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Polymers of Intrinsic Microporosity (PIMs) in Sensing and in Electroanalysis

Frank Marken *[1], Lina Wang [1], Yuanzhu Zhao [1], Zhongkai Li [1], Mandana Amiri [2], Hamideh Imanzadeh [2]

[1] *Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK*

[2] *Department of Chemistry, University of Mohaghegh Ardabili, Ardabil, Iran*

Proofs to F. Marken

Email f.marken@bath.ac.uk

Abstract

Polymers of intrinsic microporosity (PIMs) provide high surface area materials (typically 1000 m^2 g^{-1} apparent BET surface area) that are processable from organic solvents to give glassy films or composite coatings. Multi-functionality for sensing with these materials is achieved (i) based on the polymer backbone itself being fluorescent or chemically active or (ii) based on guest species (chromophores, nano-catalysts, nano-photo-catalysts, *etc*.) that are readily embedded into PIMs and accessible through micropores in the polymer host. The ease of forming uniform microporous films or composite films is linked to molecular rigidity and highlighted here for sensing/electroanalytical applications.
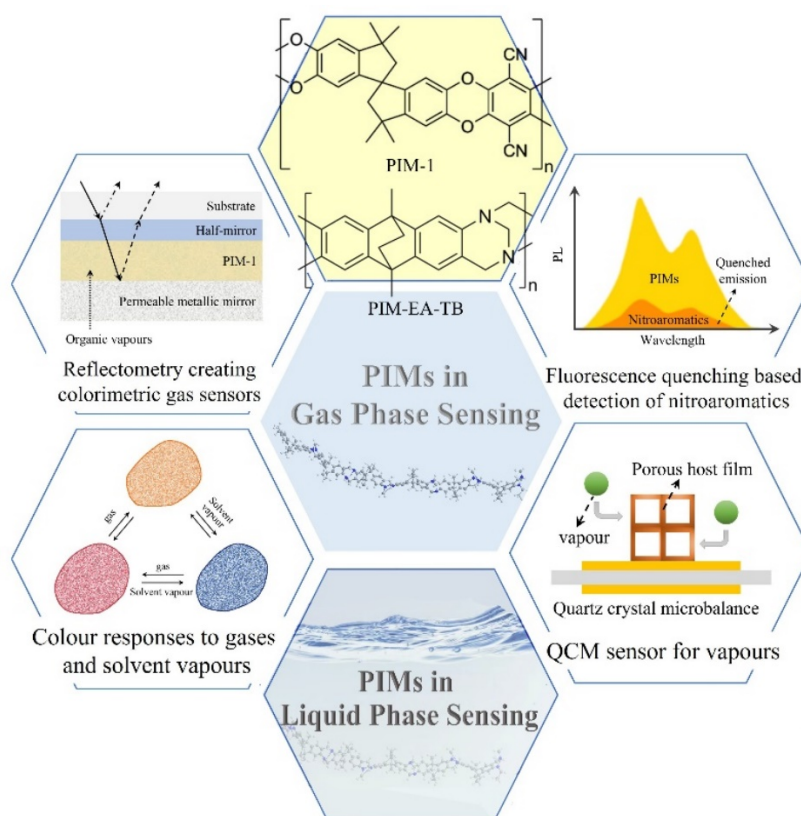
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1. Introduction

Microporous materials offer tuneable environments for effective solid|gas, solid|liquid, or solid|liquid|gas multi-phase interactions [1]. This is beneficial in particular for sensors and for electroanalytical interfaces that require effective interaction with the analyte (a gas or a solute) in high surface area absorber layers. Many types of absorber layers for sensors have been developed and polymers of intrinsic microporosity (PIMs) provide a recently emerging class of glassy materials with persistent micropores (with typically 1 nm diameter) to effectively interact with guest species or analyte species. *Extrinsic microporosity* refers to pore volume introduced by inclusion of small solvent of template molecules. In contrast, *intrinsic microporosity* is based on the rigidity of the polymer chain causing free volume elements with minimal polymer segmental motion. The key molecular feature in PIMs is the highly rigid backbone (minimising segmental motion and limiting molecular interactions in the solid) leading to both good solubility and processability. PIMs have been developed based on initial research by Budd and McKeown [2]. These materials are based on condensation reactions to build-up molecularly highly rigid chains avoiding rotational freedom without any single bonds. High molecular weight polymers of >70 KDalton provide mechanically robust non-brittle films and deposits, whereas deposits of low molecular weight materials may suffer from brittleness. Prototypical examples for these materials are PIM-1 and PIM-EA-TB (see molecular structures in Figure 1).

Related materials under development are the microporous "ladder polymers" [3] created by cross-linking materials. The cross-linking lowers processability but allows a high level of microporosity to be achieved with tunability for applications *e.g.* in gas separation. The development of covalent organic frameworks (COFs) is highly significant with applications in sensing [4]. The wider class of conjugated microporous polymers has attracted attention for applications in analysis [5]. Some specific materials such as poly-carbazoles have been reported as a related microporous class of materials with a high degree of microporosity and potential for application in sensing [6]. Many of these materials are "grainy" with properties that vary from grain to grain-boundary. The distinguishing property for PIMs here is processability and the formation of isotropic materials.

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PIMs are glassy but also highly processable due to poor interactions of rigid molecular structures and poor packing in the solid state. PIM-1 or PIM-EA-TB readily dissolve into chloroform or tetrahydrofuran to then allow cast deposition of films or anti-solvent precipitation. These processes are practical (i) when coating sensors or electrodes, (ii) for embedding molecular guests trapped in the microporous channels, (iii) for embedding nanoparticle catalysts or photocatalysts, or (iv) for introducing size-selectivity targeting smaller rapidly diffusing analyte molecules. Rigid molecular structures with microporosity result in a sieving effect at molecular scale [7] with many potential applications. In the case of PIM-EA-TB [8] and for PIM-1 [9] it has been demonstrated that heat treatment can lead to gradual crosslinking and partial carbonisation without loss of microporosity or shape, which can be important when developing electrical sensor films.
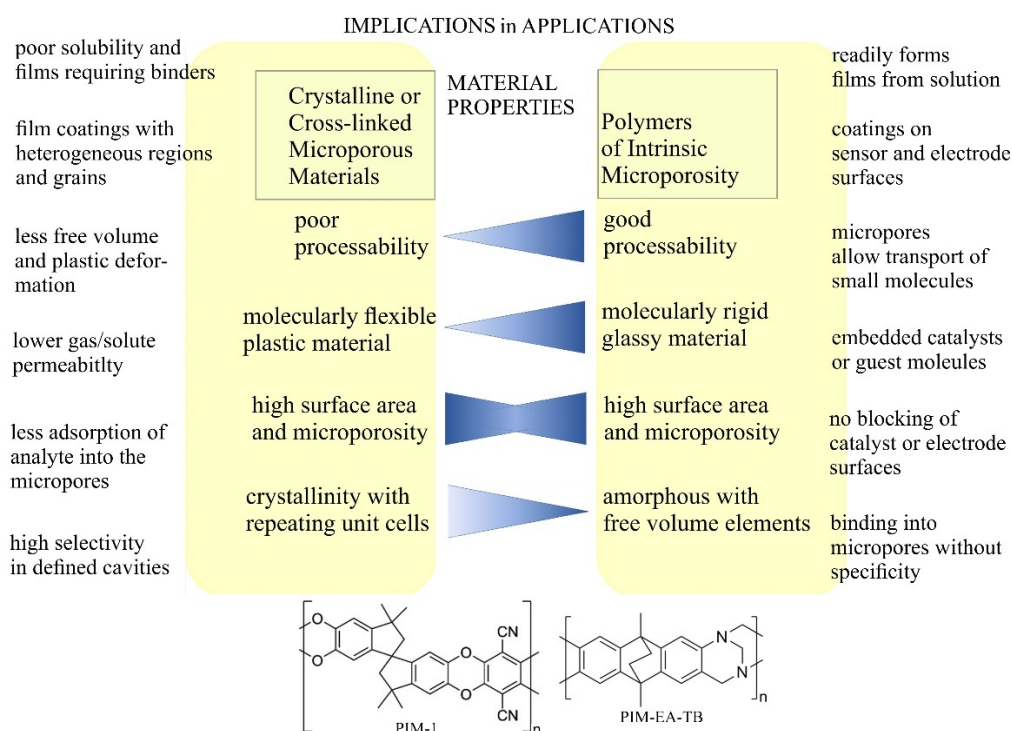
Figure 1. Overview of typical physical properties of polymers of intrinsic microporosity (PIMs) and their implications in the context of sensing and analytical electrochemistry. Molecular structures of PIM-1 and PIM-EA-TB as representative materials.

Microporosity can help in microextraction and pre-concentration, for example of chlorinated aromatics [10] or in the recovery of valuable drugs and anti-biotics [11]. In order to combine adsorption of analytes and detection, polymers with both microporosity and integrated

fluorescent groups [12] have been developed. Similarly, new applications of PIMs in electrochemistry and electroanalysis have emerged based on intrinsic microporosity [13].

2. Gaseous Phase Analysis

Microporous materials are known to be permeable to gases with molecular interactions controlling the rate of permeation in gas separation. For PIM-1 it was recognised that the interaction with volatile organic compounds (VOCs) affects optical properties such as reflectometry in thin films sandwiched between metal layers [14,15] leading to versatile visual indicators for vapour. Importantly, humidity was shown to not significantly affect the sensor responses. These types of sensor films have now been commercialised. PIM-1 being strongly fluorescent with an absorption/emission wavelengths of λ_{abs} = 291 nm and 429 nm and λ_{em} = 510 nm [16] has also been shown to be effective as laser-based emitter. PIM-1 lasing is affected by nitroaromatics that accumulate into micropores to allow chemosensor applications [17]. A number of fluorescence-based sensing systems have been proposed based on microporous films and trinitrotoluene (TNT) affecting the fluorescence [18,19,20,21,22]. The mechanism for fluorescence quenching in PIM-1 in micropores filled with hexane was investigated by Fritsch and coworkers [23]. Colour responses are commonly employed in sensing and PIMs can act as hosts for rapidly colour-changing vapour-sensitive indicators. Raithby and coworkers have demonstrated solvent vapour indicating metal complexes dispersed in the form of microcrystals in PIM-EA-TB [24]. Colour responses are rapid for small crystals embedded into highly permeable PIMs (Figure 2).
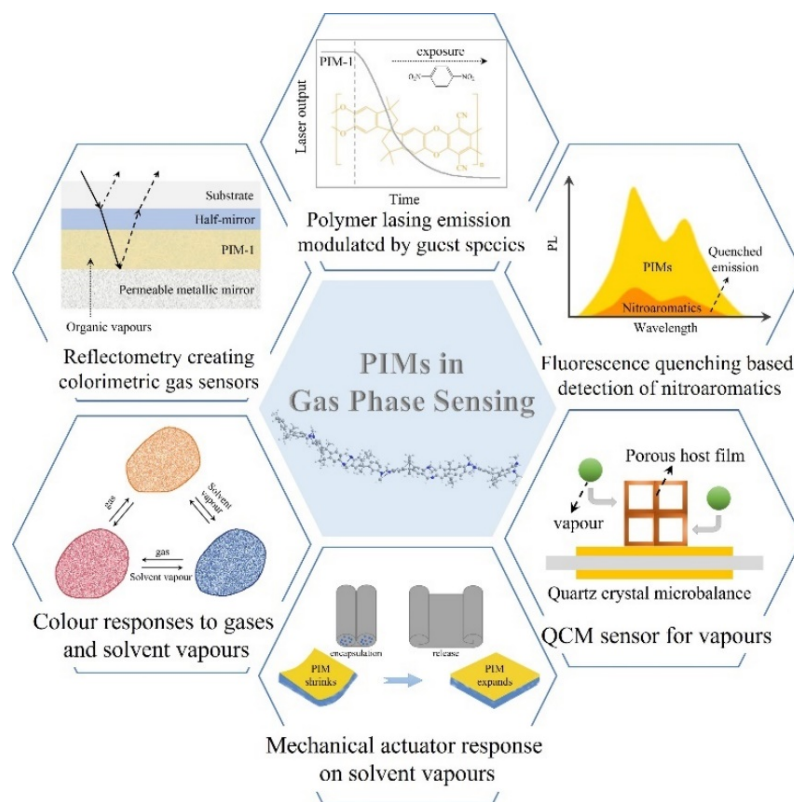
Figure 2. Summary of methodology for gas phase sensing with microporous films based on PIMs as sensor elements.

Hybrid materials with PIMs can respond to solvent vapours [25] by mechanically curling as actuators (Figure 2). Similarly, mechanical properties and weight changes are probed in quartz crystal microbalance (QCM) systems coated with PIMs that are highly sensitive for detecting weight changes down to nanogram level during adsorption of vapour molecules into microporous host films [26].

3. Liquid Phase Analysis

In liquid phase media, microporous channels are filled with solvent molecules and therefore the rate of transport and permeation are much slower. For a film of PIM-EA-TB with typically 10-20 µm thickness cast onto a carbon electrode, surface binding of caffeic acid was observed to take considerable time (several hours) and even electroosmotic transport was associated with a 10-20 minute delay for permeation of caffeic acid [27]. Therefore, transport in PIM micropores of typically 1 nm diameter filled with liquid can be slow. Microporous films need to be very thin or structured for rapid sensor responses to occur in liquid media. Larger solute molecules are size-excluded, which can be beneficial in complex sensing challenges, *e.g.*

sensing glucose in blood. It has been observed that a film of PIM-EA-TB coated over gold electrocatalyst allows glucose permeation while stopping larger proteins from interacting with the electrode [28].

Larger guest species that are immobile in the PIM environment are readily embedded by co-deposition as guests into films of PIM materials. Oxygen and H_2O_2 detection signals have been observed linked to electrocatalytic reduction at embedded iron-tetraphenylporphyrinato complexes [29]. These highly water insoluble iron complexes were embedded into PIM-EA-TB to give microporous sensor films. Molecular electrocatalysts (water-insoluble TEMPO derivatives) as guest species in PIM-EA-TB deposited onto carbon electrodes [30] were shown to oxidise aliphatic and aromatic alcohols (Figure 3). Recently, films of PIM-1 deposited onto a carbon electrode were studied for cholesterol detection [31]. The electrochemical response was induced by methylene blue adsorbed to the microporous polymer surface. In the presence of cholesterol, a displacement reaction occurred and this allowed quantitative detection of cholesterol.

The fluorescence of PIM-1 in liquid media was employed for mercury sensing. The polymer was modified with thiol functional groups to give fluorescence changes [32] in the presence of Hg(II) in solution. A heterocyclic miroporous polymer material has been shown to readily bind Ag(I) and other metal species [33] with applications in sensing. The Ag(I) loaded polymer gave a colorimetric response to traces of H_2S but did not react with molecular thiols like cysteine.

The permeation and transport of species in liquid-filled PIM microchannels can be employed in sensing and detection. PIM-EA-TB has tertiary amine functional groups on the polymer backbone and therefore allows interactions with hydrogen bond forming guests such as metal complexes [34] or herbal drugs such as catechin and quercetin [35]. Accumulation of these redox active species gave electrochemical oxidation signals proportional to the solution concentration with a Langmuir isotherm related response. The permeation of ionic species in PIMs has been investigated in ionic diode membrane devices [36], which allow accumulation/ depletion of cations/anions into a microhole region. It was demonstrated that with perchlorate in the bulk electrolyte, potassium selectivity and detection could be achieved due to local precipitation of $KClO_4$ within the ionic diode [37] (Figure 3).
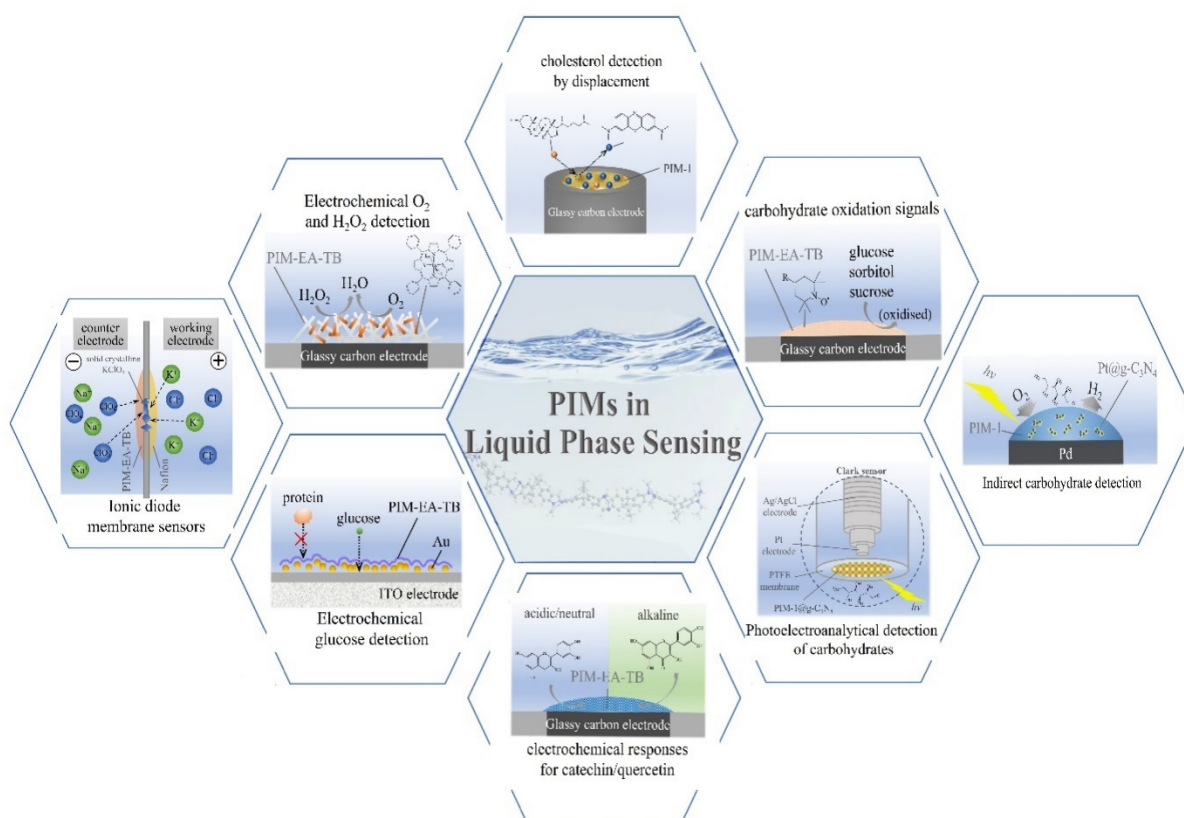
Figure 3. Summary of methodology for liquid phase sensing with microporous films based on PIMs as sensor elements.

Photoelectroanalytical processes can be desirable when the light-on current response is linked to the concentration of the analyte. A photocatalyst derived from graphitic carbon nitride, Pt@g-C$_3$N$_4$, was embedded into PIM-1 films [38] and responsive towards glucose quencher in solution. This type of sensor process could be employed in complex media, such as commercial soft drinks, to report sugar content in an indirect photoelectrochemical reaction *via* a hydrogen transport membrane. A related detection process was demonstrated for PIM-1/Pt@g-C$_3$N$_4$ coated onto a Teflon membrane of a Clark sensor [39]. Size-selectivity assigned to the PIM-1 host polymer resulted in higher photo-current responses for sorbitol and gluconic acid (small flexible molecules), with lower responses for glucose, sucrose, and raffinose (large and rigid molecules). Photoelectrochemical responses in the absence of added quencher molecules for the detection of oxygen was reported for Pt-modified titanate nanosheet materials embedded in PIM-1 and immobilised onto a glassy carbon electrode surface [40]. Generally, PIM materials can be employed as inert microporous hosts for catalysts or photocatalysts in electroanalytical processes. The lack of segmental motion in the polymer minimises chemical

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interactions of host and guest and ensures effective access to the catalyst without polymer chains blocking the surface. Table 1 summarises some recent/key publications on the application of PIMs in analytical and electroanalytical processes.

Table 1: Reports on PIM-1 and PIM-EA-TB Applications and Exploratory Studies in Sensing in Gaseous Phase Systems and in Liquid Phase Systems.

Gaseous Phase Systems							
Sensor film	PIM Type	Modified Method	Analytical Technique	Analyte	Detection Range	Detection Limit	Ref.
PIM-1 laser sensor	PIM-1	-	Photo-luminescence	Dinitrobenzene (10 ppb DNB for 5 min)	0-10 ppb	-	[17]
AgNP/PIM-1/ Ni-coated PET	PIM-1	Spin-coating	Optoelectronic	Volatile organic compounds (styrene, toluene)	0-100 ppb	$\geq$ 50 ppb (14 ppb - 32 ppb)	[15]
PIM-1	PIM-1	-	Fluorescence	Trifluoroacetic acid	-	$\geq$1.4 mM	[23]
AX21/PIM-1	PIM-1	-	Tensile testing	Organic solvents (ethanol, acetone, and DMSO)	-	-	[25]
Liquid Phase Systems							
PIM-EA-TB /AuNPs/ITO	PIM-EA-TB	Electrodeposition (AuNPs) Spin-coating (PIM-EA-TB)	Cyclic voltammetry	Glucose	2-14 mM	-	[28]
FeTPP:PIM /GCE	PIM-EA-TB	Drop-casting	Cyclic voltammetry	Oxygen, H_2O_2	-	-	[29]
4-B-TEMPO/ PIM-EA-TB/GCE	PIM-EA-TB	Drop-casting	Cyclic voltammetry	Carbohydrates (glucose, sorbitol, sucrose)	0-16 mM	-	[30]
Thiolethyl functionalized PIM-1	PIM-1	-	Fluorescence	Hg^{2+}	10-100 mg/L	-	[32]
PIM-EA-TB-Fe(CN)$_6^{3-/4-}$/GCE	PIM-EA-TB	Drop-casting	Cyclic voltammetry	Ascorbic acid	0-16 mM	-	[34]
PIM-1/GCE	PIM-1	Drop-casting	Differential pulse voltammetry	Cholesterol	0.05-0.001 µM	0.001 µM	[31]
Pt@titanate/PIM-1/GCE	PIM-1	Drop-casting	Cyclic voltammetry	Oxygen	-	-	[40]
PIM-1/Pt@g-C$_3$N$_4$/Pd electrode	PIM-1	Drop-casting	Chronoamperometry	Carbohydrates (glucose, fructose, sucrose, trehalose)	0.05-1 M	-	[38]
PIM-1/Pt@g-C$_3$N$_4$ / Teflon membrane (of a Clark sensor)	PIM-1	Drop-casting	Chronoamperometry	Carbohydrates (glucose, gluconic acid, sorbitol, sucrose, raffinose, 1-hexanol)	10-500 mM (10 µM-50 mM 1-hexanol)	-	[39]

4. Summary and Outlook

Although having emerged as a relatively recent addition to the class of microporous materials, PIMs have shown versatility and potential for applications in particular in sensing. Most studies have been performed with prototypical materials such as PIM-1 and PIM-EA-TB, but there are opportunities for this class of materials to expand and molecular structures to be tuned for specific applications. The backbone functionality has been exploited to provide fluorescence for PIM-1 and tertiary amine binding sites for PIM-EA-TB. Absorption of molecular species and selective permeation play an important role for both gaseous systems and liquid phase systems. Processability allows guest species to be embedded to lead in future to a much wider range of colorimetric, fluorometric, electroanalytical, and photo-electroanalytical sensor systems.

The concept of intrinsic microporosity and associated with this the lack of segmental motion of the host polymer are scientifically intriguing and crucial in modifying permeation and transport in PIMs. Processes linked to transport of gases have been well studied, but processes associated with transport in liquid phase or under "triphasic" conditions [41] could lead to new developments and processes. Selectivity towards transport of ions and neutral species in liquid media is crucial for example for accumulation and removal of pollutants, in electroosmotic pumps, but also integral as a process in sensing. Over the coming years and, based on current knowledge, beneficial properties of PIMs in sensing/analysis could be "pre-programmed" when designing new structures for specific application. PIMs designed based on more sustainable raw materials will add new opportunities for a wider range of application.

Conflict of Interest

The authors declare no conflict of interest.

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