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RESEARCH ARTICLE

Synthesis of polypyridyl ruthenium complexes with 2-(1-aryl)-1H-imidazo[4,5-f]-1,10-phenanthroline ligand and its application for luminescent oxygen sensing

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Polypyridyl ruthenium (Ru) complexes 1–3 were prepared. Their photophysical properties were investigated by UV-Vis absorption and luminescence emission spectra. The luminescent lifetimes of these Ruthenium complex were prolonged by more than 5 folds (τ = 2.50 μs for complex 3) when compared with the parent Ru complex 1 (τ = 0.45 μs). We propose that the extended luminescent lifetime of complex 3 is due to the equilibrium between ^{3}MLCT state and the pyrene localized $^3\pi$-π^* triplet state (^{3}IL). The luminescent O_2-sensing property of the complexes in solution and the IMPEK-C polymer film were studied, and the O_2 sensing was quantified with the two-site model. The oxygen-sensing property of the Ru complexes can be improved by 104-fold with extension of the luminescent lifetimes. For example, the quenching constant K_{SV} was improved from 0.0023 Torr^{-1} of 1 to 0.2393 Torr^{-1} for 3. Our results demonstrated a versatile approach for the preparation of Ru (II) polypyridine complexes with extended luminescent lifetimes as functional materials, for example, for luminescent oxygen-sensing applications.

Keywords phosphorescence, ruthenium, oxygen sensor, quenching, intraligand triplet state

1 Introduction

Oxygen sensors are in great interest due to their potential applications in oceanography, biology, environmental, chemical and life science [1–5]. Luminescence-based optical oxygen sensors have been developed due to their advantages over conventional amperometric electrodes in that they respond faster, do not consume oxygen, and are easy to maintain [1,2]. Among the dyes for luminescent O_2 sensing, ruthenium (II) complexes are particularly interesting because they are triplet emitters with high photochemical stability, larger Stokes shift, and long luminescent lifetime due to the metal-to-ligand charge transfer triplet excited state (^{3}MLCT) [6–9].

Recently, it has been found that the luminescence lifetime of the Ru (II) complexes can be tuned by ligand modification [10–13]. Usually, the mechanism is supposed to be either establishment of an equilibrium of triplet-triplet states or switching the emissive state from ^{3}MLCT state to intraligand triplet state (^{3}IL state) [10,11]. Herein, we prepared Ru polypyridine complexes **2** and **3** with 2-(1-aryl)-1H-imidazo [4,5-f]-1,10-phenanthroline (where aryl = phenyl and pyrenyl) as the ligand. We studied the photophysics of these complexes by steady-state absorption and emission spectra. The luminescent lifetimes (τ_{phos}) of complexes **2** and **3** were determined as 1.13 and 2.50 μs, respectively. They are extended when compared with the model complex **1** (τ_{phos} = 0.45 μs). The O_2-sensing properties of these complexes were thoroughly studied in solution and IMPEK-C polymer films. The O_2 sensitivity can be improved by up to 104-fold with tuning the luminescent lifetime of the complexes. For example, the quenching constant K_{SV} was improved from 0.0023 Torr^{-1} of complex **1** to 0.2393 Torr^{-1} for complex **3**. The K_{SV}^{app} value of complex **3** is even higher than PtOEP under similar conditions (0.15 Torr^{-1}) [14]. The sensitivity of our complex **3**/IMPES-C sensing film is much higher than that of a reported Pt-porphyrin complex in different polymer films [15,16].

2 Experimental

2.1 General methods

NMR spectra were taken on a 400-MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded on Q-TOF Micro MS spectrometer. UV-Vis spectra were taken on HP8453 UV-visible spectrophotometer. Phosphorescence spectra were recorded on a JASCO FP-6500 and Sanco 970 CRT spectrofluorometer. Phosphorescence quantum yields were measured with Ru(bpy)$_2$(Phen) as the standard (Φ =

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6.0% in CH_3CN). Luminescence lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4 (TCSPC) instrument. Gel permeation chromatography (GPC) analysis of IMPEK-C was conducted with a PL-GPC220 system at room temperature using polystyrene as the standard and tetrahydrofuran (THF) as the eluent.

2.2 Preparation of O_2 sensing film

Typical film preparation procedures are as follows. 5.0 mg of IMPEK-C polymer [14,17] was dissolved in 0.25 mL chloroform, then 0.1 mL of complex Ru(II) solution in acetonitrile (1.0×10^{-3} mol·dm^{-3}) was added into the solution. After thoroughly mixed, ca. 0.2 mL of the solution was coated on a silica glass disk (diameter: 1.6 cm). The solvent was evaporated at r.t., and a transparent film was obtained. The thickness of the film of complex **3** was estimated as 13 μm by the weight of the film (3.0 mg) and the density of the polymer (1.14 g·cm^{-3}). The thickness of the film of complex **2** was estimated as 18 μm with the same method.

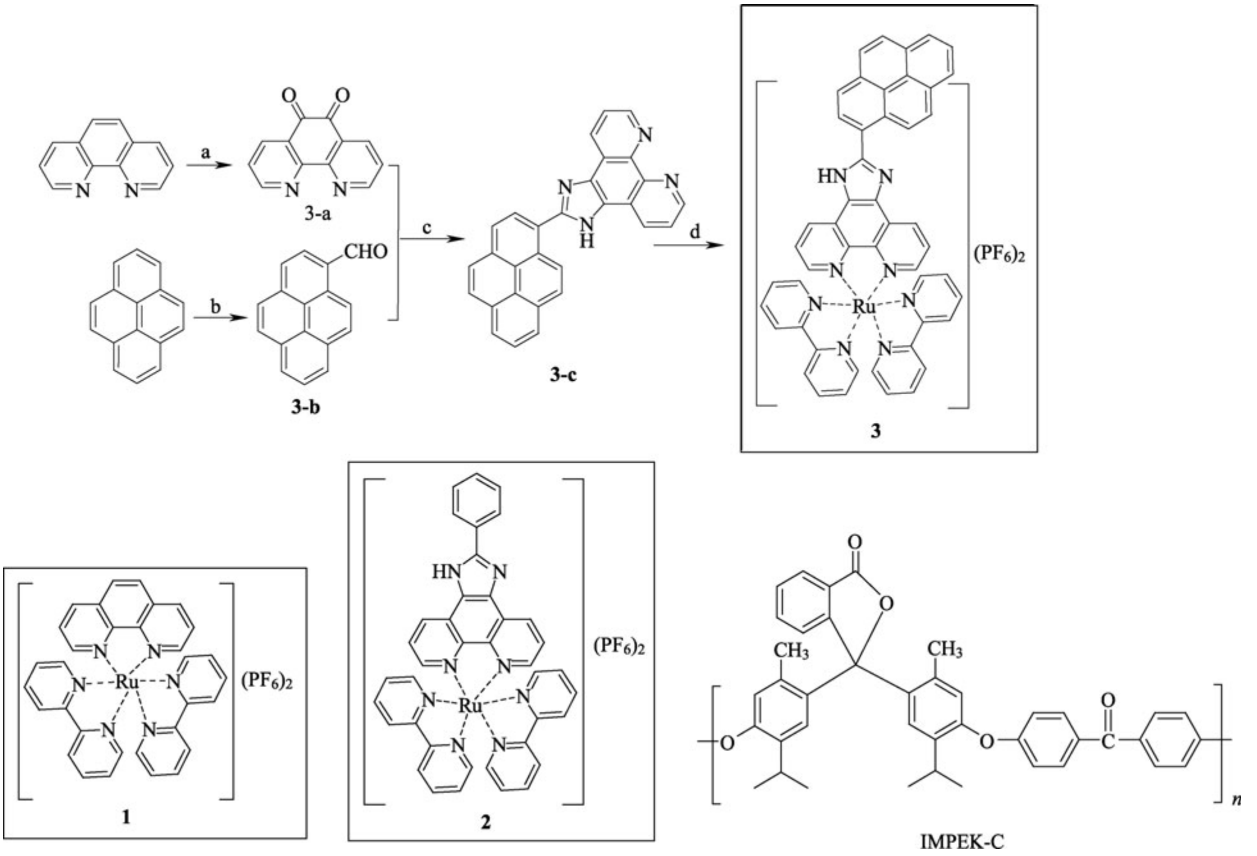
2.3 Synthesis of luminescence Ru complexes

Synthesis of the Ru complexes **2** and **3** is outlined in Scheme 1.

2-(1-Pyrenyl)-1H-imidazo[4,5-f]-1,10-phenanthroline (3-c) A solution of 1,10-phenanthroline-5,6-dione (95 mg, 0.46 mmol), pyrene-1-carbaldehyde (110 mg, 0.46 mmol) and ammonium acetate (710 mg, 13 mmol) in glacial acetic acid was refluxed for 6 h. The reacting solution was cooled to room temperature and generated a yellow precipitate, which was collected, washed with water, and dried. The crude product was then subjected to column chromatography (silica gel; eluted with dichloromethane/methanol = 30:1, *v*/*v*). Compound **3-c** was obtained as yellow solid. The yield of **3-c** is 95.0 mg (49.3%). ESI-MS $[(M+H)^+]$ calc, $m/z = 421.14$; found $m/z = 421.29$.

2-(1-Phenyl)-1H-imidazo[4,5-f]-1,10-phenanthroline (2-c) was synthesized using similar method to that of **3-c.** ESI-MS $[(M+H)^+]$ calc, $m/z = 297.11$; found $m/z = 297.02$.

$[(bpy)_2Ru(1,10\text{-phenanthroline})]^{2+}(PF_6)_2$ (1) was



Scheme 1 The structure of complexes **1** and **2** as well as the synthesis of complex **3**. a: KBr, H_2SO_4/HNO_3, 100°C, 3 h; b: $POCl_3$, DMF, $CHCl_3$, 60°C, 20 h; c: ammonium acetate, acetic acid, 60°C, 6 h; d: EtOH, r.t. 4 h, 2,2'-bipyridine, H_2O, 100°C, 24 h. The molecular structure of the IMPEK-C polymer was also shown.

synthesized as reported previously [18]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.87 – 8.81 (m, 6H), 8.45 – 8.44 (d, 2H, J = 4.8 Hz), 8.41 (s, 2H), 8.28 – 8.24 (t, 2H, J = 8.0 Hz), 8.19 – 8.13 (m, 4H), 7.95 – 7.89 (m, 4H), 7.66 – 7.62 (t, 2H, J = 6.0 Hz), 7.41 – 7.37 (t, 2H, J = 6.4 Hz). ESI-HRMS [(M-PF_6)$^+$], calcd, m/z = 739.0753; found m/z = 739.0469; [(M-2PF_6)$^{2+}$/2], calcd, m/z = 297.0553; found m/z = 297.0457.

[(bpy)2Ru(2-(1-phenyl)-1H-imidazo[4,5-f]-1,10-phenanthroline)]$^{2+}$(PF_6)$_2$ (2) was synthesized with similar method to that of **3**. ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm) = 13.38 (s, 1H), 9.18 (d, 1H, J = 8.0 Hz), 9.07 (d, 1H, J = 8.0 Hz), 8.86 – 8.81 (m, 4H), 8.37 – 8.12 (m, 10H), 7.96 (m, 4H), 7.65 – 7.56 (m, 5H), 7.40 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 158.3, 158.1, 153.8, 152.8, 152.6, 151.3, 151.1, 138.9, 138.8, 131.6, 131.3, 131.2, 130.3, 130.0, 128.7, 128.5, 127.4, 127.2, 127.0, 125.3, 125.2. ESI-HRMS: [(M-2PF_6)$^{2+}$/2] calcd, m/z = 355.0740; found, m/z = 355.0754.

[(bpy)$_2$Ru(2-(1-Pyrenyl)-1H-imidazo[4,5-f]-1,10-phenanthroline)]$^{2+}$(PF_6)$_2$ (3) A solution of [$RuCl_2$(cymene)]$_2$ (40 mg, 0.065 mmol) and **3-c** (54.0 mg, 0.13 mmol) in ethanol (5 mL) was stirred for 4 h. The reaction was monitored by TLC. Then 10 mL water and 2,2'-bipyridine (40.0 mg, 0.26 mmol) were added to the solution, the mixture was then refluxed for an additional 24 h. After cooling, the reaction mixture was concentrated under reduced pressure and treated with a saturated aqueous solution of NH_4PF_6, which gave a red precipitate. The crude product was then subjected to column chromatography (Silica gel, eluted with acetonitrile : water : saturated aqueous $NaNO_3$ = 100:9:1, v/v). The eluent was treated with a saturated aqueous solution of NH_4PF_6, which yielded a red precipitate. The solid was washed with water and dried under vacuum. Red solid was obtained in 31.0% yield. ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm) = 13.63 (s, 1H), 9.56 (d, 1H, J = 9.6 Hz), 9.27 (d, 1H, J = 8.0 Hz), 9.16 (d, 1H, J = 8.0 Hz), 8.85 (m, 4H), 8.65 (d, 1H, J = 8.0 Hz), 8.46 – 8.11 (m, 15H), 7.98 (d, 4H, J = 5.2 Hz), 7.63 (d, 2H, J = 6.0 Hz), 7.40 (s, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 158.3, 158.1, 154.4, 152.9, 151.3, 138.9, 138.8, 133.6, 132.3, 131.9, 131.7, 131.5, 130.3, 129.9, 129.8, 128.7, 128.6, 128.2, 128.1, 127.6, 127.1, 126.7, 126.2, 125.8, 125.3, 125.2, 125.1, 124.5. ESI-HRMS: [(M-2PF_6)$^{2+}$/2] calcd, m/z = 417.0896; found, m/z = 417.0901.

3 Results and discussion

3.1 UV-Vis absorptions

The UV-Vis absorptions of the Ru(II) polypyridine complexes **1**, **2** and **3** were studied. The curves were shown in Figure 1 and the absorption maxima were compiled in Table 1. Similar to the parent compound [Ru(bpy)$_2$(1,10-phenanthroline)], three main bands were observed for the UV-Vis absorption of complexes **2** and **3**, i.e., two ligand-centered π-π* transition bands at 225 nm for bpy ligand and at 262 nm for phen ligand. A broad absorption band centered at 445 nm was also observed with a higher energy shoulder at 414 nm.

The main peak and the shoulder of this absorption band are indicative of the presence of strongly overlapped ^{1}MLCT states, with similar energy levels, such as dπ(Ru)→π*(bpy) and dπ(Ru)→π*(Phen) [13,19,20]. Ru(II) complexes **2** and **3** show absorption at 285 nm, which is due to the 1H-imidazo[4,5-f]-1,10-phenanthroline ligand with extended π-conjugation framework. For complex **3**, new absorption bands appeared at 370 nm, which is due to the absorption of pyrene [21]. We propose that the pyrene unit and 1H-imidazo[4,5-f]-

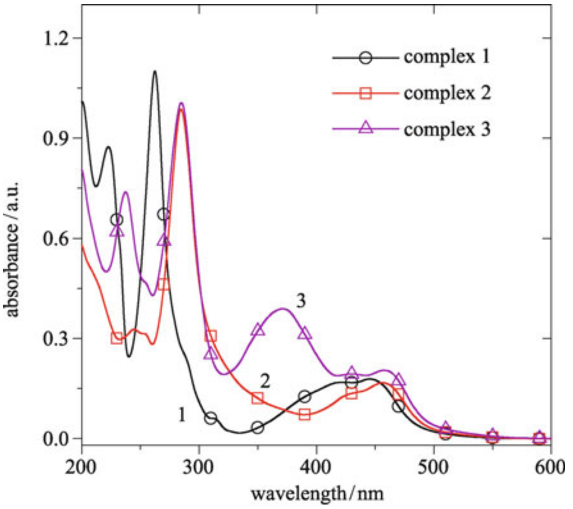


Figure 1 UV-Vis absorption spectra of Ru(II) polypyridine complexes **1**, **2**, and **3**. Measurements were carried out using 1.0 ×10^{-5} mol·L^{-1} solution in acetonitrile at 25°C.

Table 1 Photophysics parameters of the phosphorescent polyimine ruthenium complexes **1**, **2** and **3**

	λ_{ab} /nm	λ_{em} /nm	ε /(L·mol^{-1}·cm^{-1})	$\Phi^{a)}$	τ/ns$^{b)}$	$k_r$$^{c)}$/ (×10^4 s^{-1})	$k_{nr}$$^{c)}$/ (×10^6 s^{-1})	I_{Ar}/I_{O_2} (solution)	I_{N_2}/I_{O_2} (film)
1	445	594	17900	0.06	450	13.3	2.08	18.5	1.7 $^{d)}$
2	457	608	16728	0.22	1125	19.2	1.13	35.9	1.8 $^{e)}$
3	458	609	20459	0.02	2503	0.83	0.48	279.0	3.0 $^{e)}$

a) Result of deaerated solution, with complex **1** as the standard. b) The determination coefficients (r^2) for complexes **1**, **2** and **3** are 0.99, 0.99 and 0.95, respectively. c) Radiative deactivation rate constant (k_r) and non-radiative deactivation rate constant (k_{nr}). $k_r = \Phi_{em}/\tau_{em}$; $k_{nr} = 1/\tau_{em}(1-\Phi_{em})$. It is assumed that the emitting excited state is produced by ISC with unit efficiency. d) The polymer film is IMPES-C [19]. e) The polymer film is IMPEK-C.

1,10-phenanthroline are non-coplanar, which resulted in non-efficient π-conjugation between the imidazole and the pyrene fragments. The $\lambda_{\max}$ values of the MLCT transitions of complexes **2** and **3** (457 nm and 458 nm) are red-shifted in relation to that of [Ru(bpy)$_2$(1,10-phenanthroline)] (445 nm) due to the extent of π delocalization of imidazole ligands.

3.2 Steady-state emission spectra: different emission profiles and O_2 sensitivities in solution

The steady-state emissions of complexes **1**, **2** and **3** in acetonitrile solution under argon, air and O_2 atmosphere were studied (Figure 2). All complexes show broad, structureless emission that is characteristic ^{3}MLCT emission of the Ru polypyridine complexes. The emissions of **1**, **2** and **3** were quenched in the presence of O_2 to different extents. I_0/I_{100} value is usually used to evaluate the O_2-sensing property of phosphorescent dyes [1,14], where I_0 is the emission in inert atmosphere, and I_{100} is the emission intensity in neat O_2. It was found that the I_0/I_{100} value of the model complex **1** is the smallest one ($I_0/I_{100} = 18.5$). For complexes **2** and **3**, however, this value is imcreased. For example, the I_0/I_{100} value of complex **3** is as high as 279.0. Similarly improved I_0/I_{100} values (35.9) were observed for **2**. Thus, it is probable that **2** and **3** show extended lifetimes compared to the reference complex **1**[1].

Compared to the reference complex **1**, the luminescent quantum yields of **2** are increased, and the luminescent lifetime is elongated greatly (Table 1). We propose that the ^{3}MLCT state of complex **2** was stabilized with the extended π-conjugation of the Phen ligand; thus the energy gap between the ^{3}MC and the ^{3}MLCT was increased. Therefore, longer lifetime, red-shifted emission wavelength and higher luminescent quantum yields were observed for complex **2**. For complex **3**, the lifetime is extended to 2.50 µs, which is increased up to 5.5-fold compared to complex **1** (0.45 µs). We propose that the extended luminescent lifetime of complex **3** is due to the equilibrium between the ^{3}MLCT and the pyrene localized ^{3}π-π* triplet states (^{3}IL). The long-lived ^{3}π-π* state can act as energy reservoir, funneling energy to the emissive ^{3}MLCT state; thus the lifetime can be extended. The radiative and non-radiative decay rate constants (k_r and k_{nr}) of all the complexes are calculated and listed in Table 1 [22]. In general, the lifetimes of room temperature Ru(II) ^{3}MLCT-based emissions show k_r and k_{nr} values on the scale of $10^4\ s^{-1}$ and $10^6\ s^{-1}$, respectively [22]. Based on the k_r values, **1** and **2** show typical ^{3}MLCT emission. For **3**, the exceptional long lifetime and low k_r indicated that the emission is pertubed by an excited state other than ^{3}MLCT features.

3.3 Oxygen-sensing performance of the Ru complexes: effect of the lifetimes

Dyes with long luminescence lifetime are ideal for luminescence oxygen sensors. The O_2-sensing property of the Ru (II) complexes in polymer film is investigated with flow-cell/optical fiber measuring system (Figure 3 and Figure 4). For the O_2-sensing films, a modified Stern-Volmer or two-site model (Eq. (1)) is required to study the quenching effect because even in “homogenous” polymers, the dye molecules still dwell in different microenvironments [2,14]. In the two-site model, the O_2-sensitive dyes are treated as two different portions, where f_1 and K_{SV1} are the fraction of the “first” portion and the quenching constant, respectively. f_2 and K_{SV2} are the fraction of the remaining portion and the quenching constant, and $f_1 + f_2 = 1$; p_{O_2} is the oxygen partial pressure.

$$\frac{I_0}{I} = \frac{1}{\dfrac{f_1}{1 + K_{SV1}p_{O_2}} + \dfrac{f_2}{1 + K_{SV2}p_{O_2}}} \tag{1}$$

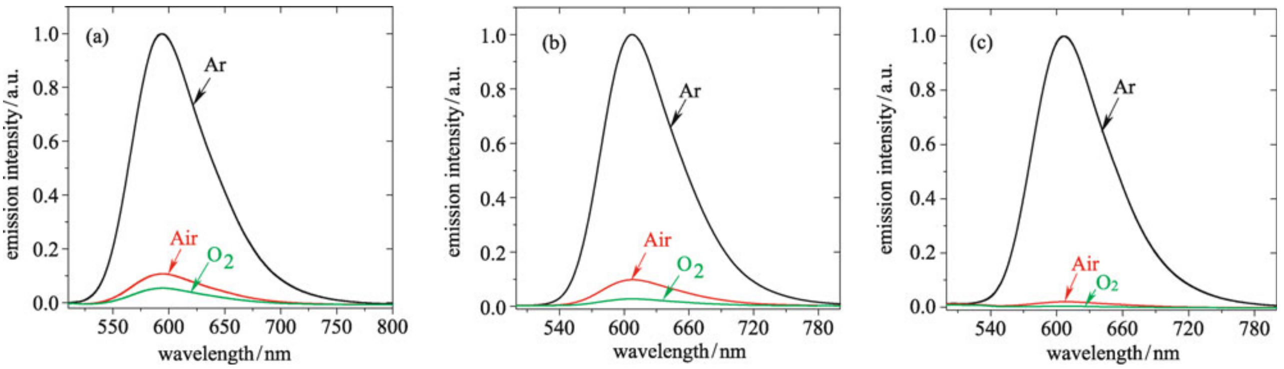


Figure 2 Room-temperature emission spectra of complexes **1**, **2** and **3** under Ar, air and O_2 atmosphere. (a) complex **1**, $\lambda_{ex} = 445$ nm, (b) complex **2**, $\lambda_{ex} = 457$ nm, (c) complex **3**, $\lambda_{ex} = 458$ nm. Measurements were taken in 1.0×10^{-5} mol·L^{-1} complexes solution in acetonitrile at 25°C.

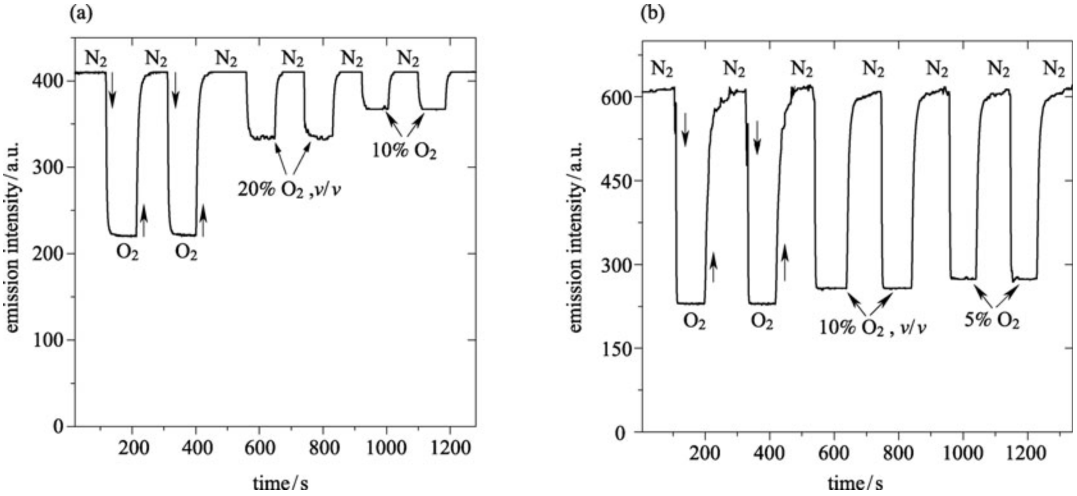


Figure 3 Phosphorescent intensity response of sensing films of the complexes **2** and **3** in IMPEK-C to O_2/N_2 saturation cycles. (a) complex **2**, λ_{ex}= 476 nm, λ_{em}= 593 nm; (b) complex **3**, λ_{ex}= 478 nm, λ_{em} = 593 nm. In order to compare the quenching properties of the films, the *y* axel is set from 0. Measurements were taken with home-assembled optical fiber/flow cell system.

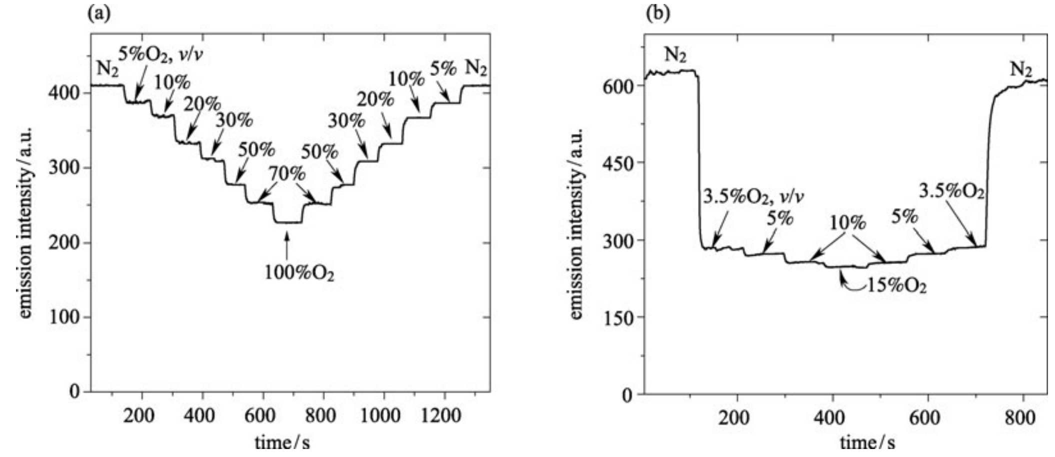


Figure 4 Phosphorescent intensity response of sensing films of the complexes in IMPEK-C to step variations of O_2 concentrations. (a) complex **2**, λ_{ex}= 476 nm, λ_{em}= 593 nm; (b) complex **3**, λ_{ex}= 478 nm, λ_{em} = 593 nm. In order to compare the quenching efficiencies of the films, the *y* axels are set from 0 for all the figures. Measurements were taken with home-assembled optical fiber/flow cell system. The numbers indicate the O_2 concentration in mixed O_2/N_2 gas (*v*/*v*).

It was found that the O_2 quenching effect on the luminescence of complex **2** is not significant under our experimental conditions with I_0/I_{100} = 1.8, as shown in Figure 3. The response time ($t\downarrow 95$) and the recovery time ($t\uparrow 95$) are 10 and 22 s, respectively [19]. A higher O_2 sensitivity is observed for complex **3** with I_0/I_{100} = 3.0. The response time ($t\downarrow 95$) and the recovery time ($t\uparrow 95$) are 4.5 and 49.9 s, respectively. The longer recovery time of complex **3** is ascribed to its high sensitivity for O_2; thus, the trace of O_2 dissolved in the polymer will quench the emission.

Sensing experiments with smaller O_2 partial pressure variation were carried out as shown in Figure 4. Complex **2** gives reasonable response to the variation of the oxygen partial pressure. For complex **3**, however, high sensitivity was found. For example, with 3.5% O_2, the emission of the complex **3** is substantially quenched (Figure 4).

The quenching effect of O_2 on the emission of complex was quantitatively studied with the two-site quenching model (Eq.(1)). With fitting of the quenching data (Figure 5), the quenching constants K_{SV1} and K_{SV2} were obtained as summarized in Table 2. Complex **3** shows an increased O_2 sensitivity compared to complex **1**. The apparent value is K_{SV}^{app} = 0.2393 $Torr^{-1}$, which is 104 folds of that of complex **1**. The K_{SV}^{app} value of complex **3** is even higher than PtOEP under similar conditions (0.15 $Torr^{-1}$) [14]. The sensitivity of our complex **3**/IMPEK-C-sensing film (K_{SV}^{app}= 0.2393 $Torr^{-1}$) is much higher than that of a reported PtOEP/polystyrene O_2-sensing film (K_{SV}^{app} = 0.0185 $Torr^{-1}$) [15]. The value of

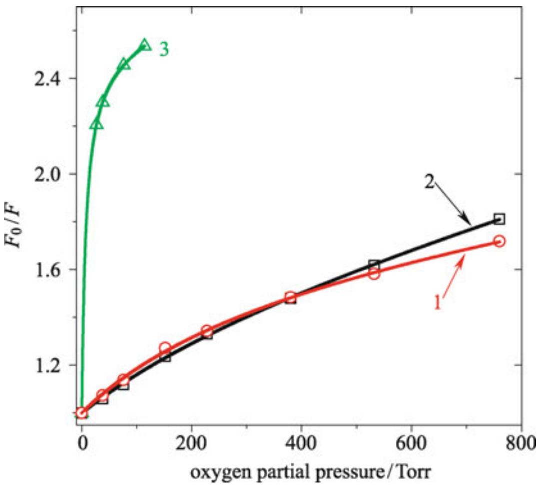


Figure 5 Oxygen sensitivity of the emission of complexes **1, 2** and **3**. The fittings are based on the data of Figure **4** and the two-site model (Eq. (1)). The supporting polymer film of complex **1** is IMPES-C, and the supporting polymer for complexes **2** and **3** are IMPEK-C. Limited oxygen partial pressure was used for complex **3** due to the significant quenching effect.

Table 2 Parameters of the O_2-sensing film of complexes **1** with IMPES-C as well as **2** and **3** with IMPEK-C as supporting matrix (fitting result with the two-site model, Eq.(1))

	f_1 a)	f_2 a)	K_{SV1} b)	K_{SV2} b)	r^2 c)	K_{SV}^{app} d)	p_{O_2} e)
1	0.5510	0.4490	0.0002	0.0049	0.99	0.0023	435
2	0.5689	0.4311	0.0004	0.0037	0.99	0.0018	556
3	0.6042	0.3297	0.3958	0.0004	0.99	0.2393	4.2

a) The ratio of the two portions of the dyes; b) The quenching constants of the two portions; c) The determination coefficients; d) Weighted quenching constant, $K_{SV}^{app} = f_1 \times K_{SV1} + f_2 \times K_{SV2}$; e) The oxygen partial pressure at which the initial emission intensity of the film is quenched by 50% and can be calculated as $1/K_{SV}$.

complex **3** is also higher than that of the O_2-sensing films of Pt-porphyrin complex in Nafion (K_{SV}^{app} in the range of 0.007–0.105 $Torr^{-1}$, with t↑95 time in the range of 350–370 s)[16].

Our experimental results show that the Ru complexes can be adopted to detect different O_2 concentration ranges through tuning their luminescence lifetime [9,23]. For example, complex **3** with long luminescence lifetime is ideal for detecting trace O_2, while complexes **1** and **2** with shorter lifetime have advantage in sensing O_2 with a wide dynamic concentration range.

4 Conclusions

In summary, we synthesized polypyridyl Ruthenium complexes **1**, **2** and **3** with 2-(1-aryl)-1H-imidazo[4,5-f]-1,10-phenanthroline (where aryl = phenyl and pyrenyl) ligand. The photophysical properties of the complexes were investigated by steady-state UV-Vis absorption spectra and emission spectra. Complex **3** shows much longer luminescence lifetime of 2.50 μs when compared to the reference complex **1** Ru$(bpy)_2$(Phen) (τ = 0.45 μs). We propose that the extended phosphorescent lifetime of complex **3** is due to an equilibrium between ^{3}MLCT and the pyrene localized $^3\pi$-π^* triplet state. The extended luminescent lifetimes were successfully employed to improve the oxygen sensitivity of the ruthenium complexes in luminescent oxygen sensing. The O_2 sensitivity of the complexes in solution, as well as in polymer film, was studied. The sensitivity of the emission of the complexes was quantified with the two-site model. The results demonstrated that, with the introduction of the pyrenyl group to the imidazole ligand, the O_2-sensing property of the Ru complexes was improved by 104 folds; for example, quenching constant K_{SV} was improved from 0.0023 $Torr^{-1}$ of complex **1** to 0.2393 $Torr^{-1}$ for **3**. Our finding may prove useful for future design of new Ru polypyridine complexes as luminescent oxygen-sensing materials with high sensitivity.

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