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Optical Sensing (Nano)Materials Based on Benzimidazole Derivatives

Ema Horak, Robert Vianello and Ivana Murković Steinberg

Abstract

Benzimidazole derivatives are well-known biologically active substances, and therefore, they are mostly synthesised for therapeutic purposes. However, such heteroaromatic molecular systems own structure-related properties that enable a variety of applications, especially in optical science. Multifunctionality of the benzimidazole unit, such as electron accepting ability, π -bridging, chromogenic pH sensitivity/switching and metal-ion chelating properties, makes it an exceptional structural candidate for the design of optical chemical sensors and functional materials. Development of smart molecular sensors and novel (nano)materials is the emerging trend observed in materials and optical sensing science in general, in which the benzimidazole molecular systems strongly contribute and participate. In this chapter, we summarised recent advances in optical sensing (nano)materials that incorporate the benzimidazole structural moiety. Solid-state optical sensing systems, including self-assembled molecular materials based on benzimidazoles, are reviewed and discussed. In addition, immobilisation of benzimidazole derivatives onto or into various substrates and matrices, such as organic and inorganic polymers, bulk membranes and nanoparticles, utilising different chemical and physical methods, is presented and analysed.

Keywords: benzimidazole, functional materials, optical sensor, solid-state, absorbance, fluorescence, aggregation-induced emission

1. Introduction

Optical chemical sensors are widely applied in chemical science and technology, as well as in other disciplines such as biology, medicine and environmental science. They enable continuous monitoring of the target analytes and exhibit high sensitivity and fast response time. The biggest advantages of optical chemical sensors, in comparison to other sensing devices, are the economic production, ease of operation and the possibility of on-site application without reference devices, which are preferred in chemical and biological applications. Performance of every chemical sensor is primarily determined by the sensing chemistry that operates in the background, that is, the recognition unit—receptor. The receptor, the core of every optical chemical sensor, is the sensing molecule that selectively responds to the presence of the target analyte by changing the photophysical properties of the observed molecular system. Fluorescence techniques are

most commonly applied for the generation and transfer of the analytical signal, while providing high sensitivity and selectivity. Therefore, fluorescent sensing molecules are the most promising candidates for the chemical sensing. Their design often starts from the heterocyclic molecular skeleton, due to its excellent spectral properties and the ability to detect diverse analytes. Heterocyclic chromophores and fluorophores are the most investigated classes of optical sensing molecules; hence, the interest for benzimidazole as a structural block of novel molecular systems is constantly increasing. Although benzimidazole derivatives are primarily known as biologically and therapeutically active substances [1], such heteroaromatic molecules have structure-related properties that enable a variety of applications in optoelectronics and non-linear optics (NLO) [2, 3], photovoltaics [4, 5], sensing [6] and bioimaging [7, 8]. Indeed, multifunctionality of the benzimidazole unit, such as electron accepting ability, π -bridging, chromogenic pH sensitivity/switching and metal-ion chelating properties, makes it an exceptional structural candidate for the design of optical chemical sensors [9, 10]. From the chemical point of view, the benzimidazole ring possesses a high degree of stability. Benzimidazole, for example, is not affected by concentrated sulphuric acid and is quite resistant to reduction. Oxidation cleaves its benzene ring, yet only under vigorous conditions. The two imidazole nitrogens are different from one another in their nature, which makes the properties of the ring system diverse in character. The hydrogen attached to the nitrogen can easily tautomerise to the other nitrogen atom. With the pK_a values 5.3 and 12.3, benzimidazoles are weakly basic, being somewhat less basic than the imidazoles and sufficiently acidic to make them usually more soluble in polar environments and less soluble in organic solvents. Benzimidazole, for example, is soluble in hot water but difficultly soluble in ether and insoluble in benzene, all of which can be modified upon the substitution. The acid/base properties of benzimidazoles are due to the stabilisation of the charged ion by the resonance effect.

However, development of optical chemical sensors is much more complicated than designing a sensing molecule (recognition unit), since the process combines molecular recognition, material science and device implementation. Employing the sensing chemistry in a form of optical sensing material is perhaps the key step towards the ultimate goal, since its implementation can directly result in a functional sensor. Although there is a large number of fluorescent indicators and sensing molecules presented in literature, many of them lose their selectivity upon the implementation in functional devices, which makes the design of optical sensing materials a very challenging task [11, 12].

Recently, developments in optical sensing molecular systems that incorporate benzimidazole structural unit are reviewed and discussed [13]. As can be deduced from a given review, molecular sensors based on benzimidazole derivatives are mainly applied in solution, while materials for optical sensing are still rare, yet very promising. Development of novel (nano)materials and especially 'smart' molecular sensors, some of which include nanotubes, nanowires and nanoparticles, is the emerging trend observed in materials and optical sensing science. Although the growth of scientific interest in benzimidazole-based materials is evident in the last decade, such systems are indeed untapped potential in the field of optical chemical sensing.

In this chapter, we summarised the recent advances in optical solid state sensing systems and (nano)materials that incorporate the benzimidazole structural moiety. Immobilisation of benzimidazole derivatives in bulk membranes, polymers, sol-gel materials, as well as self-assembled (nano)materials for optical sensing are reviewed and discussed. Representative examples have been selected and commented in next sections, based on the type of applied material.

2. Polymer-based sensing materials

Polymers are the most commonly used support for optical chemical sensors [14]. They can be utilised to immobilise the sensing component, but can also directly participate in the sensing mechanism. In general, most commonly used polymers for analyte sensing are cellulose derivatives and hydrogels because of their excellent mechanical properties, stability at broad temperature and pH ranges, as well as high permeability towards water, ions and undissolved gases. In addition, polymers like polyurethane and pHEMA are biocompatible, a fact that enables new possibilities of their application.

The simplest form of the polymeric sensing material is the polymer membrane in which the chemosensor molecule is physically entrapped [11, 12]. Such dye-impregnated polymers are widely used in sensing chemistry, due to economic and simple methods of preparation. The choice of polymer depends on its permeability towards a specific analyte, its stability, availability and potential for immobilisation. Still, the development of such membranes is a challenging task because the polymer microenvironment has a strong effect on spectral characteristics of the immobilised sensing molecule, its acid-base equilibrium, selectivity towards the analyte and fluorescence lifetime. Ion-selective optodes are well-known examples of such optical sensing systems, where the bulk membranes are mostly formed from plasticised PVC [15].

An alternative for dye-impregnated polymers are the polymers with covalently attached fluorescent molecules. Stability of covalently bonded systems provides many advantages and can significantly improve analytical performance of chemical sensor. Another class of materials for optical sensing is the luminescent polymers. Design and synthesis of novel conjugated or coordination polymers is a constantly growing area of research, due to the enormous potential for the application of these kinds of functional materials.

The polymer-based materials for optical sensing that incorporate benzimidazole unit are summarised in **Table 1**, while the representative examples have been selected and discussed in next sections.

2.1 Dye-impregnated polymers

Polymer-based sensing materials incorporating physically entrapped benzimidazole-based receptors are very often used when relying on the electrochemical detection [16, 17]. However, examples utilising optical sensing techniques are not that common. For example, novel fluorescent sensors are developed by the immobilisation of benzimidazole-based ionophores in plasticised PVC, resulting in ion-selective optode for mercury [18] and silver detection [19]. Presented ion-selective optodes are complex systems, where a number of parameters, including lipophilicity, polarity and microviscosity affect the heterogeneous ion-exchange equilibrium. The same sensing mechanism is presented for benzimidazole-based acrylonitrile derivatives [20] and Schiff bases [21], where novel colorimetric and fluorimetric sensing materials are applied for detecting the acidity changes. Moreover, immobilisation of this class of compounds into polymer matrices is demonstrated as a convenient way to overcome certain problems of organic fluorophores occurring in aqueous solution, such as hydrolysis of imino-bond or low quantum yields. For instance, a reversible spectroscopic response to pH is achieved because protonation of the immobilised benzimidazole Schiff bases occurs on the stable benzimidazole moiety (electron acceptor), while the imino bond of the Schiff base remains preserved [21]. At the same time, spectral properties of fluorescent sensing molecules are significantly altered due to the interactions between molecules in bulk, that is, in novel environment, where the molecular system becomes more rigid with partially disabled *cis-trans* isomerisation. Optical properties of developed materials

Material	Analyte	BI-based sensing molecule	Detection method	Limit of detection (mol L ⁻¹)	Ref.
PVC	Hg ²⁺	Crown-based ionophore	Fluorimetric	3.5×10^{-13}	Firooz et al. [18]
PVC	Ag ⁺	Crown-based ionophore	Fluorimetric	2.8×10^{-12}	Firooz et al. [19]
PVC	pH	Acrylonitrile derivative	Colorimetric	—	Horak et al. [20]
PVC	pH	Schiff bases	Fluorimetric	—	Horak et al. [21]
Photocrosslinked membrane	Hg ²⁺	1,8-naphthalimide derivative	Fluorimetric	2.5×10^{-6}	Fernández-Alonso et al. [22]
Amphiphilic copolymer	pH	Vinyl monomer	Fluorimetric	—	Han et al. [29]
Hydrophilic copolymer	pH	Pyridyl substituted benzimidazole derivative	Fluorimetric	—	Shen et al. [30]
Conjugated polymer	Cu ²⁺	Pendant benzimidazolyl moieties	Fluorimetric	—	Wu et al. [28]
Conjugated polymer	Fe ³⁺ and PO ₄ ³⁻	Pendant benzimidazolyl moieties	Fluorimetric	3.38×10^{-6}	Saikia <i>et al</i> (2011) [27]
Coordination polymer	Fe ³⁺	Bis(benzimidazole) derivative	Fluorimetric	3.2×10^{-6}	Hao et al. [36]
Metal organic framework	Humidity and formaldehyde	Benzimidazolyl-attached bent organic ligand	Colorimetric	—	Yu et al. (2014) [32]
Metal organic framework	Cr ₂ O ₇ ²⁻	1,6-Bis(benzimidazol-1-yl)hexane ligand	Fluorimetric	2.16×10^{-6}	Li et al. [31]
Coordination polymer	Fe ³⁺ ion and nitroaromatics	Benzimidazole ligand	Fluorimetric	3.70×10^{-7}	Zhou et al. [33]
Coordination polymer	Multi-analyte	Benzimidazole-appended tripodal tridentate ligand	Fluorimetric	—	Tripathi et al. [37]
Coordination polymer	pH	Benzimidazole-functionalized organic ligand	Phosphorescence	—	Yang et al. [38]
Coordination polymer	Fe ³⁺	Benzimidazole-functionalized organic ligand	Fluorimetric	2.53×10^{-6}	Zhao et al. [39]
Coordination polymer	Fe ³⁺	Benzimidazole-functionalized organic ligand	Fluorimetric	2.72×10^{-5}	Wei et al. [40]
Zr-UiO-66 nanocrystals	Fe ³⁺	Benzimidazole-functionalized organic ligand	Fluorimetric	—	Dong et al. [34]

Table 1.
Polymeric optical sensing materials based on benzimidazole derivatives.

can also be easily modified by tuning the ICT character of fluorescent molecules, which is often achieved by introducing electron donating groups (e.g. N,N-diethyl amino) and strong electron withdrawing moieties (e.g. -CN and -NO₂) on the opposite parts of molecular system (**Figure 1A**).

2.2 Covalently attached benzimidazole derivatives

As an alternative to dye-impregnation of polymers, fluorescent molecules can be covalently attached to polymeric materials, as demonstrated, for example, in a fluorescence solid sensor for the mercury detection based on a photocrosslinked membrane functionalised with (benzimidazolyl)methyl-piperazine derivative of 1,8-naphthalimide [22]. Benzimidazole, linked to a piperazine moiety by a methylene spacer, is responsible for the specific recognition of Hg²⁺ ions by forming a stable complex structure, that resulted in a strong fluorescence (**Figure 1B**). Materials developed by the covalent attachment of the sensing molecules usually have more advantages than those utilising physical entrapment, in which active molecules may easily leach out of the matrix. Stability and duration of covalently functionalised polymer materials are much better, and they even often provide improved analytical parameters of chemical sensor.

2.3 Luminescent polymers

Another approach to obtain fluorescent sensing materials is a clever design and synthesis of novel luminescent polymers. For instance, conjugated polymers are the constant trend in the development of novel functional materials [23, 24]. They effectively coordinate with many organic compounds or transition metals, which is very well conjoined with their excellent optical properties and exploited in optical chemical sensors. Detection methods are mostly relying on the fluorescence techniques, particularly the quenching effect ('superquenching') described by Stern-Volmer relationships. Fluorescent conjugated polymers also offer many advantages in regard to simple organic fluorophores, such as amplified sensitivity and the possibility of simple introduction of desired functional groups in order to achieve better interactions with the analyte. Benzimidazole is often found as a constituent of conjugated polymers [25–28]. Optical sensing ability of benzimidazole-based fluorescent polymers is demonstrated for the detection of pH [29, 30], metal ions [28] or inorganic anions [27], where benzimidazole moiety often plays a crucial

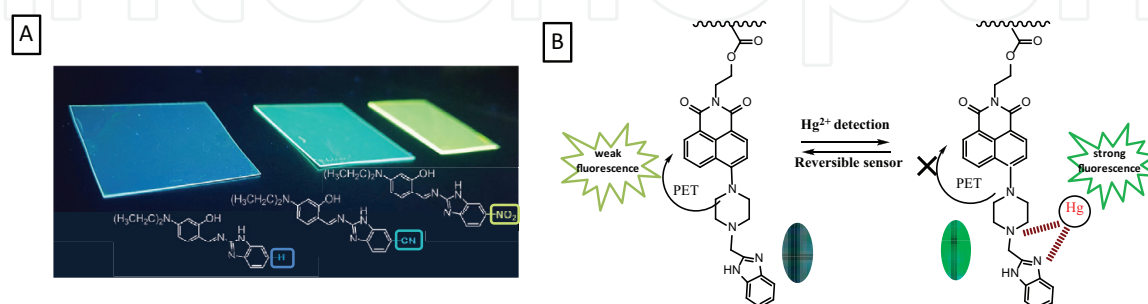


Figure 1.

(A) Fluorescent pH-sensitive bulk optodes based on immobilised Schiff base derivatives in plasticised PVC matrix. Tuneable fluorescent response of the optodes is a result of different substituents on the benzimidazole moiety. Reprinted from [21]. Copyright (2018), with permission from Elsevier. (B) Selective fluorescence solid sensor for Hg²⁺ based on N-(2-hydroxyethyl)-4-(4-(1Hbenzo[d]imidazol-2-yl)methyl) piperazine-1-yl)-1,8-naphthalimide, here presented by the author's courtesy. Fluorescence sensor undergoes fluorescence enhancement upon binding mercuric ion due to the inhibition of photo-induced electron transfer (PET) process from the piperazine to the naphthalimide moiety [22].

role in the sensing mechanism. For example, a copolymer built from *N*-(1-ethyl-2-(pyridin-4-yl)-1*H*benzo[*d*]imidazol-5-yl)methacrylamide and 2-hydroxyethyl methacrylate exhibits a pH sensitivity due to acid-base equilibria on the heteroatom of pyridyl-substituted benzimidazole moiety [30] (**Figure 2A**).

Besides conjugated polymers, benzimidazole-based materials can be developed as luminescent metal organic frameworks (MOFs) [31–35] or coordination polymers [36–42]. Such advanced functional materials have been extensively applied in the field of luminescence sensing due to their diverse structural characteristics and tunable pore sizes. For example, luminescence sensing of iron is achieved by a coordination polymer employing the linear 2,5-dichloroterephthalic acid ligand and the flexible bis(benzimidazole) derivatives. Ligand affords the capacity to strongly bind metal atoms, while bis(benzimidazole) derivatives can freely twist around two methylene -CH₂ groups with disparate angles to generate different conformations [36]. Luminescent MOFs have been exploited for the development of sensing materials for humidity and formaldehyde, such as a porous Cu(I)-MOF, constructed from CuI and 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene (**Figure 3**) [32]. 3D cadmium metal-organic framework was demonstrated as sensing material for the detection of Cr₂O₇²⁻ in water [31], while diamond-like coordination polymer exhibits selective emission quenching responses towards the Fe³⁺ ion and nitroaromatics [33].

Interesting to note is the emerging trend in the development of the so-called ‘smart’ materials, where the final product exhibit multistimuli-responsive photoluminescence sensing properties. Tripathi et al. developed Hg(II) coordination polymer with benzimidazole-appended tripodal tridentate ligand, 1,3,5-tris(benzimidazolylmethyl)benzene. Luminescent material is the first example of Hg(II) coordination polymer with multistimuli-responsive properties (**Figure 2B**). Luminescence quenching response is observed to a range of stimuli, including anions, solvents and nitroaromatic compounds [37].

2.4 Inorganic polymers

Inorganic polymers, such as networks of metal oxides obtained by sol-gel process, are also attractive substrates for immobilising sensing molecules. Sol-gel materials are very popular for the development of optical sensors, especially nanosized

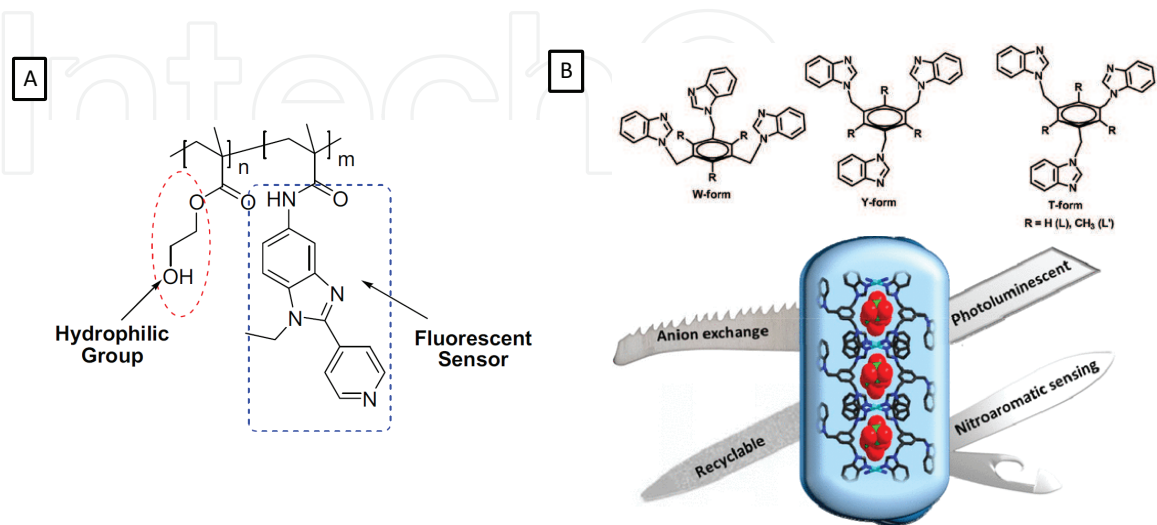


Figure 2.

(A) Chemical structure of pH-responsive copolymer of *N*-(1-ethyl-2-(pyridin-4-yl)-1*H*benzo[*d*]imidazol-5-yl)methacrylamide and 2-hydroxyethyl methacrylate, here presented by the author's courtesy. pH sensitivity is achieved by pyridyl substituted benzimidazole moiety [30]. (B) Representation of multistimuli-responsive ‘smart’ mercury(II) coordination polymer and different possible conformations of benzimidazole-based ligand in metal complexes. Adapted with permission from [37]. Copyright (2018) American Chemical Society.

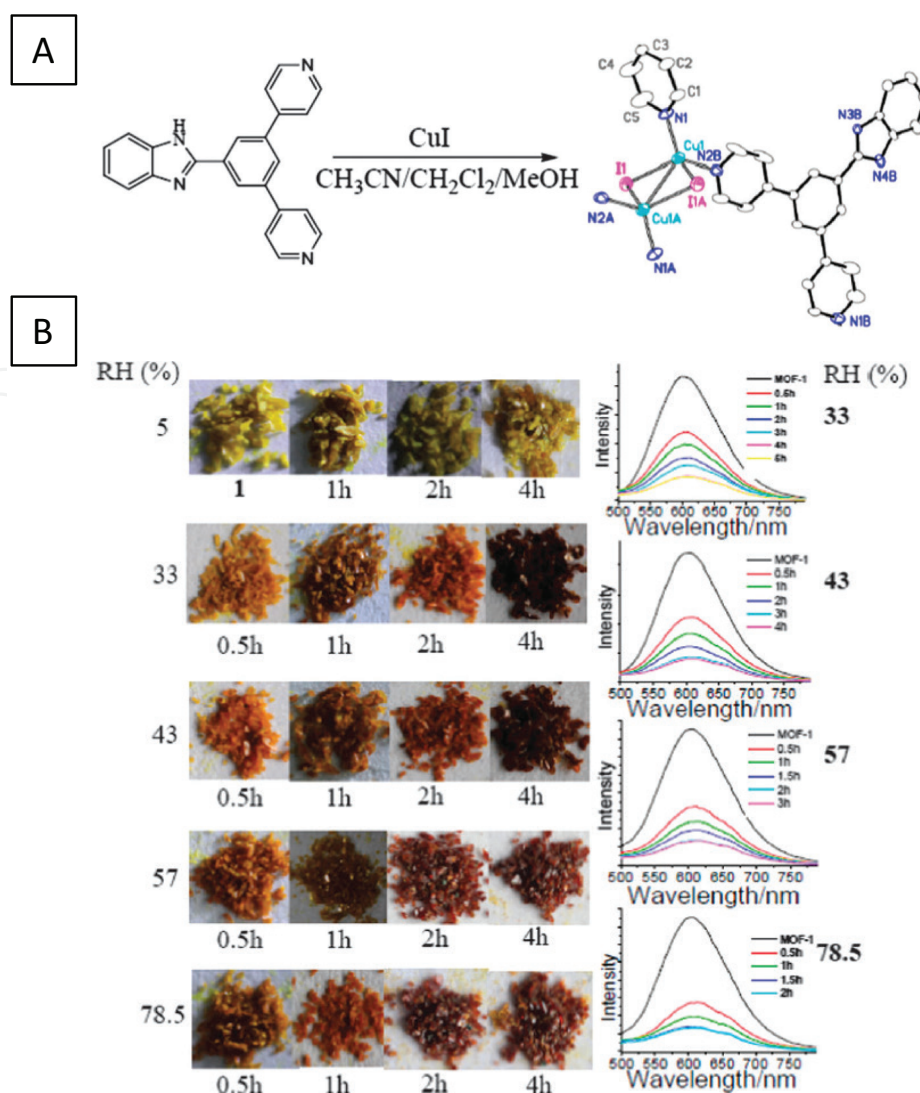


Figure 3.
 (A) Highly sensitive naked eye colorimetric sensor for water and formaldehyde detection based on a porous Cu(I)-MOF constructed from CuI and 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene. (B) The colour change of the bulk crystal samples of MOF in atmospheres with different relative humidity (RH 33–78.5%) and the corresponding solid-state emission spectra. Adapted with permission from [32]. Copyright (2013) Royal Society of Chemistry.

probes [43]. Basically, the sol-gel process is a method for the synthesis of ceramic or glass materials at low temperature, starting from the colloidal suspension ('sol'). Hydrolysis of alkoxy metal groups in the precursors followed by polycondensation results in a network structure ('gel'). Meantime, fluorescent indicators can be easily incorporated in sol-gel by impregnation, chemical or covalent immobilisation. These materials are porous, so that the analyte can freely diffuse. They are robust and biocompatible, which makes them suitable for intracellular sensing. Hoffman et al. have developed novel benzimidazole-based fluorescent materials using the sol-gel process [44]. Tetraethylorthosilicate (TEOS) was used as an inorganic precursor for the development of new silica hybrid materials. Although sol-gel chemistry is firmly embedded in the field of chemical sensors, there is a lack of benzimidazole-based sol-gel materials. The reason can be poor solubility and self-assembly properties of many benzimidazole derivatives, often inducing gelation process and thus, making the development of novel sol-gel materials, in a classical manner described above, a challenging task. However, the gelation of such compounds has been shown as an excellent method for preparing new sensing membranes, which will be discussed in further sections.

To conclude this section, we can highlight several facts. Literature shows that polymer-based materials are the most common substrates for the preparation of novel optical sensing platforms based on benzimidazole derivatives. Benzimidazole moiety retained its functional properties upon immobilisation in presented polymeric platforms. Although they are thoroughly explored and their potential for sensing applications is often emphasised, luminescent polymers that incorporate benzimidazole moiety are not adequately exploited in optical sensors. Even though polymer-based sensing materials are still relatively rare, a recent advance in developing benzimidazole-based ultralong-persistent room temperature phosphorescence (RTP) materials that exhibit reversible pH-responsive emission [38] represents a significant breakthrough of benzimidazole derivatives in materials science. Unfortunately, the biggest disadvantages of most polymer-based sensing materials are still very limited, such as selectivity, poor photostability and often leaching of indicator dyes.

3. Self-assembled sensing materials

3.1 Gels

Soft matter research and supramolecular organogels are one of the emerging scientific areas in the last decade. Functional materials based on supramolecular organogels are very attractive for the applications in tissue engineering, medical implants, controlled drug release, environmental studies etc. Small organic molecules have often been investigated as π -gelators, including benzimidazole derivatives [46, 47]. Utilising their fluorescence and self-assembling properties, benzimidazole-based gels are successfully demonstrated as novel functional materials. For example, a family of alkylpyridinium benzimidazole derivatives was synthesised in order to examine its gelation properties [48], while several fluorescent π -gelators based on benzimidazole are presented as stimuli responsive systems and sensors [49–53]. Ghosh et al. presented sensing system for Ag^+ based on the cholesterol-appended benzimidazole. Benzimidazole moiety with conformational flexibility can exhibit different alignments upon metal ion chelation, while the cholesterol is likely oriented to exert hydrophobic-hydrophobic interaction for establishing cross-linked network for solvent trapping. The addition of Ag^+ ions to the solution of presented molecules in DMF:H₂O (1:1, *v/v*) at room temperature causes instant gelation and the change of colour, visible by a naked eye [51]. Another example of multi-analyte sensor array based on benzimidazole and acylhydrazone naphthol moieties was demonstrated by Yao et al. [52]. The latter sensing system is able to detect many analytes such as CN^- , Al^{3+} , Fe^{3+} and L-Cys with a possibility for the selective identification of Fe^{3+} and Al^{3+} in the gel state (**Figure 6**).

3.2 Aggregation-induced emitters

Self-assembly of benzimidazole derivatives takes a great role in emerging mechanisms and designs of novel optical sensing materials. One of the research directions of the self-assembled molecules are the sensing materials based on the emissive (nano)aggregates. Aggregation of organic fluorophores is mostly investigated as an undesirable side effect in many biological or chemical applications due to fluorescence quenching. However, development of novel organic luminophores with aggregation-induced emission (AIE) changed the aspect of aggregation phenomena and the AIE was introduced as an analytical tool in a wide range of application, such as bioimaging, optoelectronics and chemosensors [54]. AIE or AIEE

(aggregation-induced emission enhancement) can be observed in the so called 'poor' solvents, in crystalline or powder forms. With that in mind, benzimidazole-based fluorophores capable of emitting intense fluorescence in the aggregated form (AIE emitters) can also be classified as novel sensing materials [55–58]. For example, self-assembled nanoaggregates of benzimidazole-based acrylonitrile derivative are presented as sensing system for pH, based on aggregation-deaggregation mechanism and aggregation-induced emission (AIE) [59]. 2-Benzimidazolyl-substituted acrylonitrile dye exhibits fluorescence emission in the red, green or cyan spectral regions, depending on its protonation degree. The neutral form is capable of self-assembly in the aqueous environment (pH between 5 and 9), exhibiting stable red-orange fluorescence emission at 600 nm. Thus, due to the aggregation-induced emission (AIE), from the single molecular entity, tri-state system (RGB) is derived. The aggregation and emission are pH switchable and fully-reversible. Gogoi et al. presented a novel AIE system based on a benzimidazole derivative for the detection of pyrophosphate (PPi) (**Figure 4**) [56]. The benzimidazole moiety has a functional role in assembling aggregate structures and the recognition of Ppi. Molecules of benzimidazole derivative self-assemble in nanostructures when so-called 'bad' solvent, H₂O, is added into the THF solution ('good' solvent). Self-assembled nanostructures exhibit pronounced emission at $\lambda = 530$ nm. Their π - π stacking is affected by the Ppi presence, thus assembled aggregates are of different emission properties and sizes. Another example is offered by Singh et al. by the preparation of fluorescent aggregates for sensing chemical warfare agents (diethylchlorophosphate) from benzimidazolium-based receptors containing 2-mercaptobenzimidazole and 2-mercaptobenzthiazole as functional groups, using anionic surfactants [60]. Authors presented receptors with benzimidazolium moiety in the centre, as well as receptors with two fluorescent arms as binding- and signalling units that initially interacts with chemical warfare agents and captures the hydrolysed product of an organophosphate.

An AIE phenomenon is especially exploited in solid-state, where the concentration effect commonly causes fluorescence quenching. Having in mind that fluorophores emitting in the solid states are extremely rare, especially red ones, benzimidazole-based AIE molecular systems show a great prospect for future applications of pristine powder samples or crystals as solid-state sensors and 'smart' materials [61–65].

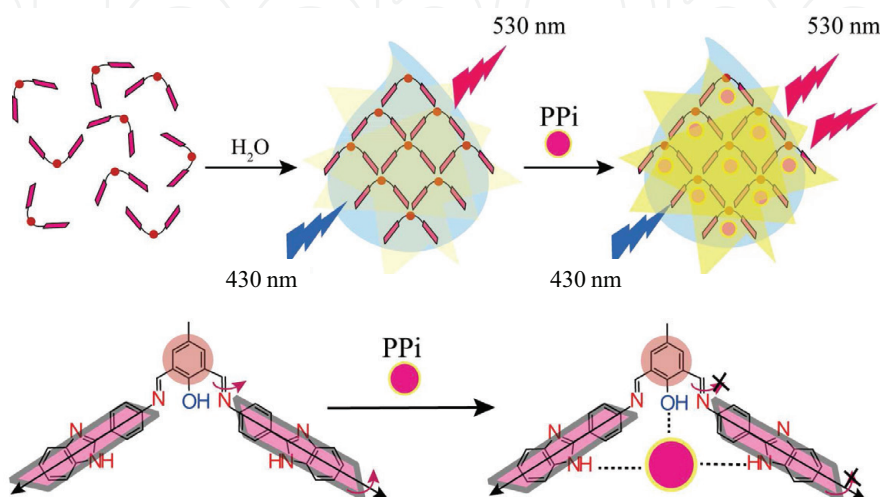


Figure 4. Aggregation-induced emission of benzimidazole-based derivative and detection of pyrophosphate (PPi). Reprinted with permission from [56]. Copyright (2015) American Chemical Society.

In conclusion, due to its emerging and multidisciplinary character, further research on optical sensing applications of benzimidazole-based gel membranes and self-assembled structures is strongly encouraged. Gelation is proven and widely investigated effect in many benzimidazole-based compounds, yet not exploited enough for the preparation of novel chemical sensors. Meanwhile, research on the aggregation-induced emission phenomena has taken momentum in all areas of application. Beside the fact that certain benzimidazole-based derivatives exhibit AIE property, which is not often found within small heterocyclic molecular systems, optical chemical sensors based on this principle are rarely found. Self-assembled materials for optical sensing that incorporate benzimidazole unit are summarised in **Table 2**.

4. Nanomaterials for optical sensing

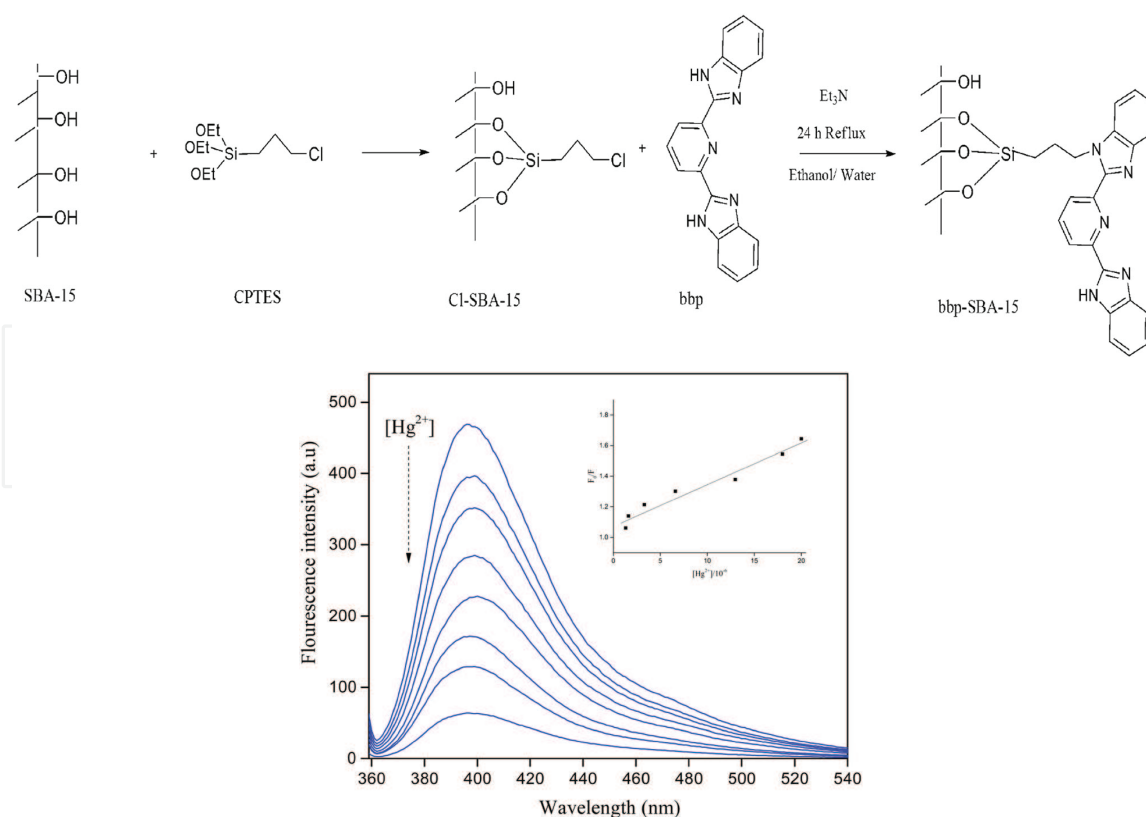
Nowadays, the term *nano* appears in all aspects of our life, technology and science, including the optical chemical sensors. In most general way, an optical nanosensor can be defined as a device smaller than 1 μm that is continuously tracking an analyte and simultaneously converting optical information into an analytically useful signal [66]. Fluorescence is the most commonly applied detection technique, due to its high sensitivity and relative simplicity of measurement [67]. Nanosensors can be macromolecular nanostructures, nano-sized polymer materials and sol-gels, multi-functional core-shell systems, multi-functional magnetic beads or nanosensors based on quantum dots or metal beads. We have previously mentioned the nanoaggregates formed by the self-assembly process. Although such type of nanomaterial can be classified as nanosensors, the emphasis in this section is placed on synthesis of nano-sized substrate materials functionalised with benzimidazole derivatives. Most commonly used method for the preparation of nanosensors is previously mentioned sol-gel process resulting in silica nanoparticles [68, 69]. Some other methods, such as precipitation, are often utilised for the preparation of polymer nanoparticles [70]. Research in the field of benzimidazole-based nanosensors is still in the early stages. Benzimidazole-based nanomaterials for optical sensing of metal ions are so far demonstrated as hybrid silica materials [44, 68, 71], ZnO nanoparticles decorated with benzimidazole-based organic ligand [72] or self-assembled nano hyperbranched polymer [73]. For example, Badiei et al. recently presented SBA-15 nanoporous silica functionalised with 2,6-bis(2-benzimidazolyl) pyridine for the selective recognition of mercury (**Figure 5**) [71]. Fluorescence intensity of the SBA-15 functionalized material quenched in the presence of Hg^{2+} ions, wherein the sensor is applicable in the physiological pH range of 6–8.

5. Other benzimidazole-based materials for optical sensing

A simple, fast and economic determination of target analyte, on-site and without a reference device is one of the key challenges of modern analytical chemistry. As mentioned in previous sections, the response to this challenge came forth in the form of optical chemical sensors. In addition, design and development of sensing materials as straightforward optical sensors enable countless possibilities of their applications, especially in modern technology where the emphasis is put on mobile, wearable and wireless devices. Simple, yet effective materials for colorimetric or fluorimetric detection of analytes can easily be achieved using filter paper or TLC plates. Paper substrates themselves are an attractive platform for the

Material	Analyte	BI-based sensing molecule	Detection method	Limit of detection (mol L ⁻¹)	Ref.
Gel	Multi-analyte	Benzimidazole and acylhydrazone naphthol moities	Fluorimetric	—	Yao et al. [52]
Gel	Ag ⁺	Cholesterol appended benzimidazole	Colorimetric	4.31 × 10 ⁻⁵	Ghosh et al. [51]
Gel	pH and anions	Benzimidazole moiety and four amide units	Colorimetric / Fluorimetric	—	Xue et al. [49]
Gel	Picric acid	Cholesterol-based anthraquinone-coupled imidazole	Colorimetric	4.30 × 10 ⁻⁶	Mondal et al. [50]
Gel	Na ₂ S	Carboxylic acid functionalized benzimidazole	Fluorimetric	—	Yao et al. [53]
AI Egen	Pyrophosphate	Dipodal benzimidazole- functionalized sensor	Fluorimetric	1.67 × 10 ⁻⁹	Gogoi et al. [56]
AI Egen	pH	Acrylonitrile derivative	Fluorimetric	—	Horak et al. [59]
AI Egen	Warfare agents	Benzimidazolium-based dipodal receptors	Fluorimetric	10 × 10 ⁻⁹	Singh et al. [60]
Powder	F ⁻ and COO ⁻	Benzimidazole derivative	Colorimetric	0.38 × 10 ⁻³	Chaudhuri et al. [64]
SBA-15 nanoporous silica	Hg ²⁺	2,6-bis(2-benzimidazolyl) derivative	Fluorimetric	2.6 × 10 ⁻⁶	Badiei et al. [71]
ZnO nanoparticles	Zn ²⁺	Benzimidazole-based organic ligand	Colorimetric	4.09 × 10 ⁻⁹	Kaur et al. [72]
Nano hyperbranched polyester	Fe ³⁺	Benzimidazole end groups	Fluorimetric	—	Wang et al. [73]
Filter paper	TNT	Pyrene-substituted benzimidazole-isoquinolinones	Colorimetric	50 × 10 ⁻⁶	Boonsri et al. [74]
Filter paper	CN ⁻	Acrylonitrile-embedded benzimidazole-anthraquinone	Colorimetric	37 × 10 ⁻⁹	Kumar et al. [76]
Filter paper	Ni ²⁺	2-(2'-hydroxyphenyl)benzimidazole	Colorimetric	—	Dhaka et al. [77]
TLC plates	Acid/amine vapours	Carbazole-based benzimidazole derivatives	Colorimetric	—	Aich et al. [75]

Table 2.
Benzimidazole-based materials for optical sensing.

**Figure 5.**

Synthesis procedure of benzimidazole functionalized SBA-15 material and fluorescence emission of the aqueous suspended nanoparticles (0.4 g L^{-1}) upon titration of increasing amount of Hg^{2+} ions. Inset: Stern-Volmer plot, $\lambda_{\text{exc}} = 353 \text{ nm}$. Reprinted with permission from [71]. Copyright (2018) Springer Nature.

use in a wide range of optical sensing, due to the possibility of a passive sample manipulation by capillary forces. So far, paper-based optical chemical sensors for neutral molecules, anions and cations, relying on benzimidazole derivatives as recognition element, have been successfully presented by several research groups. For example, Boonsri et al. demonstrated paper-based sensors for the trinitrotoluene (TNT) detection [74]. Sensing material prepared from pyrene-substituted benzimidazole-isoquinolinones can readily detect TNT in aqueous media by a naked-eye observation at concentrations as low as $50 \mu\text{M}$. Optical sensing of acid/amine vapours with three carbazole-based benzimidazole derivatives in the solid state was also demonstrated using TLC plates [75]. Plates were immersed with benzimidazole-based dyes and then exposed to trifluoroacetic acid (TFA) vapours for 1 minute. In following step, the TLC plates which were exposed with TFA vapours were further revealed to triethyl amine vapours and the restored colour was observed in each case (**Figure 6**).

Anion detection was demonstrated by the ratiometric detection of CN^- based on acrylonitrile embedded benzimidazole-anthraquinone coated on the filter paper [76]. Paper strips coated with the sensing molecule showed a distinct colour change from yellow-greenish to red under UV light in the presence of the CN^- ions. Dhaka et al. demonstrated a 'bare-eye' probe for the detection of Ni^{2+} based on 2-(2'-hydroxyphenyl)benzimidazole. Colourimetric sensing of Ni^{2+} was demonstrated on filter paper. Paper test strips exhibit distinct visual change from colourless to yellow-gold [77]. Other materials for optical sensing that incorporate benzimidazole unit are summarised in **Table 2**.

Besides optical sensing, paper-based materials coated with functional benzimidazole derivatives are also presented as 'smart', stimuli responsive materials with potential applications in security, optoelectronic or fluorescent imaging [62]. Simple sensing substrates such as paper and textile materials are perfectly suited

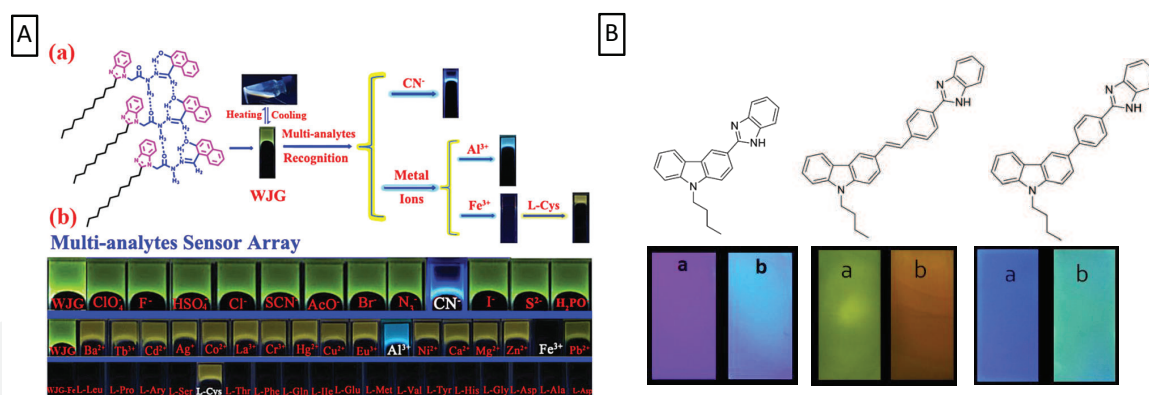


Figure 6.
 (A) Proposed self-assembly mechanism of a supramolecular AIE gel and its multiple-stimuli responsive behaviour (a) and fluorescence responses of the multi-analyte sensor array to the presence of various anions, cations and amino acids. Reprinted with permission from [52]. Copyright (2018) Royal Society of Chemistry. (B) TLC plates immersed with carbazole benzimidazole-based dyes observed under the UV light ($\lambda_{exc} = 365 \text{ nm}$) before (a) and after exposure to TFA vapours (b). Adapted with permission from [75]. Copyright (2016) Royal Society of Chemistry.

for applications in emerging mobile and wearable chemical sensors. Design and development of compatible ‘sensing chemistries’ that operate in the background of such devices is a constant challenge. The multifunctional nature of materials based on molecules such as benzimidazole can perfectly respond to this challenge.

6. Conclusion

Benzimidazole unit represents an important multifunctional building block in optical chemical sensors, with proven potential for the development of novel functional (nano)materials. Solid-state optical sensing systems incorporating benzimidazole derivatives are reviewed and discussed. Polymers are most commonly used substrates for the development of optical chemical sensors. Materials for optical sensing based on benzimidazole are also demonstrated as gels, sol-gel matrices, silica or polymer nanoparticles, (nano)aggregates and TLC or paper-based strips.

The role of benzimidazole moiety in optical sensing (nano)materials is important and crucial, since it maintains the function of the system and plays a key role in the formation of the analytical signal in the majority of chemical sensing systems reviewed here. Besides, the planar moiety significantly contributes to the conjugation of the chromo/fluorophore system. Although benzimidazole derivatives reviewed in the literature are mostly fluorescent sensors, several probes based on colourimetric switches are also demonstrated. It is very challenging to transfer the sensing chemistry from a solution to the solid state, which is successfully comprehended for the benzimidazole derivatives. It is even observed for some classes of chromophores with relatively unattractive sensing properties in aqueous solution (such as low quantum yield, decomposition upon protonation) to be drastically improved upon immobilisation in a polymer matrix.

Although examples of sensing materials presented in the literature show that benzimidazole derivatives can be successfully and easily applied in optical chemical sensors, they are yet insufficiently explored. Challenges in development of novel optical sensing (nano)materials are constantly emerging, since the scientific and industrial field of mobile and wearable sensors are experiencing great progress. Simple, fast and economic determination of target analyte, on-site and without reference device is a request that a multifunctional molecule such as benzimidazole can perfectly respond to.

Acknowledgements

This work was supported by the Croatian Science Foundation under grant number IP-2014-09-3386 entitled 'Design and synthesis of novel nitrogen-containing heterocyclic fluorophores and fluorescent nanomaterials for pH and metal-ion sensing' which is gratefully acknowledged.

Conflict of interest

Authors have no conflict of interest to declare.

Abbreviations

AIE	aggregation-induced emission
AIEE	aggregation-induced emission enhancement
DMF	dimethylformamide
ICT	intramolecular charge transfer
MOF	metal organic framework
NLO	non-linear optics
pHEMA	poly(2-hydroxyethyl methacrylate)
PPi	pyrophosphate
PVC	poly(vinyl chloride)
RGB	red, green and cyan spectrum
RTP	ultralong-persistent room temperature phosphorescence
SBA-15	porous silica
TEOS	tetraethylorthosilicate
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TNT	trinitrotoluene
UV	ultraviolet

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