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# Stern-Volmer Mechanistic Study on Transition Metals Embedded onto Optical Fibre for Dissolved Oxygen Sensing And Monitoring: A Systematic Literature Review

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**Abstract.** Dissolved oxygen (DO) concentration is the most critical parameter to evaluate water quality, commonly addressed in global freshwater, and seawater aquacultures. Research trends and patterns on optical fibre for environmental DO sensing and monitoring, specifically, photonics, are rising and revolutionising the current practices. Transition metals have emerged as a promising material for use in determining DO concentration in the water. Their unusual physicochemical and optical properties enable them to be used as an oxygen-sensitive dye and a so-called waveguide in thin-film that can be easily integrated with optical fibre. Thus, the selection of transition metals is important in the early phase of this research to design the optical-based transducers for DO sensing and monitoring. The DO concentration needs to be accurately measured in real-time, as its change is a continuous dynamic process. Gaps were identified utilising various transition metals embedded onto optical fibre for the in-situ determination of DO concentration in the water, contributing new knowledge for future scholarly work. The detection mechanism of DO concentration in the water with various transition metals is briefly outlined and concludes by addressing the real world's laboratory-scale challenges. In short, we focus on the Stern-Volmer model for mechanistic study on transition metals for DO sensing and monitoring.



## 1. Introduction

Oxygen is one of the chemical elements in the periodic table, with the symbol O and atomic number 8, which has a colourless, odourless (due to the human breathing system unable to detect it), and tasteless gas essential for nearly all biological systems on Earth [1] for aerobic respiration. Human beings will live without food for up to 1 month, without water for up to 2 weeks, but no longer than maximally 10 minutes without oxygen. Eight historians have noticed the discovery of oxygen throughout the last century between the 13<sup>th</sup> and 18<sup>th</sup> centuries, including Ibn al-Nafis, Michael Servetus, Michael Servendivogius, John Mayow, Carl Wilhelm Scheele, Joseph Priestley, Antoine Laurent Lavoisier, and Henry Cavendish [2]. No one of these eight sages can now be called the most important discoverer of oxygen.

Oceans are losing oxygen at an unprecedented rate due to climate change and other human activities. Fertiliser and fossil fuels combined with climate change are starving our oceans of oxygen, as reported by the International Union of Conservation of Nature. The ocean has absorbed more than 90% of excess heat from greenhouse emissions - for this case, carbon dioxide is the most considerable contribution, warming the ocean by around 0.13 °C every decade. The warmer water we get, the less oxygen it can store. Intensive agriculture has made the problem worse. Massive amounts of fertiliser and sewage have run off into the ocean as an essential nutrient for growth, causing algae to phytoplankton bloom, which suffocates waters even more, last from few days to several weeks. It can use up the water's oxygen, producing dead zones. Quadrupling number of dead zones in the last 70 years. There are now more than 700 areas with low oxygen levels, up from 45 in the 1960s. They keep expanding in size by an area equivalent to the European Union. Massive areas of ocean with no oxygen, where life can barely survive. Deoxygenated waters threaten the survival of marine creatures and fish. Only jellyfish, microbes, and some squid survive in low-oxygen zones and can upset the ecosystem.

Dissolved oxygen (DO) in the water is a relative measure of the oxygen concentration transported in given water as a proportion of the maximum concentration dissolved in that medium. It is also referred to as non-compound and free oxygen in the water, which is involved in various physiological and biochemical activities. The content of DO in water is a significant measure of water quality and an important factor in water purification. The concentration of DO can reflect two situations of the self-regulation of the environment. Low DO concentration results in a gradual degradation of contaminants in water. Conversely, the high concentration of dissolved oxygen, which leads to the degradation of the water's various pollutants, suggests that the water can be rapidly filtered. Consequences of unusual DO concentration may affect aquatic species' survival in global freshwater and seawater aquacultures [3]. Acceptable DO concentration is a requirement for aquatic species' healthy growth in global freshwater and seawater aquacultures. The detection of DO concentration in the water is of great significance in environmental sensing and monitoring.

The aquaculture sector from freshwater and seawater has improved food security. The outlook for 2030 is promising, globally, but more efforts need to be done to achieve sustainable water and ensure food security for everyone, as a 28-page 'in brief' copy of the report can be accessed here [4], and the complete report is available here [5]. The State of World Fisheries and Aquaculture 2020 (SOFIA 2020) statistics reveal encouraging progress towards that goal. Aquaculture is a growing, vibrant and essential supply and demand sector of high nutrients seafood, including protein, long-chain omega-3 fats (essential for optimal brain development), iodine (aiding thyroid function), vitamin D (regulates the immune system function and bone health), iron (produce additional blood for mother and the baby during pregnancy), calcium, zinc, and other minerals (useful for child development). The latest update in 2018, total global capture aquaculture production reached the highest level ever recorded at 111.4 million tonnes, with a total farm gate sale value of 263.6 billion USD. World aquaculture production of farmed aquatic animals was dominated by Asia, with an 89% share in the past two decades.

DO sensing and monitoring have attracted particular interest, as seen from the numbers of respective references. Despite an abundance of literature on dissolved oxygen sensing and monitoring, efforts to systematically review transition metal thin-film embedded onto optical fibre for the in-situ

verification of dissolved oxygen in the water. No previous methodological steps and publication standards exist for reporting realist syntheses on this subject. This research aims to fill the void in understanding the patterns and trends of research in this environmental sensing and monitoring by utilising different types of transition metal thin-film embedded onto an optical fibre. In fulfilling the critical gaps in the literature, such variables (i.e. different types of transition metal) from this systematic literature review could contribute to future scholarly work in designing and fabricating and commercialising a good performance transducer for DO sensing and monitoring. This systematic literature review also applies to policy-makers and funding agencies.

**2. Methodology on information literacy**

Information literacy is a set of useful skills in finding, evaluating, and effectively using information. Thus, information literacy framework (including capture problems, browsing and scoping the literature, keyword search and identification, and screening steps) was conducted using various highly reputable scientific databases such as Web of Science, and Scopus used information searching resources in the situation to perform this systematic literature review. This framework is used to understand the specific topic area of transition metal thin-film waveguide embedded onto optical fibre for the in-situ determination of dissolved oxygen in the water.

Keyword search and identification is the first step of the systematic review process. The method included defining keywords for information search purposes. Based on several useful sources of information, such as encyclopedias, dictionaries, thesaurus, keywords from previous literature, and keywords suggested by Scopus for keyword synonyms, possible terms associated with this other variation to the term ‘*dissolved oxygen*’ and ‘*transition metal*’ were used (refer to Table 1).

Table 1. Keywords and search strings.<sup>a</sup>

Databases	List of Keywords
Web of Science	TS=(“dissolved oxygen*” OR “oxygen saturation*” OR “oxygen solubility*” OR “oxygen concentration*”) AND (“transition metal*” OR “transition element*” OR “transi’tion el`ement*”)
Scopus	TITLE-ABS-KEY (“dissolved oxygen*” OR “oxygen saturation*” OR “oxygen solubility*” OR “oxygen concentration*”) AND (“transition metal*” OR “transition element*” OR “transi’tion el`ement*”)

<sup>a</sup> ‘*Advanced Search*’ performed on September 1<sup>st</sup>, 2020.

Screening is a method for including or removing papers based on the authors' requirements with selected studies' assistance. The eligibility, inclusion, and exclusion criteria were determined in the screening process for identifying suitable papers to be included in the systematic review process. The language was the first criterion for the inclusion and exclusion criteria. All non-English language documents were omitted in this systematic literature review to prevent misunderstanding and difficulties in translations' work. Second, as regards the timeline, it was only chosen between 1920 and 2020 (100 years period of time) based on the total number of relevant publications collected for the reviewing process. The final inclusion criterion was article types; article journals and conference proceedings containing scientific evidence were chosen. Other forms of record, such as review papers, were omitted because they were not considered primary sources of this systematic literature review as shown in Table 2.

The next step is the eligibility process that excludes or includes articles manually, according to the authors' specific criteria. The papers collected have been extensively reviewed in the process, except for any papers which did not meet the requirements. Prior to the eligibility process, duplicate documents were first withdrawn. A total of 535 papers were found as related articles were omitted in both Scopus and Web of Science databases for the next step, leaving 32 documents for the eligibility

process and manually screened for literature based on the term of ‘*dissolved oxygen*’ and ‘*transition metal*’ and requirements for earlier screening processes (inclusion and exclusion criteria).

Table 2. The inclusion and exclusion criteria.

Criterion	Inclusion	Exclusion
Timeline	Between 1919 and 2020	Less than 1919
Document type	Research articles, book, chapter in books, and conference proceedings	Review papers
Language	English	Non-English

### 3. The fundamental theory of dissolved oxygen sensing and monitoring

The study of photophysics and photochemistry in the homogeneous solvent phase of organic, inorganic, and biological compounds entered a "new and excited" period over several decades with incredible scientific novelties. The theory and equation relating to the kinetic analysis of fluorescence quenching, i.e., change in fluorescence quantum yield and fluorescence lifetime as a function of added quencher, a molecular species capable of deactivating the electronics excited state of the fluorophore or luminophore back to its electronic ground state, has been 100 years since Otto Stern and Max Volmer proposed in a seminal paper in 1919 [6]. As great scientists belonging to the emeritus group of pioneers of experimental atomic physics [7] and modern physical chemistry [8], Stern and Volmer were acknowledged. Their accomplishments have significantly altered many science fields in electronic spectroscopy studies and kinetics of chemical, inorganic, and biological compounds in the condensed phase. Specifically, in many areas of research, calculating the Stern-Volmer constant is beneficial. Thus, the determination of the Stern-Volmer constant is the central issue for many years. With the support of the Stern-Volmer relationship on the time evolution of critical molecular processes in electronics excited state; excimer and exciplex dynamics, vibronic coupling, electronic energy transfer, photo-induced charge (proton and electron) and numerous other diffusion-controlled processes that may serve as a source of luminescence quenching can be extensively investigated. Desilets with a research group from Purdue University have developed an improved method for determining Stern-Volmer quenching constants for several quenchers such as iodide (I<sup>-</sup>) and chloride ions (Cl<sup>-</sup>) that eliminate the need for a multitude of solutions and so is less prone to error [9], and believed this approach is applicable for our research interest in characterising DO concentration in the water. A ternary-gradient solvent-delivery system of the kind commonly available from liquid chromatography vendors has been adopted in the procedure. The signal loses or exponential decay of its intensity with an increase of quencher concentration due to luminescence quenching can be monitored, and a Stern-Volmer plot  $I/I_0$  and  $\tau/\tau_0$  against  $[Q]$  can easily be obtained through software manipulation of the data. The model's precision with the improved method seems to be good; after repeating three times the measurement, wherein all situations, the relative standard deviations between replicates were less than or equal to 2 %. Therefore, Volmer became famous for his impressive electrochemistry studies, where he co-developed the Butler-Volmer equation known as the Erdey-Grúz-Volmer equation, a fundamental electrochemical kinetics relationship. In comparison, Stern was awarded the Nobel Prize in Physics in 1943 for his fundamental atomic physics contributions [10].

DO concentration in the water has long been known to quench luminescence (or scientifically leads to the kinetics of photophysical- rather than photochemical-intermolecular deactivation process) where molecules and their electronics excited state are entities not fully understood or well defined until the classical Stern-Volmer model was developed. The relationship between the DO concentration and

decay time or intensity is expressed in the Stern-Volmer equation, which, in its simplest form, reads as follows in Equation 1.  $I_o$  and  $I$  are, respectively, the luminescence intensities of an oxygen-sensitive dye in the absence and presence of DO,  $\tau_o$  and  $\tau$  are, respectively, the fluorescence lifetimes in the absence and the presence of DO. While,  $[O_2]$  is the concentration of the DO quencher in the water,  $K_{sv}$  is the Stern–Volmer constant of the oxygen-sensitive dye to quantifies the luminescence quenching efficiency reflects the accessibility of the DO quencher to the electronics excited state of oxygen-sensitive dyes. The intermolecular deactivation is when non-bonded or free oxygen presence reduces its decay time and intensity. Therefore, in an ideal quencher system, the linear fitting between i) relative luminescence intensity under low light excitation,  $I_o/I$  or ii) relative luminescence decay time under low light excitation  $\tau_o/\tau$ , against  $[O_2]$  allows easy graphical determination of  $K_{sv}$ . Most optical-based transducers for DO sensing and monitoring are based on the luminescence quenching effect (i.e. spontaneous emission of light) of oxygen-sensitive dyes. The mechanism involves a dynamic collision between non-bonded or free oxygen in the water and the electronics state of the oxygen-sensitive dyes embedded onto an optical fibre. Examples of intramolecular deactivation (quenching) processes include processes such as fluorescence resulting from singlet–singlet electronic relaxation state up to nanoseconds typical lifetime and phosphorescence resulting from triplet–singlet electronic relaxation state from milliseconds up to hours typical lifetime. To support the use of the theory or model of Stern-Volmer [11] in this systematic literature review, in our humble opinion, when an additional constituent which is DO concentration in the water is added, the oxygen-sensitive dye embedded onto optical fibre is hypothesised where the luminescence quenching may occur. We may observe the reduction of luminescence intensity, increase full width at half maximum (FWHM) peak at emitted wavelength, and shortening of luminescence lifetime.

$$\frac{I_o}{I} = \frac{\tau_o}{\tau} = 1 + K_{sv}[Q] = 1 + K_{sv}[O_2] \quad (1)$$

#### 4. Transition metals thin-film waveguide embedded onto optical fibre

To minimize this environmental risk due to unstable dissolved oxygen saturation in the water, the ideal proposed design of optical fibre based transducers for dissolved oxygen sensing and monitoring:

- a) must have the right combinations of sensing material of transition metal in the form of two-dimensional thin-film embedded onto sensing region of optical fibre structure.
- b) must have a repeatable fabrication process compatible as compared with commercial dissolved oxygen transducers in the market.
- c) cost-effective, compact size, and portable, combined with less weight.
- d) must put appropriate health and safety measures during the handling process: precautions are taken to improve safety, reduce risk related to human health and the environment.
- e) must have a well characterised in terms of reliability and validity of the optical output signal such as continuous real-time, quick response, good stability for a short and long period, low detection limit, low hysteresis for reversibility measurement, long operating life, good linearity for a wide range of dissolved oxygen saturation, high-resolution and good selectivity.
- f) its permeability, solubility, and diffusion rate for DO in the water match the DO transducers' specific needs concerning quenching response and response time.

Real-time or in-situ determination of DO concentration in water requires transition metals to be firmly immobilised in a host matrix while its luminescence is measured over time. It is important in the case of water quality measurement, commonly addressed in global freshwater and seawater

aquacultures, where DO concentration should not drop below a certain level, the fish mortality rate will rise, and its consequences will reduce growth and survival rates.

From our point of view, several requirements for the transition metals to be a viable sensing element for dissolved oxygen sensing and monitoring should be highlighted:

- a) the transition metals and the matrices are compatible in solubility so that transition metals will enter and remain inside the matrix without aggregation or leaching.
- b) the transition metals have to be optically absorbance.
- c) the transition metals and matrices possess good adhesion to conceivable mechanical support such as optical fibre and should be easy to handle.
- d) the transition metals and the matrices possess good long-term stability and not to degrade.
- e) during the measurement, the transition metals are the only component to be used as the oxygen-sensitive dye. The matrices should not significantly alter the optical response (such as its spectra).

For DO sensing and monitoring, oxygen-sensitive dyes with long decay times are well suited because their long-lived excited state makes oxygen collisional quenching more likely. Also, they have good optical characteristics such as absorption in the visible range, large Stokes shifts, and often are photostable. Transition metal complexes usually undergo oxygen-sensitive dye charge transfer upon photoexcitation to form an excited triplet (or higher multiplicity) state. Triplet–singlet electronic relaxation state back transitions are spin-forbidden, and the triplet-state electronic relaxation state lifetimes are much longer than those of a singlet-singlet electronic relaxation state as brief in the previous sub-chapter. In luminescence, the wavelength of phosphorescence is longer than that of fluorescence due to the triplet state having lower energy than the singlet state. Spectral separation is facilitated by the resulting large Stokes shifts. It can be stated that an oxygen-sensitive dye's detection limits mainly depend on the lifetime of its emitting state in that quenchability is favoured by longer lifetimes. Several transition metals have been studied as an oxygen-sensitive dye, such as ruthenium(II), iridium(III), and osmium(II). Early quenching studies in liquid solution revealed that DO strongly quenches the luminescence of transition metal-ligand complexes [12]. Each transition metal has its own merits and disadvantages.

#### 4.1 Transition metal-based ruthenium(II) complexes as the oxygen-sensitive dye

The ruthenium(II) species are declared as the largest group of oxygen-sensitive dye to be utilised for DO sensing and monitoring such as Ru(bipyridine)<sub>3</sub> [denoted as Ru(bpy)], Ru(1,10-phenanthroline)<sub>3</sub> [denoted as Ru(phen)], and Ru(4,7,0-diphenyl-1,10-phenanthroline)<sub>3</sub> [denoted as Ru(dpp)]. Ruthenium(II) complexes have wide absorption bands,  $\lambda_{exc}$  most usually found in the blue region, 400 to 480 nm of the visible spectrum. They have broad Stokes shifts and are emitting,  $\lambda_{em}$  above 600 nm. Their long excited-state lifetimes (up to microseconds) make them viable DO sensing and imaging oxygen-sensitive dyes. Both lifetime and intensity are affected by DO concentration in the water. Their luminescence quenching can be tuned by changing ligands, also known as the matrix component in other observations.

In the form of its dichloride, the water-soluble probe Ru(bpy) [13] is the earliest ruthenium-based oxygen-sensitive dye ever used and investigated in the fabrication of an optical-based DO transducer. Ru(bpy) was immobilised by adsorbing it on micron-sized silicon dioxide particles, incorporated into the silicon rubber matrix. Excellent permeability to DO and its flexibility in terms of designing transducer geometries and format are the reason why silicon rubber was chosen as a matrix. The results obtained with this design of the transducer have already shown typical issues. Specifically, in

gaseous samples, such as downward exponential decay curved Stern-Volmer plot, variations its reversibility (in forward and backward response times), and sensitivity to relative humidity. Unfortunately, this transducer design does not play a role in liquid forms such as aqueous or blood samples for oxygen sensing and monitoring. The oxygen-sensitive dye that has been used in this study has an absorption maximum at 460 nm and is excited with blue light-emitting diodes (LEDs). The maximum emission peaks are shown at 610 to 630 nm give results of 150 to 170 nm of large Stokes shift due to luminescence quenching by oxygen facilitates the separation of the output optical signal in the form of luminescence (either fluorescence or phosphorescence) from scattered excitation light source, and reduces of self-absorption of luminescence.

In another experimental work, similar ruthenium(II) species have been used with an improved methodological approach, the oxygen-sensitive dye was doped into electrospun microfibres made of poly(methyl methacrylate) and ethyl cellulose and then immersed in an ionic liquid, the Ru(bpy) complex is found to have improved stability and DO sensitivity [14]. The use of polymeric-based electrospun microfibres results in increased specific surface area. However, whether the transducer is immersed in aqueous solutions or organic solvent, ionic liquids appear to be leached. It is said that the luminescence intensity of the transducer does not drift for three years and eight months.

Similar ruthenium(II) species, which is Ru(bpy), in its form of dichloride, the ionic oxygen-sensitive dye of Ru(phen)<sub>3</sub>Cl<sub>2</sub> is moderately water-soluble and has a lifetime of 1 μs unquenched. Its spectra are quite similar to that of ruthenium(II) species as described in the previous paragraph, Ru(bpy); in terms of the position of excitation and emission wavelengths, but the molar absorption coefficient is somewhat better [15-20].

A similar design of transducer with different oxygen-sensitive dye has been fabricated. Ru(dpp) has a strong absorption with a low FWHM value in the visible region at 463 nm, making it compatible with the argon-ion laser and blue LEDs, and exhibits good photostability [21-22]. These outstanding optical characteristics make Ru(dpp) the most widely used ruthenium-based oxygen-sensitive dye.

Most Ru(II) polypyridyl complexes can be excited with blue light, but more long-wavelength absorbing and emitting oxygen-sensitive dyes are needed for biological applications, especially in the red wavelength region [23]. Several long-wavelength Ru(II) complexes have been synthesised by replacing Ru(dpp) or Ru(bpy) with 6,7-dihydro-5,8-dimethyl-dibenzo[i, j][1,10]-phenanthroline [24]. Therefore, these two species of Ru(II) complexes can be photoexcited between 450 to 580 nm and have large Stokes shifts, and emitted into the near infra-red (NIR) region.

In the next approach to improving the reliability of the DO transducers, the leaching issue from the matrices must be overcome. It is possible to attach a Ru(II) complex with a polymeric acrylate group [25] to a matrix covalently. Metal-ligand charge transfer (MLCT) and spectral properties are not affected by introducing the acrylate group into the phenanthroline ring. The oxygen-sensitive dye completely preserves its oxygen sensing capacity. The co-polymerised sensing films are stable in hydrophobic organic solvents and even in aqueous solutions. Sulfonated Ru(II) complexes and immobilised them to amino-functionalised matrices such as amino-modified porous glass has been prepared [26]. When excited at 475 nm, the oxygen-sensitive dye showed a strong emission peak at 610 nm. The DO transducer design is suitable for sensing oxygen in organic solvents and aqueous solution because it was entirely resistant for leakage even on long-term usage. The Ru(II) polypyridyl complex has been functionalised by reaction with (3-aminopropyl)-trimethoxysilane in acid solution with the triethoxysilane group and condensed into the form of sol-gel glass film [27]. The results showed that the oxygen-sensitive dye in the sol-gel glass film revealed enhanced water and organic solvents' stability compared to similar films where the oxygen-sensitive dyes were incorporated physically. The respective oxygen-sensitive dye exhibited almost linear Stern-Volmer characteristic and good quenchability.

#### 4.2 Transition metal-based iridium(III) complexes as the oxygen-sensitive dye

Low-lying, non-emitting metal-centred excited states are found in Ru(II) complexes. It contributes to early deactivation by thermal depopulation [28] of the luminescent MLCT excited states.



Cyclometalated Ir(III) complexes have remarkable optical properties; excellent triplets emitters and widely used in LEDs. Besides, they also have good physicochemical characteristics; soluble in organic polymeric films, long lifetimes to display remarkable strong luminescence. The Ir(III) complexes are therefore attractive candidates for use as oxygen-sensitive dyes. It has been shown that crystalline iridium(III)-containing coordination polymers are viable materials integrated with optical fibre for oxygen sensing [29].

The oxygen-sensitive dye of  $[\text{Ir}(\text{ppy})_2(\text{dpt-NH}_2)](\text{PF}_6)$  [28] has been studied in the deoxygenated acetonitrile solutions showing good photostability, strictly linear Stern-Volmer plot with  $K_{sv}$  value of 2.5 and fully reversible response, for the emission peaks at 490 nm and 530 nm.

Two mono- and di-nuclear Ir(III) cyclometalated complexes were prepared and immobilised in polymeric matrices, as investigated by the same research team with a similar transducers design [30]. The resulting transducers emit intense luminescence with a maximum range of 500 to 650 nm and having a linear Stern-Volmer plot with  $K_{sv}$  in the range of 1.61 up to 2.76. Thus, they concluded a) the particle size, lifetime, and charge of the chromophore in the mono- and di-nuclear Ir(III) cyclometalated complexes, and b) permeability of polymeric used may affect the collisional quenching by oxygen.

In the following design of the DO transducer, the immobilisation of the oxygen-sensitive dye  $\text{Ir}(\text{ppy})_3$  in the fluoropolymer poly(styrene-co-TFEM) was investigated [31]. It showed an excellent optical response where it displays a strong luminescence in the green region, with a relatively long lifetime 1.5  $\mu\text{s}$ . Moreover, this DO transducer is photostable, and its fluorescence is strongly quenched by oxygen with  $K_{sv}$  of 15.3, as calculated from the Stern-Volmer plot. In the same study, they found that selecting the matrices itself may affect the transducers' sensitivity. By replacing the fluoropolymer with polystyrene, the  $K_{sv}$  value drops to 1.1.

The cyclometalated Ir(III) with aromatic organic chemical compound with the coumarin complexes have been synthesised to study the oxygen's collisional quenching [32]. It displayed a strong luminescence in the purple and blue region, with a relatively long lifetime on the order of 8 to 13  $\mu\text{s}$ , using respective mono- or di-meric complexes and tuning the use of coumarin ligand.

In another study, the use of Ir(III) complex (referred to as Ir-N-948) as the oxygen-sensitive dye was reported [33]. It has outstanding optical behaviour: a) strong absorption bands between 400 and 500 nm, b) longwave emission maximum at 650 nm, c) long lifetime up to 102  $\mu\text{s}$ , and having a good response to collisional quenching of the oxygen with  $K_{sv}$  value of 8.0, make this material most suitable for oxygen sensing and monitoring.

Similar to the situation with the previous choice of oxygen-sensitive dye for oxygen sensing and monitoring, using  $\text{Ir}(\text{ppy})_2(\text{H}_2\text{dcbpy})\text{PF}_6$  as the bridging ligand ( $\text{H}_2\text{dcbpy}$ =4,4'-dicarboxy-2,2'-bipyridine), four oxygen-sensitive dye of Ir(III)-containing coordination crystals were successfully synthesised [34]. In this methodological step, bridging ligand was crystallised with  $\text{M}(\text{ClO}_4)_2$  ( $\text{M}=\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Co}$  and  $\text{Ni}$ , respectively) to form Ir(III)-containing single crystals, and correspond to  $K_{sv}$  values of 0.83, 2.82, 1.33, 1.11, and 2.48, respectively. The lifetime of these crystals is rather long, more than 70 s.

#### 4.3 Transition metal-based osmium(II) complexes as the oxygen-sensitive dye

Os(II) polypyridyl complexes are another form of oxygen-sensitive dye widely used to study the oxygen's collisional quenching. A series of the Os(II) polypyridyl complexes have been synthesised and characterised in degassed acetonitrile solution ambient. They found the luminescence lifetime in the range of 101 to 3462 ns was obtained [35-36]. They also claimed that Os(II) species' excited state properties could be precisely designed by variation of ligands so that the oxygen's sensitivity can be adjusted. Os(II) polypyridyl complexes can excite even in the NIR region, to make it suitable for in vivo biological applications. It is due to any matter related to biological is poorly penetrated by shortwave visible and ultra-violet light regions [37]. Oxygen luminescent quenching of a series of Os(II) complexes with  $\alpha$ -diimine ligands in polydimethylsiloxane and related polymers [38] was also

studied. They can be efficiently excited in yellow and the region, with broad absorption spectra. Thus, the excited-state lifetime was in the range of 400 ns, and emitted in the NIR region.

### Conclusions and future outlook

Research on transition metals got underway following the promise of its application to the optical sensing. Any question about the ideal DO transducer cannot be answered unless the issue is stated. Thousands of types of DO transducers are identified or can be envisaged. In the future, DO transducer will predictably become much smaller (in the scale of optical fibre), and this will pave the way for mass production for commercialisation. Numerous applications of optical-based DO transducer have been explored. Such a DO transducer can be used in large-scale applications to measure the water quality in marine and freshwater research. It is noted that DO transducer has also seen extremely exciting applications include sensing of oxygen in the blood and the vascular system, imaging of the distribution of oxygen inside biological cells, the detection of hypoxia (a condition in which there is an insufficient amount of oxygen) in skin tumours diagnosis and therapy, sensing of oxygen in food technology and packaging, sensing of oxygen in drug screening and many more. All this indicates that research and development will continue to advance vigorously and in several directions in this optical-based sensing area. We concluded that the Stern-Volmer model as a versatile approach to be used on the mechanistic study of the collisional quenching of oxygen with different types of the transition metal, and we believe many other transitional metals can be explored for the future outlook.

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### Competing interests

The authors have identified no possible conflict of interest regarding the publication of this manuscript.

### Authors' contributions

The authors provided equal contributions to this manuscript. The authors approved the final manuscript.

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