Modulation of Optical Oxygen Sensing Properties of Iridium (III) Complexes By Changing Their Substitution Groups

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Abstract

The series of bis-cyclometalated iridium (III) complexes bearing different substituents (-H, -OCH₃, -F, -CH₃) at the aryl moiety (**Ir-1**, **Ir-2**, **Ir-3** and **Ir-4**) have been synthesized and characterized by MASS and ¹H NMR spectrometries, and IR, absorption and emission spectroscopies. The effects of the substituents on their oxygen sensing properties as well as optical properties and decay kinetics have been investigated systematically in tetrahydrofuran (THF) and ethyl cellulose (EC) thin films. The Ir (III) complexes embedded in EC-based thin films showed more advanced sensor dynamics, higher oxygen sensitivity, and superior relative signal changes when compared with their solution phase. The I₀/I₁₀₀ values of **Ir-1**, **Ir-2**, **Ir-3** and **Ir-4** immobilized in EC thin film were calculated as 11.3, 5.2, 7.0 and 25.6 for the concentration range of 0-100% pCO₂, respectively. These results show that the weak electron-donating properties of the methyl groups at the aryl moiety improve remarkably the optical oxygen sensing abilities of the Ir (III) complexes.

Introduction

The optical chemical sensing approach has been used many times in the development of sensors. The oxygen-sensible dye is of great importance to enhance the sensitivity of such sensors. Iridium (III) complexes are known to exhibit oxygen-sensitive room temperature phosphorescence emission and lifetime (microsecond to millisecond range) [1, 2]. In addition, syntheses of iridium complexes are easy and high yielding which is also quite important to develop cheaper sensors. The Ir (III) complexes that have been studied so far showed quite good sensitivity to oxygen (Table 1). Liu and co-workers reported the oxygen sensitivity studies of bis-cyclometalated-diphenylamino equipped iridium (III) complexes in ethyl cellulose (EC) film. The influences of substituents (-H, -CH₃, -F, -CF₃) at the pyridyl moiety of ppy of these complexes were investigated systematically, and I₀/I₁₀₀ values of the Ir-1, -2, -3 and -4 complexes in EC thin film were 16.2, 16.4, 15.2 and 14.1, respectively [3]. Toro and co-workers presented the nanostructured materials that including four various Ir (III) dyes associated either with polystyrene or metal oxide. The most oxygen-sensitive films based on dye N1001 incorporated into the aluminium oxide-hydroxide nanostructured solid support presented a K_{SV} constant equal to 2848 ± 101 bar⁻¹ and a pO₂ (S = 1/2) equal to 0.0006 [4]. Yoshihara et.al proposed a ratiometric molecular probe-based on dual emission of a coumarin dye and red phosphorescent cationic iridium (III) complex for intracellular oxygen sensing [5]. The new cyclometalated iridium (III) complexes in nanocomposites made of AP200/19 and in polystyrene film were presented by Marín-Suárez and co-workers, and the results have been found promising for the detection of low oxygen concentrations [6]. Xing et al. reported that I₀/I₁₀₀ values of the Ir (III) complexes; IrC1, IrC2, and IrC3 substituted with 4-(diphenylamine)phenyl, 4-(9H-carbazol-9-yl)phenyl, and 9-phenyl-9H-carbazol-3-yl moieties were found as 33.0, 8.2 and 16.5, respectively [7]. Zhang and co-workers reported amino methyl substituted phenyl pyridine ligands including series of iridium (III) complexes and researched their dual-phosphorescence properties. One of them exhibited response naked-eye distinguishable colour changed emission response to oxygen in solution [8]. Ho and co-workers reported four iridium (III) coordination polymers, and their K_{SV} values in single crystal form

were quite promising [9]. Liu and co-workers presented trifluoromethyl-substituted cyclometalated iridium (III) complexes which showed improved photostability against irradiation and the favourable response time of Lx4 incorporated in the EC film (2.6 s) on going from N₂ to O₂ [10]. The oxygen responses of the new designed Ir (III) complexes with different numbers of F atoms in electrospun fibrous films were recently studied by Wang and co-workers, and large conjugation planes and F atoms in their ligands were affected positively sensing performance [11]. Kai et al. offered three Ir (III) dyes with diverse numbers of fluorine substituents. They found that the presence of F atoms developed oxygen sensing properties of the complex in the form of fibrous polystyrene films (I_0/I_{100} value of 12.89) [12]. The oxygen sensing properties of cyclophosphazene equipped- iridium (III) complexes in electrospun fibrous ethyl cellulose (EC) mats were reported by Ongun and co-workers [13]. It was found that: i) the substitution with cyclophosphazene moiety enhanced the oxygen sensitivity of Ir (III) complexes, and ii) distinct oxygen-induced blue shifts extending from 22 to 75 nm were observed. In another study, Borisov and co-workers produced novel optical nanochemosensors by entrapped Ir (III) complexes in nanobeads using different polymers [14]. By the way, it is still a challenge to enhance their photostability and improve their biocompatibility so the design/synthesis of new complexes exhibiting optimized emission characteristics or lifetimes are ongoing to answer all needs. These studies encouraged us to study the design/synthesis of new iridium (III) complexes with different substituents to overcome these problems.

In this work, we encoded iridium (III) complexes bearing -H, -OCH₃, -F, -CH₃) at the aryl moiety on **Ir-1**, **Ir-2**, **Ir-3** and **Ir-4**, respectively. Corresponding Ir (III) complexes were embedded in two different matrices; EC and poly(methyl methacrylate) (PMMA) to define the most advantageous material to improve their oxygen permabilities. The influences of substituents (-H, -OCH₃, -F, -CH₃) at the aryl moieties on the oxygen sensing properties of corresponding complexes have been investigated systematically in THF and EC films.

Table 1
Some of Ir(III) complexes used as oxygen sensing probes.

Dye (Measured Parameter: Luminescence Intensity)	Matrix Materials	Sensitivity (I_0/I_{100} or K_{SV})	Range	Response Time	Photo-stability	[Ref]
(CS) ₂ Ir(μ -Cl) ₂ Ir(CS) ₂	PS	K_{SV1} at 25 °C (hPa ⁻¹) 0.00701	25–175 hPa O ₂	-	poor	[1]
Ir2 (with two pyrene moieties)	oxide hydroxide nanostructure (AP200/19)	K_{SV} (kPa ⁻¹) 26.96 ± 0.25	0–10 kPa pO ₂	-	-	[2]
Ir2 (with –CH ₃ group)	EC	I_0/I_{100} 16.40	0 to 100 % O ₂	4.0 s	58%, after 90 min	[3]
N969	aluminium oxide/ hydroxide (AlOOH)	I_0/I_{100} 47.60 ± 0.50	0 to 10 % O ₂	2 s	long-term stability (for 1 year)	[4]
3	AP200/19	K_{SV} (kPa ⁻¹) 780.77 ± 18.28	0 to 10 % O ₂	-	-	[6]
IrC1	EC	I_0/I_{100} 33.00	0 to 100 % O ₂	3.7 s	52.8% after 60 min of irradiation	[7]
Lx4	EC	I_0/I_{100} 5.75	0 to 100 % O ₂	2.6 s	long-term stability	[10]
Ir(FBT) ₂ (acac-F6) 7.0%	PS fibrous film	I_0/I_{100} 15.56	0 to 100 % O ₂	8s	-	[11]
Ir(BT) ₂ (acac-F6) 6.5%	PS fibrous film	I_0/I_{100} 12.89	0 to 100 % O ₂	9s	-	[12]
Ir-III	EC	I_0/I_{100} 6.20	0 to 100 % O ₂	5s	24 months	[13]

Dye (Measured Parameter: Luminescence Intensity)	Matrix Materials	Sensitivity (I ₀ /I ₁₀₀ or K _{SV})	Range	Response Time	Photo-stability	[Ref]
Ir-1	EC	I ₀ /I ₁₀₀	0 to 100	6s	18 months	This study
Ir-2		11.30	% O ₂			
Ir-3		5.20				
Ir-4		7.00				
		25.60				

Experimental

2.1. Materials

Dichloromethane (DCM), tetrahydrofuran (THF), phenol, sodium hydride (NaH) (60% dispersion in mineral oil), *n*-hexane, 2-naphthol, magnesium sulphate (MgSO₄), absolute ethanol (EtOH), sodium sulphate (Na₂SO₄), ammonium acetate, 4-hydroxybenzaldehyde, ammonia solution, 1,10-phenanthroline, potassium bromide (KBr), acetic acid, sulphuric acid (H₂SO₄), nitric acid (HNO₃), THF-d₈ were purchased from Merck. 1,10-Phenanthroline-5,6-dione was supplied from Sigma Aldrich. All of the solvents were purified by conventional methods.

The poly(methyl methacrylate) (PMMA) (MW: 120,000), ethylcellulose (EC) (ethoxy content of 46%), nonadecafluorodecanoic acid (PFC), room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) and bis-(2-ethylhexyl)phthalate (DOP) were supplied from Sigma Aldrich to obtain thin films.

To record luminescence spectra, 10 mm path length quartz cells with septum were supplied from Hellma. Nitrogen and oxygen gas cylinders were 99.99% pure and supplied from Linde Gas Company, Izmir.

2.2. Characterization

Thin-layer chromatography (TLC) was carried out on Merck Silica gel plates (Merck 60, 0.25 mm thickness) with an F254 indicator. Column chromatography was performed on silica gel (Merck 60, 0.063-0.200 mm; 120 g of silica gel was used in a column of 3 cm diameter and 110 cm length for 3 g of crude mixture). Elemental analyses synthesized dyes were measured by a Thermo Finnigan Flash 1112 Instrument. Mass analyses were recorded on a Bruker MALDI-TOF (Matrix Assisted Laser Desorption / Ionization-Time-of-Flight mass, Rheinstetten, Germany) spectrometer using 2,5-dihydroxybenzoic acid as a matrix. Fourier Transform Infrared (FT-IR) spectra were recorded on a Perkin Elmer 100 spectrophotometer. The ¹H spectra for the compounds were examined on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference. Microstructure SEM images were captured with Philips XL 30 SFEG scanning electron microscopy. Electronic absorption spectra in the UV-Vis region were

recorded with a Shimadzu 2101 UV-Vis spectrophotometer. The steady-state photoluminescence (PL) emission/excitation measurements were studied by using a red-sensitive photomultiplier tube equipped spectrofluorometric system (FLSP920 Fluorescence Spectrometer, Edinburgh Instruments) in a quartz cell with a septum at room temperature. The decay times were measured in time-correlated single photon counting mode (TCSPC) of the FLSP920. The gases, O₂ and N₂ were mixed in the concentration range of 0–100% with a Sonimix 7000A gas blending system for oxygen sensing measurements. The output flow rate of the gas was maintained at 550 mL/min. Gas mixtures were introduced on the sensing agents via a diffuser needle under ambient conditions. Relative luminescence quantum yields were determined according to the William Method [15]. The solutions of the dyes were deoxygenated thoroughly by bubbling nitrogen.

2.3. Synthesis and characterization

The starting compounds, 11,12-dichloro-dipyrido [3,2-a: 2', 3'-c] phenazine (**Cl₂dppz**) [16, 17] and **Ir-dimer** [18–20] were synthesized according to the literature. Synthetic pathways (See Scheme S1 and S2) and characterization (See Figs S1-S4) of these compounds were given as in a supplementary file. Synthetic pathways of **L1–L4** ligands and **Ir-1**, **Ir-2**, **Ir-3**, **Ir-4** complexes were given in Scheme 1 and Scheme 2, respectively. The same synthetic procedure was employed for obtaining **L1–L4** complexes. So experimental details were given for only **L1**. Also, the similar synthesis process was used for producing **Ir-1–Ir-4** compounds, and experimental data were given for only **Ir-1**.

2.3.1. Synthesis of L1

Cl₂dppz (5 mmol), phenol (10 mmol) and K₂CO₃ (15 mmol) reacted in dry DMF (25 mL) under argon atmosphere by refluxing for 2 days. The reaction mixture was cooled to room temperature and filtered off and the solid phase was washed with water. The crude solid product was purified by preparative TLC on silica with DCM:EtOH (30:1) as the eluent (60% yield). Anal. Calc. for C₃₀H₁₈N₄O₂; C, 77.24; H, 3.89; N, 12.01. Found: C, 77.54; H, 3.99; N, 12.10 %. MALDI-TOF-MS (m/z): [M]⁺, 466.97 (cal cd. 466.14). FT-IR (ATR /cm⁻¹): 3070 (ArC-H), 3003 (C-H) 1589 (ArC = C), 1470(C = N), 1254-1214-(C-O-C), 1070 – 1024 (C-O). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.48 (d, 2H, CH), 9.24 (t, 2H, CH), 7.73 (m, 2H, CH), 7.61 (s, 2H, CH), 7.53 (m, 4H, CH), 7.32 (m, 6H, CH).

2.3.2. Synthesis of L2

The crude solid product was purified by preparative TLC on silica with DCM:EtOH (25:1) as the eluent (75% yield). Anal. Calc. for C₃₂H₂₂N₄O₄; C, 72.99; H, 4.21; N, 10.64. Found: C, 71.83; H, 4.08; N, 10.49 %. MALDI-TOF-MS (m/z): [M]⁺ 526.31 (calcd. 526.16). FT-IR (ATR /cm⁻¹): 3096 (ArC-H), 2839 (C-H) 1573 (ArC = C), 1472 (C = N), 1251-1208-(C-O-C), 1070 – 1022 (C-O). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.48 (d, 2H, CH), 9.24 (t, 2H, CH), 7.75 (t, 2H, CH), 7.48 (t, 2H, CH), 7.29 (t, 4H, CH), 7.08(t, 4H, CH), 3.92 (t, 6H, CH₃).

2.3.3. Synthesis of L3

The crude solid product was purified by preparative TLC on silica with DCM:EtOH (40:1) as the eluent (70% yield). Anal. Calc. for $C_{30}H_{16}N_4O_2$; C, 71.71; H, 3.21; N, 7.56. Found: C, 71.85; H, 3.28; N, 7.70 %.

MALDI-TOF-MS (m/z): $[M]^+$ 502.95 (calcd. 502.12). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3077 (ArC-H), 2925 (C-H), 1570 (ArC = C), 1469 (C = N), 1255 (C-O-C), 1089 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.49 (d, 2H, CH), 9.24 (t, 2H, CH), 7.74 (t, 2H, CH), 7.54 (t, 2H, CH), 7.28 (t, 4H, CH), 7.23 (t, 4H, CH).

2.3.4. Synthesis of L4

The crude solid product was purified by preparative TLC on silica with DCM:EtOH (35:1) as the eluent (65% yield). Anal. Calc. for $C_{32}H_{22}N_4O_2$; C, 77.22; H, 4.48; N, 11.33. Found: C, 77.30; H, 4.29; N, 11.20%.

MALDI-TOF-MS (m/z): $[M]^+$ 494.71 (calcd. 494.17). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3066 (ArC-H), 2922 (C-H) 1575 (ArC = C), 1470 (C = N), 1256-1212 (C-O-C), 1072 – 1032 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.48 (d, 2H, CH), 9.22 (t, 2H, CH), 7.72 (t, 2H, CH), 7.54 (d, 2H, CH), 7.33 (d, 4H, CH), 7.22 (d, 4H, CH), 2.46 (s, 6H, CH_3).

2.3.5. Synthesis of Ir-1

Ir-dimer (10 mmol) and L1 (21 mmol) and 30 mL EtOH was added to a flask and refluxed at night under an inert medium. The mix was cooled to 25 C and the solvent was removed under pressure. The obtained precipitate was washed by CH_2Cl_2 /EtOH mixture several times and dried to give **Ir-1** as solid (75 % yield.) Anal. Calc. for $C_{55}H_{36}F_6IrN_6O_4$; C, 57.83; H, 3.12; N, 7.23. Found: C, 57.75; H, 3.20; N, 7.45 %. MALDI-TOF-MS (m/z): $[M + H]^+$, 1164.56 (calcd. 1163.13). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3070 (ArC-H), 1560 (ArC = C), 1480 (C = N), 1113 – 1014 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.76 (t, 2H, ArH), 8.28 (dd, 2H, ArH), 8.28 (d, 1H), 8.02 (dd, 2H, ArH), 7.86 (s, 1H, ArH), 7.61–7.49 (m, 8H, ArH), 7.44–7.31 (m, 8H, ArH), 7.22 (d, 1H, ArH), 7.20 (d, 1H, ArH), 6.87 (d, 1H, ArH), 6.86 (d, 1H, ArH), 6.58 (d, 1H, ArH), 6.56 (d, 1H, ArH), 3.98 (s, 6H, CH_3).

2.3.6. Synthesis of Ir-2

Ir-2 was obtained as solid (65 % yield.) Anal. Calc. for $C_{58}H_{40}F_6IrN_6O_6$; C, 56.95; H, 3.30; N, 6.87. Found: C, 56.65; H, 3.25; N, 6.95 %. MALDI-TOF-MS (m/z): $[M + H]^+$, 1224.10 (calcd. 1223.25). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3067 (ArC-H), 1559 (ArC = C), 1475 (C = N), 1112 – 1015 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.47 (d, 2H, ArH), 8.27 (d, 2H, ArH), 8.01 (m, 2H, ArH), 7.86 (s, 2H, ArH), 7.49 (d, 4H, ArH), 7.43 (d, 2H, ArH), 7.30 (t, 4H, ArH), 7.21 (d, 2H, ArH), 7.10 (d, 4H, ArH), 6.83 (dd, 2H, ArH), 6.57 (d, 2H, ArH), 3.98 (s, 6H, AO- CH_3), 3.92 (s, 6H, O- CH_3).

2.3.7. Synthesis of Ir-3

Ir-3 was obtained as solid (60 % yield.) Anal. Calc. for $C_{56}H_{34}F_8IrN_6O_4$; C, 56.09; H, 2.86; N, 7.01. Found: C, 56.15; H, 2.95; N, 6.90 %. MALDI-TOF-MS (m/z): $[M]^+$, 1199.13 (calcd. 1199.21). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3100 (ArC-H), 1560 (ArC = C), 1480 (C = N), 1110 – 1020 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.71 (d, 2H, ArH), 8.27 (d, 2H, ArH), 7.98 (t, 1H, ArH), 7.87 (s, 2H, ArH), 7.70 (d, 2H, ArH), 7.49 (m, 6H, ArH), 7.27 (m, 6H, ArH), 7.10 (m, 4H, ArH), 6.77 (m, 1H, ArH), 6.54 ppm (dd, 2H, ArH), 3.94 (s, 6H, O- CH_3).

2.3.8. Synthesis of Ir-4

Ir-4 was obtained as solid (80 % yield.) Anal. Calc. for $C_{56}H_{40}F_6IrN_6O_4$; C, 58.48; H, 3.38; N, 7.06. Found: C, 58.40; H, 3.25; N, 7.30 %. MALDI-TOF-MS (m/z): $[M]^+$, 1191.23 (calcd. 1191.26). FT-IR (ATR / cm^{-1}): $\bar{\nu}$ 3070 (ArC-H), 2910 – 2850 (CH_3), 1559 (ArC = C), 1480 (C = N), 1115 – 1021 (C-O). 1H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.74 (d, 2H, ArH), 8.27 (d, 2H, ArH), 8.02 (t, 2, ArH), 7.86 (s, 2H, ArH), 7.58–7.16 (m, 16H, ArH), 6.84 (d, 2H, ArH), 6.57 (d, 2H, ArH), 3.98 ppm (s, 6H, O- CH_3), 2.47 (s, 6H, O- CH_3).

2.4. Preparation of solid-state sensing materials

In this study, the different compositions of EC based composites were prepared by mixing 120 mg of EC, 24 mg of ionic liquid ($BMIMBF_4$), 96 mg of DOP, and 2.0 mg of Perfluorodecanoic acid (PFC), 0.5 mg of the Ir (III) complex in 2.0 mL of $CHCl_3$:EtOH (75:25) solvent. The PMMA based cocktails were prepared with 0.5 mg of Ir (III) compound, 24 mg of ionic liquid ($BMIMBF_4$), 2.0 mg of PFC and 120 mg of PMMA in 2.0 mL of toluene. The PFC was added to enhance the O_2 solubility of both sensing materials. The cocktails were knife-coated onto a Mylar sheet, and located in a solvent saturated desiccator to result in $\sim 5.9 \mu m$ sensor film.

2.5. Choice of matrix materials

The relative signal intensity (I_0/I_{100}) changes of the related the Ir (III) complexes were measured in the gas-permeable PMMA and EC polymeric matrix. The highest sensitivities were obtained in the EC matrix for all four complexes matching with literature knowledge [3, 13]. Therefore, the EC polymer matrix was chosen as a suitable material to investigate the O_2 sensitivities of the synthesized Ir (III) complexes (**Ir-1**, **-2**, **-3** and **-4**) for further studies.

Results And Discussion

3.1. Synthesis and characterizations of the compounds

The series of new Ir(III) complexes (**Ir-1-Ir-4**) were synthesized by the reaction of **Ir dimer** and pyrazine fused phentrolin ligands **L1-L4** bearing -H, - OCH_3 , -F, - CH_3 groups, respectively. The complexes were isolated by precipitation. Each compound (**L1-L4** and **Ir-1-Ir-4**) was characterized by using elemental analysis, FT-IR spectroscopy and mass, and 1H NMR spectrometry techniques. NMR and mass spectra of all the compounds were given in the supplementary file as Figs S5-S20.

3.2. Absorption and phosphorescence emission-based properties

Figure 1 demonstrates the UV-Vis absorption spectra of the complexes in THF (5.0 μM) solution at room temperature, also the corresponding data are presented in Table 2. Corresponding Ir (III) complexes all showed similar and typical absorption in THF, similar to other cyclometalated Ir (III) complexes previously reported [3]. The **Ir-1** and **Ir-4** complexes exhibited intense absorption bands in the UV area belong to $\pi-\pi^*$ transitions of intra-ligands (ILCT) [7, 11]. Their lower energy absorption bands around 380 nm and 405 nm can be attributed to the overlap of metal-ligand charge transfer (MLCT), inter-ligand charge transfer (ILCT) and ligand-ligand charge transfer (LLCT) interactions. It should be noted that these charge-

transfer-based transitions generally have low molar absorption coefficients, resulting in poor absorption bands. Moreover, the weak absorption bands of MLCT / LLCT transitions (400 nm) are quite effective in exciting emitting centers [11].

The photoluminescence based emission/excitation spectra of the Ir (III) complexes were measured in THF under nitrogen atmosphere (Fig. 2). Upon excitation at 400 nm corresponding to the MLCT/LLCT transitions, **Ir-1**, **Ir-2**, **Ir-3** and **Ir-4** in THF showed dense long-wavelength emission bands with and no detectable fluorescence at 576, 590, 570 and 562 nm, respectively. Notably, the emission spectra change upon the substitution groups. The emission maximum of **Ir-2** complex was remarkably red-shifted according to others, owing to the moderate electron-donating ability of -OCH₃ moieties.

Ir-1, **Ir-2**, **Ir-3** and **Ir-4** in THF presented large Stoke's shift values of 176, 182, 168 and 156, respectively. When compared to the others, **Ir-2** exhibited the largest Stoke's shift because of having -OCH₃ moieties. The observed bright phosphorescence emission and large Stoke shifts are evidences of room temperature phosphorescence around 560–600 nm [21].

The phosphorescence quantum yields (Φ_p) of the corresponding compounds in THF were determined by Williams Method [15] using a solution of Rhodamine 6G in ethanol as a standard (0.95 in ethanol) [22]. Φ_p values of **Ir-1**, **-2**, **-3**, **-4** in THF were calculated as 0.03, 0.03, 0.04 and 0.02, respectively (Table 2). The trifluoromethyl (-CF₃) group has both a strong electron-withdrawing property and also is an important substituent in many organic electroluminescent materials. It has an effect on the ligand system and provides steric protection around the metal that is an important consideration for increasing the quantum efficiency of the complexes. However, the quantum values of the corresponding compounds were very close to each other in this study.

Under nitrogen atmosphere, **Ir-1**, **Ir-2**, **Ir-3** and **Ir-4** in EC presented intense long-wavelength phosphorescence emission bands at 552, 550, 546 and 554 nm with no detectable fluorescence, respectively. It should be noted the emission spectra change only slightly upon the substitution groups and bathochromic shift does not exceed 10 nm. Stoke's shifts were 148, 144, 148 and 144 nm for **Ir-1**, **Ir-2**, **Ir-3** and **Ir-4**, respectively (Table 3).

Table 2. Absorption and phosphorescence emission-based data of the Ir(III) complexes in THF.

Dye	Solvent	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	ϵ $\text{L}\times\text{mol}^{-1}\text{cm}^{-1}$	$\lambda_{\text{max}}^{\text{em}}$ (nm)	$\lambda_{\text{max}}^{\text{ex}}$ (nm)	Stoke's Shift	Φ_p
Ir-1	THF	405	8.10×10^7	576	405	176	0.03
Ir-2		408	8.16×10^7	590	408	182	0.03
Ir-3		407	8.14×10^7	570	407	168	0.04
Ir-4		406	8.12×10^7	562	406	156	0.02

3.3. Oxygen sensing properties

Herein, we investigated the O₂ induced emission-based response of the Ir(III)-based sensing materials embedded in EC thin films. Fig. S21-23 and Fig. 3 show the intensity-based fluorescence spectra of the **Ir-1**, **-2**, **-3** and **-4**, respectively. All of the studied forms exhibited a spectral response between 0-100% p[O₂]. When the Ir (III)-bearing sensing slides were excited at 400 nm, the emission peaks were observed at 552, 550, 546, 554 nm, for of **Ir-1**, **-2**, **-3** and **-4** based EC thin films, respectively, and they also exhibited a quenching-based signal response to oxygen. The **Ir-1**, **-2** and **-3** doped sensing slides yielded 68.5, 84.2, 86.0 and 88.6% signal changes under the concentrations of 0.0–100.0% [O₂], respectively. However, all of the Ir (III)-based sensing composites in EC matrixes exhibited more than 80% of the response for the oxygen between the concentration ranges of 0–40% [O₂]. Therefore, in further studies, we focused on the 0–40% [O₂] range. Figure 3 reveals the emission based response of the **Ir-4** in EC thin film towards oxygen for the concentration range of 0–100% p[O₂]. The linearized calibration plot can be described by; $y = 0.1326x + 1$ and the correlation coefficient of 0.9845 for the concentration range of 0–40% [O₂] (See inset of Fig. 3).

Table 3 shows the composition, excitation, emission and sensitivity information (I_0/I_{100}) of the utilized EC sensor slides with the related calibration plots and regression coefficients for the concentration range of 0–40% [O₂]. The I_0/I_{100} values of **Ir-1**, **-2**, **-3** and **-4** immobilized in EC film were found as 11.3, 5.2, 7.0 and 25.6, respectively. The I_0/I_{100} value of **Ir-4** was about 5 times higher than that of **Ir-2**, indicating negative impact of electron donating properties on oxygen sensitivity. Consequently, it was found that the inclusion of the substituents (-H, -OCH₃, -F, -CH₃) in the aryl portion of the iridium (III) complexes has a strong effect on the sensitivity of the oxygen sensors. In a previous study, it was found that the inclusion of substituents (-H, -OCH₃, -F, -CH₃) in the pyridyl moiety of cyclometalizing ligands had relatively little effect on the sensitivity of the sensors [3]. It can be concluded that not only substituted group but also the binding position of the substituted group in the Ir(III) complexes is very effective.

Table 3. Phosphorescence emission-based characteristics and O₂ sensitivity data of the Ir (III) complexes immobilized in EC matrix.

Dye	Matrix/ Thin film	λ_{ex}	λ_{em}	Stoke's Shift	I_0/I_{100}	Equation Range (Concentration range 40% [O ₂])	of 0–	R ²
Ir-1	EC	404	552	148	11.3	$y = 0.0324x + 1$		0.9340
Ir-2	EC	406	550	144	5.2	$y = 0.0710x + 1$		0.9452
Ir-3	EC	398	546	148	7.0	$y = 0.0647x + 1$		0.9964
Ir-4	EC	410	554	144	25.6	$y = 0.1326x + 1$		0.9845

Stern-Volmer plots exhibiting nonlinear behaviour are compatible with the two-site model showing the presence of two various microenvironments for encapsulated Ir (III) dyes; where f_1 and f_2 are the total emission fractions for each component, respectively, and K_{SV1} and K_{SV2} are the Stern-Volmer constants for each component, and $[O_2]$ is the concentration of the triplet oxygen (See Eq. 1) [1]

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{f_1}{1+K_{SV1}[O_2]} + \frac{f_2}{1+K_{SV2}[O_2]} \quad (1)$$

The **Ir-4** showed the highest K_{SV} value amongst the others (See Fig. 4 and Table 4). Besides the K_{SV} values, the linear properties of the Stern-Volmer plots can be evaluated as evidence of the super-sensitivity of the related Ir (III) sensor agents towards oxygen.

The detection limit (LOD) was calculated by dividing 0.003 / slope where the slope is expressed as %⁻¹ units at a signal-to-noise ratio of 3.0 (See Eq. 2);

$$LOD = 3.0 \times S/K_{SV}[O_2] \quad (2)$$

Assuming the uncertainty of the measurement as 0.1%, the detection limits of the **Ir-1**, **-2**, **-3** and **-4** immobilized in EC thin films were found to be 1.17×10^{-4} , 1.58×10^{-4} , 1.47×10^{-4} , and 1.42×10^{-5} , respectively (See Table 4).

Table 4
Stern-Volmer constants (K_{SV}) and LOD values of the Ir (III)-based complexes embedded in EC membranes.

Dye	K_{SV1} (% ⁻¹)	K_{SV2} (% ⁻¹)	LOD (% ⁻¹)
Ir-1	0.0291	0.0143	1.17×10^{-4}
Ir-2	0.0735	0.0262	1.58×10^{-4}
Ir-3	0.0840	0.0456	1.47×10^{-4}
Ir-4	0.1114	0.0640	1.42×10^{-5}

3.4. Decay time measurements

The luminescence-based oxygen sensing process involves dynamic collision between the excited state of the oxygen-sensitive probes and triplet oxygen, causing a decrease of intensity and decay kinetics of sensing slides [10]. In order to figure out the high O_2 sensitivity of corresponding Ir (III) molecules in oxygen-free and fully-oxygenated moieties, we measured the oxygen-induced decay kinetics subsequent to the signal within the THF and EC thin film in a microsecond time scale (Fig. 5). The multi-exponential of the decays and their distribution results for the **Ir-1**, **-2**, **-3** and **-4** were shown in Table S1. The decay kinetics of all of the Ir (III)-based sensors decreased upon exposure to fully-oxygenated conditions. The average decay times of **Ir-4** embedded in EC decreased from 417.68 μ s to 21.59 μ s when exposed to the oxygen-free and fully oxygenated conditions. According to these results, since rotational movements in

the EC phase are prevented compared to the solution phase, the best decrease of decay time values was observed in the solid phase. Also, **Ir-4** in the EC thin film matrix, exhibited a higher τ_0 value of 417.68 μ s when compared to the value of **Ir-4** in THF. The luminophores with longer τ_0 lifetimes are known to have higher oxygen sensitivities, and those molecules are preferred for oxygen sensor studies. **Ir-4** has decay time-based higher oxygen sensitivity and that is advantageous for the sensor studies. When the Stern–Volmer plots and the decay kinetics were evaluated together, it can be concluded as the evidence of the dynamic quenching for all of the moieties.

3.5. Response time, repeatability and photostability

The time-based oxygen-induced responses of the **Ir-1**, **-2**, **-3** and **-4** doped thin films were determined under 100.0% N₂ and 100.0% O₂ (See Figs S24-S26 for **Ir-1**, **-2**, **-3** and Fig. 6 for **Ir-4**). The response and regeneration times of the sensing slides were measured as ~ 6 sec (n = 3) and ~ 12 sec, respectively. The values of I_0 and I_{100} were almost constant and the cycles of quenching and recovery cycles were entirely reversible with no reduction of the original emission intensity based signal for all of the sensing slides (89.0 % recovery of original intensity for **Ir-4**). **Ir-1**, **-2**, **-3** and **-4** exhibited excellent operational stability for continuous monitoring of molecular oxygen. Also, no remarkable reduction was monitored in the decay time-based values and the emission-based intensities of the **Ir-1**, **-2**, **-3** and **-4** doped EC thin films which were stored in ambient laboratory conditions during the 18 months. The sensor membranes had lost their original intensity values less than 5%, but they still had the potential for O₂ measurements.

The photostability of iridium complexes is every time of important concern for applied experiences such as high-light densities definition or long-time continuous monitoring of oxygen. Figure 7 shows the photo-degradation histograms of the Ir (III) dyes embedded in EC thin films with continuous 60 min illumination. All data were normalized to let a comparison of the decrease in intensity in each sample. About 48.0% of **Ir-1**, 55.0% of **Ir-2**, 59.0% of **Ir-3** and 56.0% of **Ir-4** were destroyed under irradiation. This limits the potential application of the optodes to short-time measurements.

Conclusions

Ir (III) complexes-based oxygen-sensitive thin films showed quite good sensitivity, complete reversibility with short response times. The oxygen sensitivities of the optodes modulated by introducing the changing substituted group of the complex. Although the I_0/I_{100} value of **Ir-2** (-OCH₃ substituted group) immobilized in EC film was 5.2, **Ir-4** with methyl group exhibited the best sensitivity upon oxygen with the value of 25.6. It can be concluded that the presence of oxygen atom in the substituted group effected the oxygen sensitivity of the molecule negatively. The results demonstrate that the position of the substitution group in the complexes is an attractive one for tuning the photophysical and oxygen sensitivity properties of the corresponding Ir (III) complexes. All of the complexes exhibited relatively short response time (~ 6s) and good photostability when they are stored in ambient laboratory conditions in the dark. The only disadvantage of the corresponding Ir (III) complexes is low photostability under

continuous illumination for 60 min. This limits the potential application of the optodes to short-time measurements.

Declarations

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Authors Contributions

The authors Sevinc Z Topal and Devrim Atilla conceived this research and designed experiments, wrote the paper and participated in the revisions of it; Merve Zeyrek Ongun and Sibel Oguzlar participated in specifically performing the analytical experiments and data/evidence collection; Murat Şahin and Tugce Akbal Aytan participated in the specifically performing the inorganic experiments and data/evidence collection. The author(s) read and approved the final manuscript.

Data Availability

The authors declare that the data supporting the findings of this study are available in the article and the supplementary materials.

Declarations

Not applicable

Conflicts of Interest

“The authors declare that they have no potential conflict of interest in relation to the study in this paper”.

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Figures

Figure 1

Electronic UV-Vis absorption spectra of Ir-1, Ir-2, Ir-3 and Ir-4 in THF (concentration: 5.0 μ M).

Figure 2

Excitation/emission spectra of Ir-1, -2, -3 and -4 in THF (concentration: 2.5 μM).

Figure 3

The emission spectra of Ir-4 in EC thin film under various oxygen partial pressure conditions. Inset: Stern-Volmer plot for 0-40% [O₂].

Figure 4

Stern-Volmer plots for oxygen sensing films of Ir (III) complexes; Ir-1, Ir-2, Ir-3 and Ir-4 immobilized in EC matrix.

Figure 5

Stern-Volmer plots for oxygen sensing films of Ir-1, Ir-2, Ir-3 and Ir-4 immobilized in EC matrix.

Figure 6

Time-based kinetic response of Ir-4 in thin film in an alternating atmosphere of 100.0% N₂ and 100.0% O₂.

Figure 7

Photo-degradation histograms of Ir-1, Ir-2, Ir-3 and Ir-4 immobilized in EC matrix under continuous illumination for 60 min under ambient atmospheric conditions. Irradiation is performed using 15 W Xenon lamps.

Supplementary Files

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