except Pt/Al₂O₃ was used instead of Pt/C. After taking the processes as well as the first reaction, the crude product was distilled at 70 °C under reduced pressure (<1 mm Hg) to obtain 4.0 g of colorless liquid (yield 80%). Deuterium content rate was determined to be over 95% in average by ¹H NMR analysis with using 1,2-dibromoethane as an external standard. ESI-MS (relative abundance%) 163 (20), 164 (100), 165 (10), (MH⁺); ¹H NMR ((CD₃)₂CO 400 MHz) δ(ppm); 8.67, 8.13, 7.93, 7.86, 7.49, 7.43, 7.31 (every peak was observed as singlet); FT-IR (wavenumber of peaks) 2272, 2253, 2201, 2103, 1549, 1525, 1411, 1366, 1333, 1307, 1274, 1230, 995, 847, 821, 736, 598, 580, 562, 546.

*Ir(ppy-d₈)*₃: A mixture of iridium trichloride hydrate (IrCl₃·3H₂O) 35 mg (0.1 mmol), 2-phenylpyridine- d_9 165 mg (1 mmol) and 1 mL of ethylene glycol were set in a 10 mL glass vessel. The reaction was carried out by microwave irradiation at 200 °C for 30 min. After cooling to room temperature, 1 M aqueous hydrochloric acid was added to the solution. The precipitated product was filtered, washed with 1 M HCl (aq) followed by water. The collected crude product was reacted with 165 mg of 2-phenylpyridine- d_9 in ethylene glycol 1 mL by microwave irradiation; and this was repeated twice. The desired product was purified by a silica gel column chromatography with dichloromethane as an eluent (yield 55 mg 81%). ESI-MS (relative abundance %) 675 (20), 676 (50), 677 (80), 678 (90), 679 (100), 680 (30), 681 (10), (MH⁺); ¹H NMR

(400 MHz, δ(CD₃)₂SO) 8.11, 7.77, 7.73, 7.46, 7.10, 6.78, 6.66, 6.63; FT-IR (wavenumber of peaks) 2277, 2251, 1566, 1548, 1529, 1502, 1401, 1349, 1328, 1297, 1260, 1234, 1021, 986, 974, 850, 822, 757, 636, 577.

3. Result and discussion

3.1. Synthesis of deuterated compounds

Deuterated 2-phenylpyridine-d₉ was prepared by catalytic H–D exchange reactions with deuterium oxide (D₂O), aluminum powder and platinum on carbon or on aluminum oxide at 180 °C for 24 h as a modified literature procedure [28-30]. One of our advantages in preparing deuterated ligands is to reduce the use of deuterium oxide by stepwise deuteration reaction. Since the deuterium content rate of the desired product depends on the protium-todeuterium molar ratio (%) in the reaction system, we first run a reaction with $[D] \sim 90\%$ and enriched by a second reaction with the same volume of fresh deuterium oxide; this will lead the final deuterium content rate to $[D] \sim 99\%$ and reduce the use of deuterium oxide by 5 times. A series of iridium complexes Ir(ppy $h_8)_n(\text{ppy-}d_8)_{3-n}$ (n = 0, 1, 2, 3) were synthesized by microwave assisted reactions [27]. The advantage of the microwave technique is the reduction of reaction time. Differently from the preparation of [Ru(bpy)₃]²⁺, Ir(ppy)₃ requires dehydrogenation processes for complexation and long reaction time may cause de-deuteration of the ligands. Thus, microwave assisted reaction is a preferred approach. Fig. 2 shows the FT-IR spectrum of fac-Ir(ppy- h_8)₃ and Ir(p $py-d_8$)₃. The highest energy of observed absorption bands is shifted from 3050 to 2280 cm^{-1} by deuteration. The low frequency shift should reduce extent of vibronic coupling and thus energy dissipation process of excited $Ir(ppy)_3$. It has been pointed out that energy reduction in the fingerprint region such as CCC and CCH modes can also contribute to the deactivation processes of $\operatorname{Ru}(\operatorname{bpy-}d_n)_3^{2+}$ [31,32]. Recently, Raman and infrared absorption energies and intensities of [Ru(bpy)₂(CN)₂] and [Ir(bpy)₂(CN)₂]⁺ have been calculated based on the density functional theory [33]. By following the provided information, we have assigned the experimentally given low energy modes ($v < 1500 \text{ cm}^{-1}$) of Ir(ppy- h_8)₃ and Ir(ppy d_8)₃. The vibrational frequencies of the components are listed in Table 1 accompanied by relevant data. Both the deuterated complexes show lower energies than their corresponding normal complexes. Since several modes often contribute together in the low energy frequencies, the extent of energy decrements by deuteration is not simply same in each absorption. Larger overtone factors results in poorer vibronic coupling between the states so that



Fig. 2. FT-IR spectra of $Ir(ppy-d_8)_3$ (top) and $Ir(ppy-h_8)_3$ (bottom) of KBr tablet under nitrogen atmosphere at room temperature.

Table 1
Selected vibration modes and frequencies of infrared and Raman peaks.

Types of vibration ^{a,b}	$[Ir(bpy-h_8)_2(CN)_2]^+$	b	Ir(ppy) ₃ ^c		[Ru(bpy) ₃]Cl ₂ ^a	
	I _{Ram} ^d	v ^e	v (-h ₈)	v (-d ₈)	$v(-h_8)$	$v(-d_8)$
ν(C–C), δ(CH)	100.8	1325	1310	1260	1320 ^e	1255 ^e
$v(C-C)$, $\delta(CH)$, $v(C-N)$	317.3	1324	1299	1234	1310 ^c	1227 ^c
$v(C-N), v(C-C), \delta(CH)$	14.1-51.0	1279-1285	1261	1021	1264 ^e	1020 ^e
δ (CH), ν (C–C), α (CCC)	32.4	1110	1124	872	1121 ^c	867 ^c
δ (CH), v(C–C), α (CCC)	31.2	1059	1058	850	1067 ^e	851 ^e

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^a Ref. [31]. ^b Ref. [33].

^c Infrared absorption frequency (cm⁻¹).

^d Calculated Raman intensity in Ref. [33].

^e Resonance Raman frequency (cm⁻¹).

depression of the thermal relaxation of the excited $Ir(ppy)_3$ is plausible.

3.2. Luminescence and photophysical properties of Ir(ppy)₃

The luminescence peak wavelength of the $Ir(ppy-h_8)_3$ and $Ir(p-h_8)_3$ $py-d_8)_3$ were located at 523 nm with the identical waveform at 293 K in acetonitrile- h_3 (Table 2). A slight bathochromic shift was observed compared with that of toluene solution (λ_{max} = 511 nm), tetrahydrofuran solution ($\lambda_{max} = 514 \text{ nm}$) and dichloromethane solution (λ_{max} = 516 nm). The energy shift behavior was similar to ionic $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ [34], suggesting that emission energy of neutral $Ir(ppy)_3$ is also affected by solvents polarity. The luminescence quantum yield determined for $Ir(ppy-h_8)_3$ by a relative measurement method was 0.87 ± 0.05 in toluene, whereas that of Ir(ppy d_8)₃ was 0.93 ± 0.05. These results are in good agreement with the recently reported Ir(ppy- h_8)₃: Φ_{PL} = 89 ± 3 (%) in dichloromethane [35]. It has been brought up that absolute method is a useful technique to obtain Φ [36], and we measured them in the same fashion. Deuterated Ir(ppy- d_8)₃ exhibited $\Phi = 0.80 \pm 0.03$, 0.90 ± 0.04 and 0.92 ± 0.04 which was slightly larger than $Ir(ppy-h_8)_3$ in each entry of Table 2. To interpret this difference, we compared the corresponding rate constants. The nonradiative rate constant (k_{nr}) of the deuterated complex in each solution was considerably reduced from that of the normal complex. Exchanging the C-H for C-D vibrational oscillators reduced the nonradiative deactivation as a result of reduced probability of vibronic coupling between the states and this is attributed to the ligand deuteration effect of $Ir(ppy)_3$. By contrast, the k_r is more likely to play a key role in controlling the Φ and τ because it is about an order magnitude larger than k_{nr} in this Ir(ppy)₃ system. As regards this role, the solvent dependence of Φ is attributable to the k_r , in other words, the solvent contributes less to the k_{nr} . Thus, it is not reasonable to consider a strong quenching process model in terms of the interaction between excited Ir(ppy)₃ and solvent. To discuss this

Table 2				
Photophysical	properties	of $Ir(ppy-h_8)_3$	and I	$lr(ppy-d_8)_3$

	λ _{max} nm	Φ	τ µs	$k_r \ 10^5 \ { m s}^{-1}$	$k_{nr} \ 10^5 \ { m s}^{-1}$	Solvent
Ir(ppy-h ₈) ₃	511	0.87^{a}	1.5	5.8	0.9	Toluene
	514	0.84^{b}	1.6	5.1	1.0	Tetrahydrofuran
	519	0.89^{b}	1.4	6.4	0.8	Dichloromethane
	523	0.74^{b}	1.8	4.1	1.4	Acetonitrile
Ir(ppy- <i>d</i> ₈) ₃	511	0.93 ^a	1.6	5.8	0.4	Toluene
	514	0.90 ^b	1.8	5.1	0.6	Tetrahydrofuran
	519	0.92 ^b	1.7	5.5	0.5	Dichloromethane
	523	0.80 ^b	2.1	3.9	0.9	Acetonitrile

^a Values obtained from relative quantum yield measurement.

^b Values obtained from absolute quantum yield measurements.

in detail, we consider the nonradiative pathways of $Ir(ppy)_3$ in possible distributions, namely nonradiative relaxation through a thermal transition to a metal-centered MC state, intermolecular quenching through energy transfer via solvents, and intramolecular deactivation as rapid horizontal transitions from excited to ground state electronic surfaces. Here, the ligand field parameter of $Ir(ppy)_3$ is sufficiently large and hence the MC state is inaccessible from the lowest excited state around room temperature [5]. To discuss the inter- and intramolecular deactivation processes, we measured the temperature dependent luminescence lifetime of $Ir(ppy-h_8)_3$ and $Ir(ppy-d_8)_3$ in acetonitrile- h_3/d_3 from 273 to 308 K, as summarized in Table 3. Both the complexes $Ir(ppy-h_8)_3$ and Ir(ppy- d_8)₃ in acetonitrile- h_3 were $\tau = 1.8 \,\mu s$ (1.76–1.79 μs) and $\tau = 2.1$ us (2.07–2.13 us), respectively. The deuterated sample showed a slight increase in τ ; however, neither sample exhibited temperature dependence. Moreover, the result of deuterated solution were $\tau = 1.8 \ \mu s \ (1.77 - 1.82 \ \mu s)$ and $\tau = 2.1 \ \mu s \ (2.06 - 2.10 \ \mu s)$, thus no deuteration solvent effect was observed. It is worth noting that the lack of temperature and solvent deuteration dependence is unique for Ir(ppy)₃ since this behavior contrasts with that of ruthenium(II) and osmium(II) complexes [37,38]. It has been reported that the k_{nr} of Os(bpy)²⁺₃ increases with temperature as a result of activated intermolecular quenching, such as an energy transfer from the excited complex molecule to the solvent [38]. Solvent deuteration suppresses this interaction between the energy donor and the acceptor, therefore the isotope effect is observed in the enhancement of the Φ and τ . The fact that the k_{nr} is independent of temperature and solvent deuteration indicates that there is weak solvent-chromophore quenching of excited Ir(ppy)₃ by energy transfer processes. Fig. 3 clearly shows that only the ligand deuteration effect is observed as the logarithm of k_{nr} decrease from 11.8 ± 0.2 to 11.4 ± 0.2 . Accordingly, we interpret this to mean that intramolecular deactivation is a main pathway for the nonradiative processes of $Ir(ppy)_3$.

The luminescence quantum yield and excited state lifetime of partially deuterated $Ir(ppy-h_8)_2(ppy-d_8)$ and $Ir(ppy-h_8)(ppy-d_8)_2$, which were prepared by combining $ppyH/D-h_9/d_9$ ligands, were

able 3			
uminescence	lifetime of $Ir(ppy-h_8)$	$_3$ and Ir(ppy- d_8) ₃	in acetonitrile- h_3/d_3 .

	τ µs							
	273 K	278 K	283 K	288 K	293 K	298 K	303 K	308 K
Ir(ppy-ha CH₃CN CD₃CN	⁸⁾ ₃ 1.76 1.78	1.76 1.81	1.77 1.77	1.77 1.80	1.78 1.82	1.79 1.79	1.79 1.80	1.77 1.81
Ir(ppy-da CH₃CN CD₃CN	₈) ₃ 2.07 2.10	2.09 2.07	2.09 2.09	2.13 2.06	2.13 2.10	2.07 2.09	2.13 2.10	2.12 2.08



Fig. 3. Plot of the nonradiative rate constants versus temperature of $Ir(ppy-h_8)_3$ and Ir(ppy- d_8)₃ in acetonitrile- h_3 : \Box/\blacksquare , and acetonitrile- d_3 : \bullet/\bigcirc . Error regions are represented by broken and dotted line for the normal complex and the deuterated one, respectively.

Tuble 1						
Photophysical	properties of	f Ir(ppy- h_8)	$(ppy-d_8)_{3-n}$	(n = 1,	2) in acetonitrile-	h3.

	Φ	τ μs	$k_r \\ 10^5 \text{ s}^{-1}$	$k_{nr} \ 10^5 { m s}^{-1}$
Ir(ppy- h_8) ₂ (ppy- d_8)	0.74	1.9	4.0	1.4
Ir(ppy- h_8)(ppy- d_8) ₂	0.70	1.8	3.9	1.7

 Φ = 0.74 ± 0.03, 0.70 ± 0.03 and τ = 1.9 µs, 1.8 µs in acetonitrile at room temperature, respectively. The values were identical to or less than that of $Ir(ppy-h_8)_3$ (Table 4). Unlike the proportional excited state lifetime increment of $\operatorname{Ru}(\operatorname{bpy-}h_8)_n(\operatorname{bpy-}d_8)_{3-n}^{2+}$ (*n* = 0, 1, 2, 3) [39], slight but a clear difference was only observed for a fully deuterated sample in a series of $Ir(ppy-h_8)_n(ppy-d_8)_{3-n}$ (*n* = 0, 1, 2, 3). Therefore the excited state energy of $Ir(ppy)_3$ seems to be trapped by a vibronic coupling with hydrogen involved vibrational modes. This result is similar to the ligand selective emission of $Pt(bpy-h_8)_n(bpy-d_8)_{2-n}^{2+}$ (n = 0, 1, 2) which is led by the effective intramolecular energy transfer at low temperature [21,40]. Although it is not easy to determine emission selectivity from room temperature measurements, the nonradiative process of Ir(ppy)₃ would be driven through intramolecular deactivation rather than intermolecular quenching through solvents.

We have prepared a series of deuterated $Ir(ppy-h_8)_n(ppy-d_8)_{3-n}$ (n = 0, 1, 2, 3) and studied the luminescence quantum yield and excited state lifetime of their solutions around room temperature. The Ir(ppy- d_8)₃ was Φ = 0.80, 0.90, 0.92, 0.93 in acetonitrile, tetrahydrofuran, dichloromethane and toluene, respectively, which was slightly higher than that of $Ir(ppy-h_8)_3$ in each system. The ligand deuteration isotope effect was observed as a result of the reduced k_{nr} when the sample was fully deuterated. A comparison of the rate constants for non-deuterated and fully deuterated Ir(ppy)₃ showed that the k_{nr} was independent of temperature (273–308 K) and solvent deuteration. Our observation of only the ligand deuteration effect suggests that intramolecular deactivation is a main pathway for the nonradiative process, and therefore $Ir(ppy)_3$ would have a Φ

as high as 0.9. We are presently in the pursuance of studies on OLED devices with these deuterated iridium emitters and the results will be reported in elsewhere.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2010.03.084.

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Table 4