DOI 10.5162/IMCS2018/OS1.1

Luminescence-based Chemical Sensors

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Abstract

Optical chemosensors became increasingly popular in the last decades due to many new possibilities and applications offered by them compared to conventional analytical methods. Particularly, they are free of electromagnetic interferences, enable non-invasive or minimally invasive read-out with compact and inexpensive read-out devices, imaging of analyte distribution on surfaces as well measurements in small samples such as cells and organelles. Among optical sensors and probes, those based on luminescent materials are probably the most numerous ones. In this talk we will briefly discuss the general concepts of sensing with luminescence-based chemosensors and provide an overview of the materials developed in our group along with some application examples. Particularly, sensors for oxygen, pH, basic and acidic gases, ions and temperature will be discussed.

Key words: optical sensor, luminescence, nanoparticles, imaging, oxygen, pH, ions, temperature

General design of a luminescent sensor and current challenges

The key component of a luminescent sensor is a (metal)organic indicator dye/inorganic phosphor which luminescent properties (emission spectrum, intensity, decay time) respond to the analyte of interest. In most cases, the indicator is covalently immobilized or physically entrapped into a matrix (most commonly a polymer) to enable continuous measurement in a variety of samples. This sensing material can be coated on a planar transparent support (planar optodes), a tip of optical fiber (fiber-optic sensors and microsensors), 3D surfaces (sensor paints) or can be used on its own in form of nanoparticles. The flexibility of formats allows for a great variety of potential applications.

Although the basic principles of luminescent sensors are generally known for long time, there is still a lack of high performance materials which fulfill the necessary requirements. For instance, the indicator should have desired spectral properties, possess high luminescence brightness (which is the product of the molar absorption coefficient and quantum yield), be reasonably photostable and show minimum cross-sensitivities to other parameters. Additional requirements are applied to the sensing material depending on the application, for instance fast response time, good storage and operational stability, suitability for sterilization etc.

The research of our group attempts to address these challenges and is focused on preparation of new high performance materials for luminescent sensors. Particular attention is given to the materials operating in the red and near-infrared parts of the electromagnetic spectrum due to their compatibility with the biological “optical window” and low interference from background fluorescence and light scattering.

Optical oxygen sensors

Oxygen sensors rely on dynamic quenching of the luminescence of indicator by molecular oxygen which implies no consumption of the analyte during the measurement. We investigated numerous systems based on metalloporphyrins and particularly the π-extended derivatives such as benzoporphyrins [1] (Fig. 1), naphthoporphyrins, azabenzoporphyrins etc. However alternative systems including iridium(III) cyclometallated complexes, lanthanide chelates, complexes of Schiff bases etc. have also been prepared and characterized. We also addressed the challenge of measuring low and ultra-low oxygen concentrations by manufacturing trace oxygen sensors with detection limits in pM range [2].

pH and ion sensors

Different fluorescent pH indicators have been prepared, mostly based on BODIPY (Fig. 1),

aza-BODIPY [3], perylene [4] and diketo-pyrrolo-pyrrol [5] chromophores. They mostly utilize quenching via photoinduced electron transfer (PET, Fig. 1). Different quencher groups (aliphatic and aromatic amines, phenolates) have been used to adjust the dynamic range of the pH indicators to particular application [6]. We also prepared a sensor which covers significantly wider pH range than the sensors based on a single indicator dyes (~ 3 pH units) [6].

Sensors for carbon dioxide and ammonia

pH indicators with comparably high and low pK_a values have been used to manufacture carbon dioxide [7] and ammonia [8] sensors, respectively (Fig. 1). In an alternative concept of ammonia sensing we utilized a neutral NH_4^+ fluoroionophore along with internal buffer [9]. This system resulted in elimination of cross-sensitivity to amines.

Optical ion sensing

A palette of new NIR fluoroionophores (FIs) base on π-extended BODIPY dyes have been prepared to enable sensing of K^+, Na^+ and Ca^{2+} [10, 11]. The FIs rely on PET effect (Fig. 1).

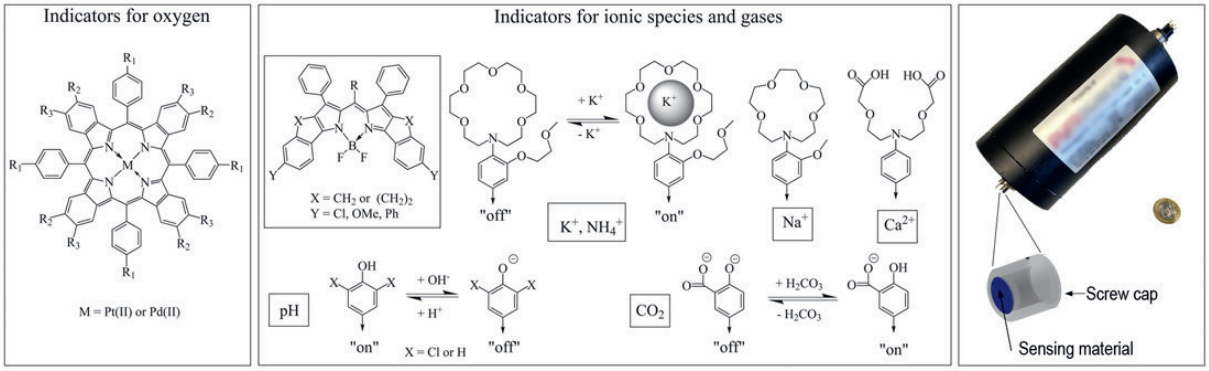

Fig.1.Chemical structures of new luminescent indicators covering red/NIR part of the spectrum. Right panel illustrates optode system developed for oceanographic applications

Optical temperature sensors

Similarly to other chemosensors, optodes show temperature cross-talk. We have proposed different systems based on metal-organic complexes and inorganic phosphors for optical sensing and imaging of temperature. Recent development includes highly sensitive molecular thermometers utilizing thermally-activated delayed fluorescence [12].

Applications

In cooperation with collaboration partners, new optical sensors have been applied in many fields, most prominently biology, biotechnology, marine biology and oceanography. For instance, in frames of EU project SenseOcean, the new materials were combined with loggers designed by PyroScience (Aachen, Germany) to enable autonomous monitoring of oxygen, pH or carbon dioxide in seawater for up to 1 year (Fig. 1, right).

Acknowledgements

Financial support by the European Research Council Project "Oxygen" (N 267233), European Union FP7 Projects SenseOCEAN (N 614141) and SCHeMA (N 614002) H2020 Project STEMM-CCS is gratefully acknowledged.

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