Highly luminescent Langmuir–Blodgett films of amphiphilic Ir(III) complexes for application in gas sensing†

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Received (in Victoria, Australia) 28th November 2009, Accepted 4th January 2010
First published as an Advance Article on the web 15th February 2010
DOI: 10.1039/b9nj00714h

Four members of mixed ligand cyclometalated iridium(III) complexes, *fac*-[Ir(ppy)$_n$L$_{3-n}$] (ppy = 2-phenylpyridine; L = 2-(3-octadecyloxyphenyl)pyridine; n = 0–3), were prepared in a one-pot reaction between [Ir(ppy)$_2$(O^O)] (O^O = acetylacetonato) and LH in glycerol at 170 °C. Each compound was purified and optically resolved to Δ- and Λ-enantiomers chromatographically on a chiral column. A film of *fac*-[Ir(ppy)$_n$L$_{3-n}$] floating at an air–water interface was transferred horizontally onto a hydrophobic glass plate as a Langmuir–Blodgett (LB) film. The emission from a single layered LB film was monitored under the atmosphere of various kinds of gases. As a result, molecules with functional groups such as –OH, >C=O and –CN were found to quench efficiently excited *fac*-[Ir(ppy)$_n$L$_{3-n}$] in a film. The effects of isotope and molecular chirality on energy transfer were also investigated, comparing the quenching ability between H_2O and D_2O or between *R*-2-butanol and *S*-2-butanol on a racemic or chiral film of *fac*-[Ir(ppy)$_2$L], respectively.

Introduction

There has been an intensive interest in developing photo-responsive devices based on luminescent transition metal complexes.[1] Polypyridyl metal complexes with d^6-metal ions such as Ru(II) and Os(II) are the main applicants for these purposes.[2] Recently, attention has been paid to a group of cyclometalated iridium(III) complexes because of their highly luminescent properties in the visible region.[3–22] They are regarded as a promising component for constructing emitting functional devices such as photo-diodes and oxygen sensors.[4]

The stereochemical aspects of cyclometalated iridium(III) complexes are also an interesting issue since they provide a stable example of chiral meridional (*mer*)- and facial (*fac*)-isomers.[7–10] The iridium(III) complex of a phenylpyridyl ligand attached with a chiral auxiliary, for example, is synthesized, and its chiral structures and photophysical characteristics are examined.[10] The introduction of alkoxy groups to a phenylpyridine ligand was performed to investigate the spontaneous formation of molecular arrays on highly oriented pyrolytic graphite.[12] The work demonstrated the chirality effect on two-dimensional packing with a scanning tunneling microscope. From the synthetic approach, novel types of blue emitting iridium(III) complexes were prepared with terdentate ligands.[13] The circularly polarized luminescence spectra of the resolved enantiomers were measured to determine Δε for emission.

In spite of these extensive works, however, there have been a limited number of works reporting on the properties of molecular films involving cylcometalated iridium(III) complexes.[15,22] One of such attempt is the preparation of Langmuir–Blodgett (LB) films by mixing water-insoluble iridium(III) complexes with amphiphilic molecules such as stearic acid and lipid phosphates.[15] It remains to be clarified yet how the photophysical properties of these complexes are affected when they form a pure molecular film with no additives. Information of this kind would be important to construct a film device using iridium complexes.

Motivated by these circumstances, the present work has intended to prepare LB films by using amphiphilic tris(chelated) iridium(III) complexes. A mixture of cyclometalated iridium(III) complexes (*fac*-[Ir(ppy)$_n$L$_{3-n}$]: ppy = 2-phenylpyridine, L = 2-(3-octadecyloxyphenyl)pyridine and n = 0–3) was obtained by reacting [Ir(ppy)$_2$(O^O)] (O^O = acetylacetonato) with LH. Each of the complexes was purified and optically resolved chromatographically. The emission from the single layered LB films of these complexes was measured under the atmosphere of various kinds of gases. The results would be a benchmark to explore a gas sensing film based on cyclometalated iridium(III) complexes.

Results and discussion

Formation of a series of mixed ligand iridium(III) complexes

All members constituting mixed ligand complexes, *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 0–3), were obtained in a single reaction between LH (2-(3-octadecyloxyphenyl)pyridine) and [Ir(ppy)$_2$ (O^O)]

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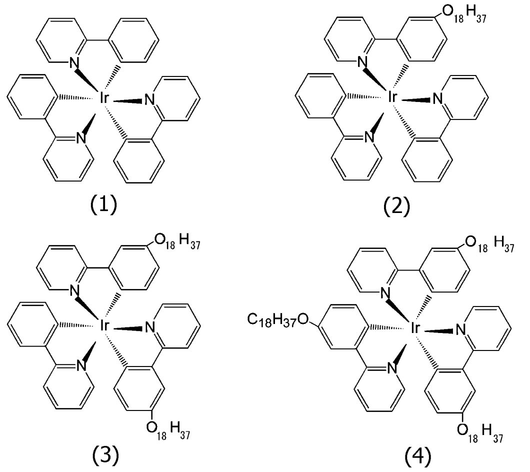
† Electronic supplementary information (ESI) available: The HPLC chromatograms to separate each of the iridium(III) complexes (*fac*-[Ir(ppy)$_3$], *fac*-[Ir(ppy)$_2$L], *fac*-[Ir(ppy)L$_2$] and *fac*-[IrL$_3$]) from the reaction product; the NMR spectra of the iridium(III) complexes; the HPLC chromatograms to resolve the enantiomers of these metal complexes; the deposition of a floating film of iridium(III) complexes onto a glass substrate, the AFM images of the LB films of *fac*-[Ir(ppy)$_3$] and *fac*-[Ir(ppy)$_2$L]; the luminescence spectra of the cast films and the effect of methanol vapor. See DOI: 10.1039/b9nj00714h



Scheme 1 Structures of Ir(III) complexes: (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$] (ppy = 2 phenyl-pyridine and L = 2-(3-octadecyloxyphenyl)pyridine).

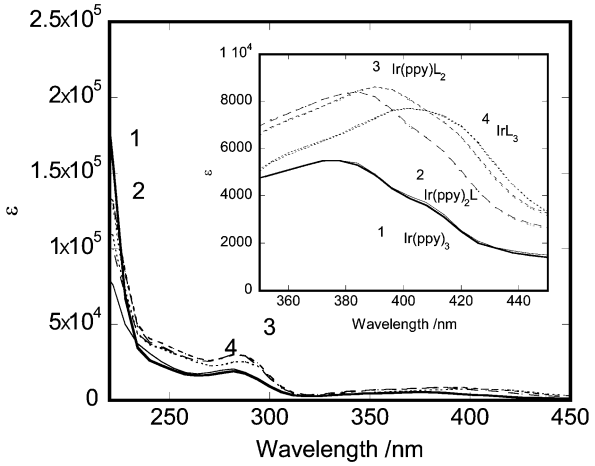


Fig. 1 The electronic absorption spectra of the chloroform solutions of (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$].

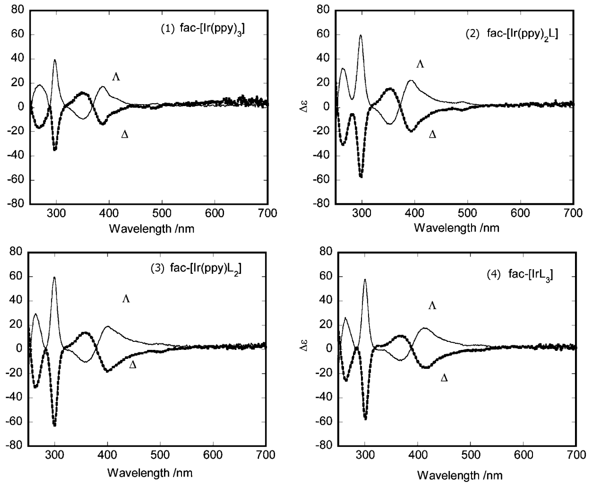


Fig. 2 The circular dichroism spectra of the chloroform solutions of (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$].

(O^O = acetylacetonato) in glycerol at 170 °C for three days (Experimental section) (Scheme 1). The results implied that the ligand exchange reactions took place under the experimental conditions as below:

$$[\mathrm{Ir(ppy)_2(O\hat{}O)}] + \mathrm{LH} \leftrightarrow [\mathrm{Ir(ppy)_2L}] + \mathrm{acacH}$$

$$[\mathrm{Ir(ppy)_2L}] + \mathrm{LH} \leftrightarrow [\mathrm{Ir(ppy)L_2}] + \mathrm{ppyH}$$

$$[\mathrm{Ir(ppy)L_2}] + \mathrm{LH} \leftrightarrow [\mathrm{IrL_3}] + \mathrm{ppyH}$$

$$[\mathrm{Ir(ppy)_2(O\hat{}O)}] + \mathrm{ppyH} \leftrightarrow [\mathrm{Ir(ppy)_3}] + \mathrm{acacH}$$

The above reactions might be driven by the different coordination strength of ligands or LH > ppyH > acacH. From the HPLC chromatogram of separation (Supporting Information), the relative abundance of amphiphilic complexes was found to be [Ir(ppy)$_2$L] > [Ir(ppy)L$_2$] > [IrL$_3$].

Spectroscopic properties of iridium(III) complexes

The obtained series of iridium complexes provided an example for systematically studying the effect of the amphiphilic alkoxy chains on the spectroscopic properties and the functions of their molecular films. Fig. 1 shows the UV-visible spectra of four kinds of prepared complexes, *fac*-[Ir(ppy)$_3$], *fac*-[Ir(ppy)$_2$L], *fac*-[Ir(ppy)L$_2$] and *fac*-[IrL$_3$]. The intense band appearing in the ultraviolet region (260–300 nm) was assigned to the π–π* transitions of phenylpyridyl ligands.[7] The weaker band extending into the visible region (300–450 nm) was assigned mainly to the charge transfer transition from Ir(III) to the ligand (MLCT band).[7] It was noticed that the MLCT bands displaced towards longer wavelengths as the number of attached alkoxy chains the increased. The shift to lower energy indicated a tendency that the electron-donating alkoxy groups lowered the π*-orbitals in phenylpyridine ligands.

The circular dichroism (CD) spectra of the resolved enantiomers are shown in Fig. 2. On the basis of the reported CD spectra of analogous iridium(III) complexes, the less and more retained fractions were identified to be Λ-and Δ-enantiomers for all of the complexes, respectively.[11] The peak position of the first band around 400 nm displaced toward the longer wavelength with the increase of the attached alkoxy chains. This was the reflection of the same shift of the MLCT band in the electronic spectra. In contrast, the position of the CD bands due to the π–π* transitions of phenylpyridyl ligands in the region of 320–260 nm varied little among these complexes.

All of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 0–3) were luminescent in solution at room temperature. Fig. 3 shows the luminescence spectra of these complexes dissolved in chloroform. Among the four complexes, [Ir(ppy)$_3$] gave the peak of luminescence at a shorter wavelength than other three. The band was assigned to be phosphorescence from a mixed state of MLCT and ligand-centered triplet states.[7] It implied that the attached alkoxy chain had the effect of lowering that excited triplet state. Since there was no distinct difference in the emission maxima among *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 1–3), that effect was concluded to saturate already at the attachment of the first alkoxy chain. Quantum yield (Φ) was determined for their air-saturated chloroform solutions: Φ = 0.046 (*fac*-[Ir(ppy)$_3$]),

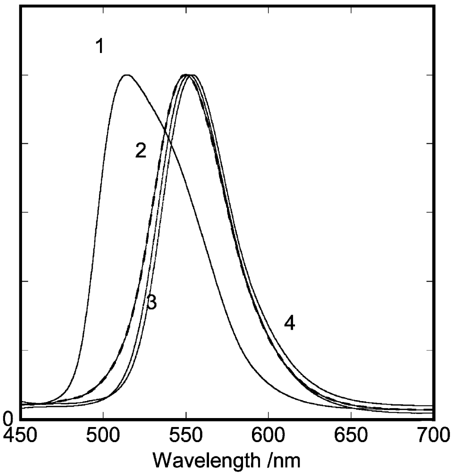


Fig. 3 The emission spectra of the chloroform solutions of (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$], when the solutions were excited by the light at 430 nm under air. The horizontal axis indicates the luminescence intensity, which is normalized to unity at the maximum wavelength.

0.016 (*fac*-[Ir(ppy)$_2$L]), 0.015 (*fac*-[Ir(ppy)L$_2$]) and 0.016 (*fac*-[IrL$_3$]). These values were comparable for that of [Ru(bpy)$_3$]$^{2+}$ (0.028) under the same conditions.

Preparation of LB films

For preparing a monolayer film at an air–water interface, a chloroform solution of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 0–3) was spread onto pure water. All of these complexes gave a reversible surface pressure *versus* molecular area (π–A) curve, indicating that they form a floating molecular film reversibly at an air–water interface (Fig. 4). The surface pressure leveled off from zero in the region of the molecular area below 0.8 nm^2 per molecule. The critical molecular area (S_c) was obtained by extrapolating the linear region of the π-curve to zero surface pressure: S_c = 0.35, 0.40, 0.50, 0.65 nm^2 for *fac*-[Ir(ppy)$_3$], *fac*-[Ir(ppy)$_2$L], *fac*-[Ir(ppy)L$_2$] and *fac*-[IrL$_3$], respectively. Since the sectional area of the head groups of these complexes was calculated to be 0.50 nm^2, the floating layers were thought to be composed of mono- or partly double-molecular layers. The fact that S_c increased with the increase of the number of attached alkyl chains suggested that the area occupied by the packed alkyl chains also contributed to the critical surface area.

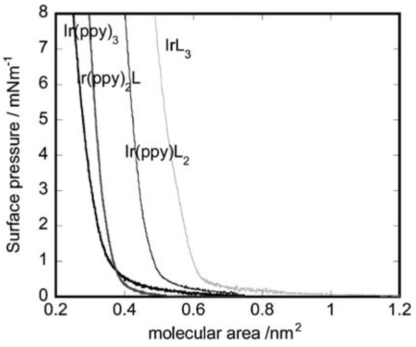


Fig. 4 The π–A curves of (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$], when the surface was compressed after a chloroform solution of the complex (1–4) was spread onto pure water.

A floating film of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 0–3) was transferred by horizontal deposition onto a hydrophobic glass substrate at the surface pressure of 15 mN m^{-1} (see the ESI†). The transfer ratio was estimated to be 0.9 ± 0.1 for all complexes. The AFM images of deposited films of *fac*-[Ir(ppy)$_3$] and *fac*-[Ir(ppy)$_2$L] are shown in the ESI.† According to the images, the LB film of *fac*-[Ir(ppy)$_3$] consisted of islands with a height of *ca.* 2 nm. Thus, the floating film on a water surface might shrink into multi-molecular domains. The LB film of *fac*-[Ir(ppy)$_2$L] was composed of thin flat particles. They were thought to maintain the character of a crystalline molecular film even after being deposited onto a substrate. The similar images were also obtained in the cases of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 2 and 3).

Emission properties of the LB films of iridium(III) complexes

A hydrophobic glass substrate modified with a single-layered LB film was placed in a quartz cell. The emission spectra were measured in vacuum under the excitation wavelength of 430 nm as shown in Fig. 5. The band was computationally decomposed into several composites as indicated by the dotted curves in the figure. For the case of *fac*-[Ir(ppy)$_3$], the spectrum consisted of five bands with the peaks at 460, 500, 530, 560 and 580 nm. For the cases of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 1–3), the spectra consisted of one main peak at 560 nm and a small peak around 580 nm. The results indicated that *fac*-[Ir(ppy)$_3$] took several different states, while *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 1–3) took one or two states in the LB films. These are related to the difference in the surface structures as observed in the AFM

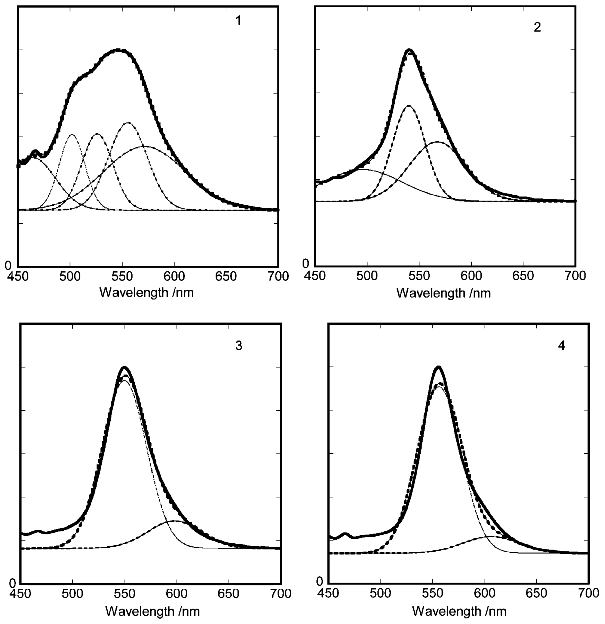


Fig. 5 The luminescence spectra from the single layered LB films of iridium(II) complexes: (1) *fac*-[Ir(ppy)$_3$], (2) *fac*-[Ir(ppy)$_2$L], (3) *fac*-[Ir(ppy)L$_2$] and (4) *fac*-[IrL$_3$]. The horizontal axis is the intensity of luminescence at an arbitrary unit. Each band was decomposed into several composite bands (denoted by dotted curves) computationally.

images. The attachment of long alkoxy groups resulted in the increase of homogeneity in the film states of metal complexes.

Effects of gaseous molecules on the emission from the LB films

Various kinds of gases were introduced into a quartz cell containing a glass substrate modified with a single-layered LB film. The effect of methanol gas on the luminescence intensity was investigated for the LB film of [Ir(ppy)$_3$] (Fig. 6). As shown in the figure, the emission spectrum underwent a remarkable change on the introduction of methanol gas. It was seen that the peaks at 560 and 580 nm decreased their intensity, while the peaks at 460, 500 and 530 nm were indifferent to methanol gas. Thus it was suspected that the former two peaks arose from the excited metal complexes located on the surface of the film, while the latter three peaks arose from the metal complexes present in the inner part. Under the atmosphere of methanol gas, only the iridium(III) complexes present on the surface of the film were thought to be deactivated. The dependence of quenching efficiency on the pressure of a gas was expressed in terms of the following equation (Stern–Volmer plots):

$$\frac{I_F}{I'_F} = 1 + \frac{k_q}{k_F}[q] \tag{1}$$

$[q]$, I_F and I'_F are the gas pressure, the luminescence intensity without and with a quencher, respectively. If the quenching takes place by the collision of a gaseous molecule with an excited complex, k_q and k_F represent the bimolecular rate constant of quenching and the rate of spontaneous luminescence, respectively. The luminescence intensity was taken at the wavelength of 600 nm, at which only the component with the peak at 580 contributed to the emission intensity. The plot of I_F/I'_F against the pressure of a gas, $[q]$, is shown in the inset of Fig. 6. From the slope of the plot, k_q/k_F was obtained to be 0.035 mm Hg. Other gases were introduced and their quenching ability was determined in the same way. The results are summarized in Table 1. It was noted that a small molecule with a functional group such as –OH, >C=O, –CN –CO–CH$_3$ and >N quenched the excited iridium complexes efficiently. At this point, the mechanism of quenching with an introduced gas was not clear. One possibility was that the triplet sate of the iridium complex was quenched by the nuclear spin such as oxygen or nitrogen. If that was the case, the contact with the iridium complex and a gaseous molecule would be required for the occurrence of quenching.

Table 1 The slopes of Stern–Volmer plots for the luminescence from the singly deposited racemic LB films of [Ir(ppy)$_{3-n}$L$_n$] (n = 0–3) when various kinds of gases were introduced

Slope (k_q/k_F)/mm Hg^{-1} ($\times 10^3$)	n = 0	1	2	3
Methanol	35.0	2.7	2.0	1.1
Pyridine	8.5	1.8	2.1	0.7
Acetone	15.6	0.1	0.9	0.5
Ethyl acetate	6.2	−0.9	0.07	−0.2
Acetonitrile	7.0	−1.4	0.7	−0.8
Diethyl ether	1.0	−0.6	−0.03	−0.2
Benzene	5.7	−0.05	−0.8	−1.0
Cyclohexane	1.9	0.4	−0.9	−1.3
Water	15.3	1.43	0.16	0.78

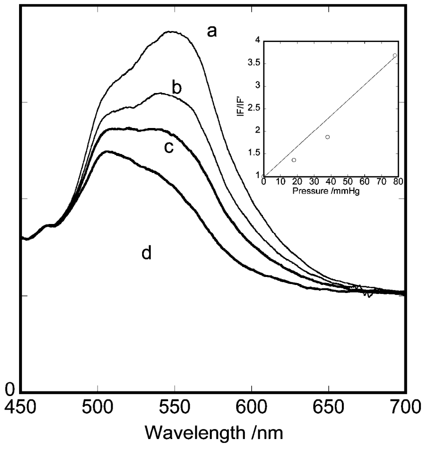


Fig. 6 The effect of methanol vapor on the emission spectrum from the singly deposited LB film of [Ir(ppy)$_3$]: the pressure of methanol was (a) 0, (b) 18, (c) 38 and (d) 78 mm Hg. The inset is the Stern–Volmer plots for the quenching by methanol. The luminescence intensity was taken at 600 nm. The excitation wavelength was 430 nm.

Similar experiments were performed on the LB films of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 1–3). In these films, the introduction of methanol gas resulted in the uniform decrease of intensity over the whole emission spectra (not shown). The slopes of the Stern–Volmer plots, k_q/k_F, for the investigated gases are summarized in Table 1. It was noted that the quenching ability by methanol diminished in the LB films of *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 1–3) in comparison to that of [Ir(ppy)$_3$]. The presence of alkoxy chains might prohibit these molecules to access the head groups of the iridium(III) complexes. Notably, some molecules increased emission intensity instead of acting as a quencher or they gave negative values for k_q/k_F. The effect was seen for the molecules with no specific functional groups such as benzene, diethylether and cyclohexane. These results suggested that the inclusion of these inert molecules might cause the structural change of the alkoxy layers in the films. The resultant disordering of the alkoxy chains, for example, might diminish the degree of self-quenching among the neighboring iridium(III) complexes in a film.

Isotopic effects were investigated by comparing the quenching ability between H$_2$O and D$_2$O. Fig. 7 shows the results of such experiments in the case of the LB films of [Ir(ppy)$_2$L]. As a result, the quenching ability of D$_2$O was smaller than that of H$_2$O, giving k_H/k_D = 1.2 at the pressure of 20 mm Hg. The background level of the emission intensity showed a gradual decrease by *ca.* 3% over 5 min. The error caused by this drift, however, was much lower than the observed isotope effect (20%). The observed isotope effect was partly ascribed to the difference of collision frequency because a D$_2$O molecule was heavier than a H$_2$O molecule. The collision frequency of H$_2$O was calculated to be 1.05 times larger than that of D$_2$O. Considering this effect, the true isotopic effect of quenching was estimated to be 1.15. The situations were contrasted with the quenching of polypyridyl Ru(II) or Os(II) complexes by water molecules. The much larger isotope effect is reported in quenching [Ru(bpy)$_3$]$^{2+}$ or k_H/k_D = 2.2.[2] These results are rationalized in terms of the difference of zero point

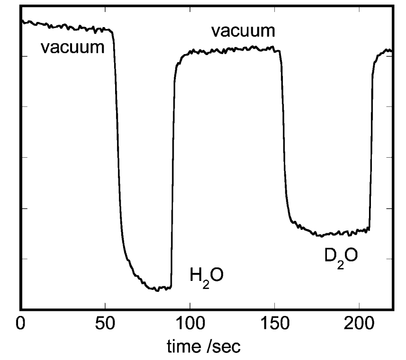


Fig. 7 The time course of luminescence intensity from a singly deposited LB film of *fac*-[Ir(ppy)$_2$L], when H_2O and thereafter D_2O gases were introduced to 20 mm Hg and evacuated alternatively. The horizontal axis is the intensity of luminescence at an arbitrary unit.

energy of the vibration of O–H or O–D bonds. Thus, the smaller isotope effect observed in the present cases suggested that the O–H or O–D bonds in water molecules were not involved in the deactivation processes of excited iridium(III) complexes.

The possibility of chiral effects on quenching was also investigated by comparing the time course of emission intensity on introducing chiral molecules. For that purpose, *R*- or *S*-2-butanol was chosen as a quenching gas molecule on the emission from the chiral LB film of Δ-*fac*-[Ir(ppy)$_2$L]. As shown in Fig. 8, no difference between these enantiomers was detected. If the quenching occurred through the Förster-type mechanism,[4] the quenching molecule might not be in contact with the excited iridium(III) complex in a film. Under such situations, it was hardly possible to discriminate the absolute configuration of a quenching molecule by the iridium complex.

Experimental

Materials

$IrCl_3$, 2-phenylpyridine (Hppy) and acetylacetone were purchased from Aldrich and used to synthesize [Ir(ppy)$_2$(O^O)] (O^O = acetylacetonato). 1-Bromooctadecane, 2-(tributylstannyl)pyridine and [Pd(PPh$_3$)$_4$] were purchased from Wako Pure Chemical Inc. (Japan) and used to synthesize 2-(3-octadecyloxyphenyl)pyridine (LH).

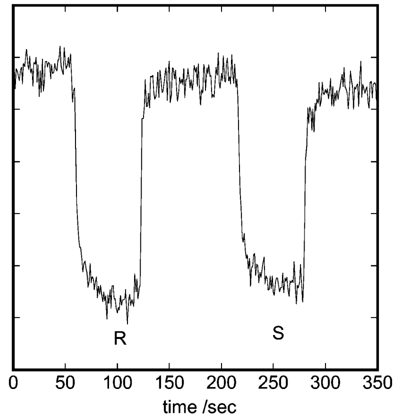


Fig. 8 The time course of luminescence intensity from a singly deposited LB film of *fac*-[Ir(ppy)$_2$L], when either *R*- or *S*-2-butanol gas was introduced and evacuated in a cell. The horizontal axis is the intensity of luminescence at an arbitrary unit.

Instruments

UV-visible electronic spectra were recorded with a spectrophotomer (Hitachi U-2810). Circular dichroism (CD) spectra were recorded with a J-720 spectropolarimeter (JASCO. Japan). High-performance liquid chromatography (HPLC) was performed with a PU-2080 PLUS chromatograph (JASCO, Japan) equipped with a Hitachi-L2400 detector (Hitachi, Ltd. Japan). Emission spectra were measured with a FP-6500 fluorometer (JASCO, Japan). Quantum yield (Φ) was calculated according to the following equation:[23] Φ = 0.028 × {(the area of emission band by iridium complex)/(the area of emission band by [Ru(bpy)$_3$]Cl$_2$)} × {(the absorbance of [Ru(bpy)$_3$]Cl$_2$ at 430 nm)/(the absorbance of iridium complex at 430 nm)}. Molecular weight was determined with a JMS-700 Mstatin mass spectrometer (JEOL, Japan) with calibration of nitrobenzyl alcohol as a standard sample. NMR spectra were recorded with a JNM-AL400 spectrometer (JEOL, Japan). Langmuir–Blodgett films were prepared with a LB trough (USI System, Japan). The trough had an area of 10.0 cm × 13.0 cm LB. The temperature was maintained at 20 °C by circulating water.

Syntheses of [Ir(ppy)$_{3-n}$L$_n$] (n = 0–3; L = 2-(3-octadecyloxyphenyl)pyridine)

[Ir(ppy)$_2$(O^O)] (O^O = acetylacetonato) and 2-(3-octadecyloxyphenyl)pyridine (LH) were synthesized according to the reported procedures.[12] A mixture of 0.35 g of [Ir(ppy)$_2$(O^O)] (0.5 mmol) and 0.64 g of LH (1.5 mmol) in 30 mL of glycerol was refluxed at 170 °C for 3 days. After cooling, 100 mL of water was added to the reaction mixture and extracted with chloroform. The chloroform phase was separated and dried in vacuum. The residue was eluted on a reversed phase HPLC column (2 mm (i.d.) × 250 mm) (CAPCELL Pack, Shiseido Ind. Co. Japan) with an eluent of 3 : 1 (v/v) methanol–chloroform. Four peaks appeared as shown in the ESI.† From the molecular weight and ^{1}H NMR spectra (ESI†), the species in these fractions were identified to be *fac*-[Ir(ppy)$_{3-n}$L$_n$] (n = 0–3) in this order. The analytical results were as follows: *fac*-[Ir(ppy)$_3$]: (0.9 mg, yield 2.8%) (*m*/*z* = obs. 656.1; calc. 654.8) ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.88 (d, J = 8.54 Hz, 3H), 7.65 (d, J = 7.32 Hz, 3H); 7.58 (t, J = 6.74 Hz, 3H), 7.53 (d, J = 6.08 Hz, 3H), 6.89 (m, 6H), 6.84 (m, 6H), ε (5100 at 380 nm); *fac*-[Ir(ppy)$_2$L]: (yield 4.3%) (*m*/*z* = obs. 923.5; calc. 923.7) ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.88 (d, J = 7.80 Hz, 2H), 7.82 (d, J = 7.84 Hz, H), 7.64 (d, J = 7.80 Hz, 2H); 7.56 (m, 6H), 7.24 (d, J = 2.44 Hz, H), 6.83 (m, 9H), 6.67 (d, J = 11.68 Hz, H), 6.56 (dd, J = 8.32 Hz, J = 3.52 Hz; H) 3.91 (t, J = 6.54 Hz, 2H), 1.74 (m, 2H), 1.43 (m, 2H), 1.25 (m, 28H), 0.87 (t, J = 6.8, 3H), ε (8400 at 384 nm); *fac*-[Ir(ppy)L$_2$]: (2.0 mg, yield 3.3%) (*m*/*z* = obs. 1191.7; calc. 1193.7) ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.86 (d, J = 8.28 Hz, H), 7.81 (d, J = 8.28 Hz, 2H), 7.63 (d, J = 7.32 Hz, H); 7.57 (m, 6H), 7.23 (d, J = 2.44 Hz, 2H), 6.87 (m, 9H), 6.69

(d, J = 8.11 Hz, 2H), 6.56 (dd, J = 8.30 Hz, J = 3.52 Hz; 2H) 3.91 (t, J = 6.54 Hz, 4H), 1.74 (m, 4H), 1.43 (m, 4H), 1.25 (m, 56H), 0.87 (t, J = 6.8, 6H), ε (8600 at 390 nm); *fac*-[IrL$_3$]:(1.2 mg, yield 1.6%) (m/z = obs. 1460.0; calc. 1460.2) ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.80 (d, J = 8.00 Hz, 3H), 7.56 (t, J = 7.44 Hz, 3H), 7.53 (d, J = 5.68 Hz, 3H), 7.23 (d, J = 2.32 Hz, 3H), 6.83 (t, J = 6.35 Hz, 3H), 6.69 (d, J = 8.12 Hz, 3H), 6.56 (dd, J = 8.28 Hz, J = 2.48 Hz; 3H) 3.91 (t, J = 6.54 Hz, 6H), 1.74 (m, 6H), 1.43 (m, 6H), 1.25 (m, 84H), 0.87 (t, J = 6.8, 9H), ε (7700 at 402 nm).

Optical resolution

The optical resolution of [Ir(ppy)$_{3-n}$L$_n$] was performed chromatographically on a column of 4 mm (i.d.) × 25 cm (length) (CHIRAL PACK IC, Daicel Co. Japan) in eluting 2 : 1 (v/v) hexane–dichloromethane. The pure Δ and Λ enantiomers were obtained. The assignment of Δ and Λ isomers were carried out by comparing their CD spectra with those of [Ir(ppy)]$_3$.[10]

Film preparation

A chloroform solution of an Ir(III) complex was spread onto a water phase. After 40 min, the surface was compressed at a rate of 10 cm^2 min^{-1} until the surface pressure reached 15 mN m^{-1}. After 10 min at 15 mN m^{-1}, the film was transferred onto a hydrophobic glass plate by the horizontal dipping method. Quenching experiments on a LB film were performed by use of glass-made vacuum line equipped with a quartz cell, gleaseless valves, an oil rotary pump and a pressure gauge. A gas was introduced after the line was evacuated below 0.1 mm torr. For the measurement of emission spectra from a LB film, a glass substrate in a quartz ell was oriented at 45 degrees with respect to the incident light.

Computational analyses of emission spectra

The peak fitting of the measured emission spectra into several composite bands was performed by use of the commercial program, Origin (OriginLab Co.). Each peak was assumed to take a Gaussian spectral shape. The number of composite peaks was increased from two to five until the best agreement was attained between the observed and simulated spectra.

Conclusion

A series of mixed ligand Ir(III) complexes, *fac*-[Ir(ppy)$_n$L$_{3-n}$] (n = 0–3), were prepared for constructing a luminescent Langmuir–Blodgett (LB) film. A glass substrate was modified with a single layered LB film and placed into a quartz cell. Luminescence was monitored under the atmosphere of various kinds of gases. As a result, molecules with functional groups such as OH, $>$C=O and –NH$_2$ were found to quench excited Ir(III) complexes efficiently. When the behavior was compared with that of the cast films of the same complexes, it was deduced that the LB films were superior to the cast films because of their higher sensitivity for sensing gasses (ESI†). The work presented the potentiality of the LB films of cyclometalated Ir(III) complexes as a luminescent gas sensing device.

Acknowledgements

We thank Dr Kentaro Okamoto (Ochanomizu University) and Ms. Keiko Hashiguchi (Ochanomizu University) for AFM observation and the syntheses of iridium(III) complexes. We also thank Prof. Yutaka Fukuda and Dr Yukie Mori (Ochanomizu University) for their useful discussion.

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