

Electronic Acknowledgement Receipt

EFS ID:	25436384
Application Number:	62319895
International Application Number:	
Confirmation Number:	8755
Title of Invention:	ROBUST, AND PLASTICIZER-FREE IODIDE-SELECTIVE SENSOR
First Named Inventor/Applicant Name:	Sergio Granados-Focil
Customer Number:	58406
Filer:	Christopher J. Lutz/Debra Gilbride
Filer Authorized By:	Christopher J. Lutz
Attorney Docket Number:	CLK16-01P
Receipt Date:	08-APR-2016
Filing Date:	
Time Stamp:	12:42:32
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$ 130
RAM confirmation Number	9531
Deposit Account	503735
Authorized User	CHAPIN INTELLECTUAL PROPERTY LAW, LLC

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 CFR 1.16 (National application filing, search, and examination fees)

Charge any Additional Fees required under 37 CFR 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 CFR 1.19 (Document supply fees)

Charge any Additional Fees required under 37 CFR 1.20 (Post Issuance fees)

Charge any Additional Fees required under 37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Specification	CLK16-01P_Application.pdf	369490	no	13
			667738552cc6d6ec0dd0a5105dd46edf43841c81		
Warnings:					
Information:					
2	Provisional Cover Sheet (SB16)	CLK16-01P_Provisional_Cover_Sheet.pdf	1477545	no	3
			53123c0072a11aa1022010781bf95534a731db10		
Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	29940	no	2
			69440cc2cc7d64fed69759d29ac671f30ba3ed92		
Warnings:					
Information:					
Total Files Size (in bytes):			1876975		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Electronic Patent Application Fee Transmittal

Application Number:				
Filing Date:				
Title of Invention:	ROBUST, AND PLASTICIZER-FREE IODIDE-SELECTIVE SENSOR			
First Named Inventor/Applicant Name:	Sergio Granados-Focil			
Filer:	Christopher J. Lutz			
Attorney Docket Number:	CLK16-01P			
Filed as Small Entity				
Filing Fees for Provisional				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Provisional Application Filing Fee	2005	1	130	130
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Extension-of-Time:				
Miscellaneous:				
Total in USD (\$)				130

Invention Disclosure Information

1. **Brief Descriptive Title of the Invention**

Robust, and plasticizer-free iodide-selective sensor.

2. **Inventor(s) - Name, position, department, phone. Identify all individuals who have made significant intellectual contributions to this invention's advance over prior technology, but do not include anyone merely because s/he has carried out some of the experimental work.**

..... Dr. Sergio Granados-Focil, Associate Professor, Gustaf Carlson School of Chemistry and Biochemistry.

3. **Specify any other inventor(s) who is/are an employee of an organization other than Clark and their institutional affiliation.**

Dr Aleksandar Radu; Lecturer in Chemistry (Environmental Sustainability), School of Physical and Geographical Sciences, Keele University, Keele, ST5 5BG, United Kingdom

Lukasz Mendecki; PhD student; School of Physical and Geographical Sciences, Keele University, Keele, ST5 5BG, United Kingdom

When it comes to dividing the contribution, I think it would be reasonable if Lukasz and I share contribution allocated to Keele only. In other words, let's say we distribute 50-50 between Clark and Keele, then Keele's contribution is shared 50-50 between Lukasz and I leaving the distribution of the total as 50% to you, 25% to Lukasz and 25% to me.
(Makes sense?)

4. **Background - to successfully determine the patentability of this invention, it will be necessary to compare it to existing technology, referred to as "prior art." Provide any references to assist in this evaluation.**

A. **If possible, identify any references to the prior art by patent number or journal article identification.**

Using long alkyl chains to increase overall lipophilicity of membrane:

Gehrig, P.; Rusterholz, B.; Simon, W. *Anal. Chim. Acta* **1990**, 233, 295–298.

Using plasticizer-free membranes:

Heng, L. Y.; Hall, E. A. H. *Anal. Chim. Acta* **2000**, 403 (1-2), 77–89.
 Heng, L. Y.; Toth, K.; Hall, E. A. H. *Talanta* **2004**, 63 (1), 73–87.
 Qin, Y.; Peper, S.; Radu, A.; Ceresa, A.; Bakker, E. *Anal. Chem.* **2003**, 75 (13), 3038–3045.
 Qin, Y.; Peper, S.; Bakker, E. *Electroanalysis* **2002**, 14 (19-20), 1375–1381.
 Mendecki, L.; Fayose, T.; Stockmal, K. A.; Wei, J.; Granados-Focil, S.; McGraw, C. M.; Radu, A. *Anal. Chem.* **2015**, 87 (15), 7515–7518.

Covalent attachment of ionophore and ion exchanger:

Püntener, M.; Fibbioli, M.; Bakker, E.; Pretsch, E. *Electroanalysis* **2002**, 14 (19-20), 1329–1338.
 Reinhoudt, D. N.; Engbersen, J. F. J.; Brzozka, Z.; van der Vlekkert, H. H.; Honig, G. W. N.; Holterman, H. A. J.; Verkerk, U. H. *Anal. Chem.* **1994**, 66 (21), 3618–3623.
 Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, 57 (9), 2600–2604.
 Rosatzin, T.; Bakker, E.; Suzuki, K.; Simon, W. *Anal. Chim. Acta* **1993**, 280 (2), 197–208.
 Qin, Y.; Bakker, E. *Anal. Chem.* **2003**, 75 (21), 6002–6010.
 Kimura, K.; Sunagawa, T.; Yajima, S.; Miyake, S.; Yokoyama, M. *Anal. Chem.* **1998**, 70 (20), 4309–4313.

Use of ionic liquids:

Cicmil, D.; Anastasova, S.; Kavanagh, A.; Diamond, D.; Mattinen, U.; Bobacka, J.; Lewenstam, A.; Radu, A. *Electroanalysis* **2011**, 23 (8), 1881–1890.
 Shvedene, N. V.; Chernyshov, D. V.; Khrenova, M. G.; Formanovsky, A. A.; Baulin, V. E.; Pletnev, I. V. *Electroanalysis* **2006**, 18 (13-14), 1416–1421

Using of triazole-based ligand for sensing of iodide:

Hua, Y.; Flood, A. H. *Chem. Soc. Rev.* **2010**, 39 (4), 1262.
 Zahran, E. M.; Hua, Y.; Li, Y.; Flood, A. H.; Bachas, L. G. *Anal. Chem.* **2010**, 82 (1), 368–375.

Other iodide-based ISEs:

Malon, A.; Radu, A.; Qin, W.; Qin, Y.; Ceresa, A.; Maj-Zurawska, M.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2003**, 75 (15), 3865–3871.

Other prior art relevant for using polymerized ionic liquids:

Benjamin Schazmann, Aleksandar Radu; *European Patent Application No: 14184047.0*; **Filing Date: 9 September 2014** (attached for reference)

B. Specify any deficiency in the prior art improved upon by this invention or any limitation which it extends.

Current technical problems solved by this invention are:

- Improved detection limit: Single-piece membrane avoid using traditionally used inner-filling solution in ion-selective electrodes (ISEs) which are the biggest branch of IBSs. The inner solution is known to introduce significant bias in detection limit and its absence is considered advantageous. It should be noted that the last decade has seen substitution of inner solution with a layer of conductive polymer. This practice solved some of the existing issues with so called coated-wire electrodes. However, it still uses a number of components and more importantly heavily relies on somewhat involved and tedious pretreatment (conditioning) of electrodes in order to achieve optimal detection limit. Therefore, this renders such ISEs difficult for real-life applications.

- Stable signal: data presented indicate that there are no water layer formation that is identified as the major factor contributing to drifts in coated-wire electrodes.
- Conditioning: An important step in traditional preparation of ISEs is conditioning — a process where the membrane is exposed to solution of primary ion in order to allow its partition into the membrane and formation of primary ion-ionophore complex. Furthermore, achieving optimal detection limit typically requires two condition steps thus making the process of sensor preparation tedious. In our invention the membrane inherently contains association of primary ion and ionophore which renders conditioning unnecessary. This is major advantage in respect to traditional IBSs.

5. Briefly describe the invention. Indicate specifically what is considered to be the invention, as distinct from the prior art.

The most significant advantage of this invention is the creation of material that can be used as chemical sensor (of the ionophore-based sensors (IBSs) class) that contains only one component. In other words, classical (IBSs) typically contain polymer (typically polyvinyl chloride (PVC)), plasticizer (material for reducing polymer's glass transition temperature and solvent for other components), ionophore (ligand that selectively binds ion of choice, or as typically referred to as primary ion), and ion exchanger (compound used to address the ion-exchange mechanism of response of IBSs and maintain charge balance in the polymer membrane).

In our invention, we use polymerized ionic liquid (IL) whose cation part is formed of moieties that are selective to desired primary ion which is actually anionic part of IL. We therefore prepared a plasticizer-free polymer that *inherently contains ionophore*. Moreover, since primary ion is also inherently present in the membrane, the ion exchanger is not necessary and more importantly, there is *no need for any pretreatment of sensor*. Finally, due to large diversity of ILs and the possibility of their structure with relative ease, we suggest the possibility that the same principle is used to create sensors for many other ions (synthetically modifying a ligand to become cationic part of an IL and have primary ion as anionic part of the same IL) thus making this invention very general and *procedure for sensor preparation generic*.

6. Conception is the recognition that a novel arrangement of structural elements, composition of matter, manner of implementing a process, etc. will produce a useful result. Does there exist an earlier, dated record of the invention's conception (e.g., a sketch, report, laboratory notebook entry, etc.) that describes this invention and can be independently corroborated? Please indicate what it is and where it is.

Laboratory notebooks and progress reports stored at Clark University

7. Indicate the first successful reduction to practice of this invention (date, place, record, witnesses).

July 18th, 2015, Keele University, laboratory notebook, Aleksandar Radu.

8. Has this invention been disclosed to others, either verbally or in written form (date, place, to whom, method of disclosure)?

No disclosure yet.

9. Indicate any pending disclosures (date, place, to whom, method of disclosure).

Simple, robust, and plasticizer-free iodide-selective sensor based on copolymerized triazole based ionic liquid

Lukasz Mendecki,[†] Xiaorui Chen,[§] Nicole Callan,[‡] David F. Thompson,[†] Benjamin Schazmann,[‡] Sergio Granados-Focil,^{*,§} and Aleksandar Radu^{*,†}

Accepted for publication to *Analytical Chemistry*

10. List patents, publications, and/or commercial products or processes known to you showing a) technology closest to this invention, and b) closest known use of those elements or steps of this invention that differ from a.).

11. Indicate the potential commercial use of this invention (e.g., fields of use, advantages, estimate of value).

12. Indicate any potential commercial licensees that may be interested in this invention.

AR had initial discussions with Dr Duncan Hill (Scientific Officer) from Polyphotonix (<http://www.polyphotonix.com/>) about the use of their experimental technology for spooling polymers. There is an interest in mass production of sensors and our invention can potentially make impact in this regard.

13. Identify any sponsors and projects under which either conception or first reduction to practice occurred, including partial funding. Also list any related projects and/or inventions and any other potential claimants to rights in this invention.

This work has been generously supported by Royal Society (RG120118) and Marie Curie IRSES Grant (IBS Network; R6810 B475). LM gratefully acknowledges support from Keele University.

14. Were any University funds or other resources used in making this invention (if yes, please explain). SQF used some start up funds to purchase reagents for this work.

15. If funded by an external sponsor, has the sponsor been notified of this invention, either directly, in a progress or other report, or in an application for additional funds (date, sponsor, method of disclosure)?

Signed and Submitted By:

Name

Date

Simple, robust, and plasticizer-free iodide-selective sensor based on copolymerized triazole based ionic liquid

Lukasz Mendecki,[†] Xiaorui Chen,[§] Nicole Callan,[‡] David F. Thompson,[†] Benjamin Schazmann,[‡] Sergio Granados-Focil,^{*,§} and Aleksandar Radu^{*,†}

[†] Lennard-Jones Laboratories, Birchall Centre, Keele University, Keele, Staffordshire ST5 5BG, United Kingdom

[‡] School of Chemical & Pharmaceutical Sciences, Dublin Institute of Technology, Kevin Street, Dublin, Republic of Ireland

[§] Sackler Sciences Center, Department of Chemistry, Clark University, Worcester, Massachusetts 01610, United States

ABSTRACT: Novel solid contact iodide selective electrodes based on covalently attached 1,2,3 triazole ionic liquid (IL) were prepared and investigated in this study. Triazole-based IL moieties were synthesized using click chemistry and were further copolymerized with lauryl methacrylate via a simple one step free radical polymerization to produce a "self-plasticized" copolymer. The mechanical properties of the copolymer are suitable for the fabrication of plasticizer-free ion-selective membrane electrodes. We demonstrate that covalently attached IL moieties provide adequate functionality to the ion selective membrane thus achieving a very simple, one component sensing membrane. We also demonstrate the presence of iodide as the counter-ion in the triazole moiety has direct influence on membrane's functionality. Potentiometric experiments revealed that each electrode displays high selectivity towards iodide anions over a number of inorganic anions. Moreover the inherent presence of the iodide in the membrane reduces the need for conditioning. The non-conditioned electrodes show strikingly similar response characteristics compared to the conditioned ones. The electrodes exhibited a near Nernstian behavior with a slope of -56.1 mV per decade across large concentration range with lower detection limits found at approximately 6.3×10^{-8} M or 8 ppb . These all-solid state sensors were utilized for the selective potentiometric determination of iodide ions in artificial urine samples in the nanomolar concentration range.

Potentiometric chemical sensors, with primary responses based on extraction and molecular recognition processes are a well-studied and understood class of sensing devices.¹ Ion selective electrodes (ISEs) have been already widely used in a variety of fields such as clinical analysis,² process control³ and environmental monitoring.⁴ Ion selective membranes are typically composed of plasticized polymers, ion exchange salts, and one or more ionophores. Each constituent plays a specific role in the proper functioning of these membrane based ISEs.⁵ Spontaneous and non-specific extraction of analyte ions from the sample into the membrane bulk is primarily suppressed due to the highly hydrophobic nature of the polymer backbone. Ideally, polymer matrix should provide a homogenous medium in which all active components can move freely. This strongly resembles the composition of liquid membrane electrodes since their sensing components were simply dissolved in an organic medium. However, the performance of polymer-based membranes can be drastically reduced if such sensors are used for the measurements of ions within more lipophilic environments in biological samples including undiluted whole blood. The cross contamination of chemical sensors coupled with leaching of the sensing components from the ion selective membrane into the sample fundamentally limited the applications of ISEs as a robust analytical tool for long-term trace level analysis.⁶

Over the years, a number of approaches have been developed to minimize the extent to which the active components diffuse out of the membrane bulk and therefore to improve the response characteristics of ISEs. The most logical step involved chemical modifications of sensing components including addition of long alkyl chains to parent molecules in order to increase their overall lipophilicity.⁷ However, changes in the solubility of the functionalized species may result in their macroscopic phase separation from the polymeric matrix. One promising approach that increases the stability of a homogenous sensing layer is the covalent attachment of the sensing components to the polymer backbone.

In recent years, the use of ISEs based on plasticizer-free membrane has been studied and the response characteristics of such membranes were evaluated in terms of their selectivity towards various cations and anions. Methacrylic-acrylic copolymers synthesized via free radical polymerization are particularly attractive candidates as their physical and mechanical properties finely tuned by simply choosing either different combinations of monomers, or polymerization routes, or both.^{8,9} Bakker's group reported that sensing membranes composed of self-plasticized methyl methacrylate and decyl methacrylate (MMA- DMA) copolymer are viable for the detection of Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} ions.^{10,11} Our research group has demonstrated recently that methacrylate based membranes are also excellent candidates for the trace-level analysis of carbonate ions.¹²

Furthermore, the covalent attachment of ionophore was recognized as a viable strategy to develop ion se-

lective membranes with significantly improved lower limits of detection.¹³ It has been shown that such modifications reduce the zero current transmembrane ion fluxes producing ISEs with nanomolar detection limits. Recently, several attempts were undertaken to attach cation and anion exchangers to the polymeric matrix of the sensing material. Reinhoudt already attached tetraphenylborate (TPB^-) anion to the polysiloxane membrane¹⁴; however an unsubstituted TPB^- anion can undergo irreversible decomposition in the presence of acids, oxidants and light.^{15,16} Qin and Bakker successfully polymerized a C-derivative of the closo-dodecacarborane anion with MMA-DMA monomers to produce a plasticizer-free membrane with cation-exchange properties and significantly reduced rate of leaching of ionic sites.¹⁷ Kimura reported on the covalent immobilization of anionic lipophilic salts (tetradecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride) into sol-gel based membranes.¹⁸

Other attempts to improve the robustness and sensing properties of ISEs were aimed towards finding appropriate replacement to the conventional plasticizers such as dioctyl sebacate (DOS) or 2-nitrophenyl octyl ether (NPOE) since the nature of the plasticizer plays a pivotal role in the analytical performance of polymer based sensors.¹⁹ Here, the authors have used polymeric plasticizer (polyester sebacate (PES) to be more precise) and demonstrated that polymeric nature of the plasticizer increases retention of membrane components thus resulting in robust membranes exhibiting significantly longer life-times relative to traditional ones. Recently, room temperature ionic liquids (RTILs) have been proposed as alternative materials to these traditionally used sensing components. RTILs are attractive due to their versatile and tunable physicochemical properties.^{20,21} These molten salts are composed of two asymmetrical ions (usually large organic cation and a charge delocalized anion) that exist in liquid state at ambient temperature.²² The ability of ILs to undergo almost unlimited structural variations,²³ opens up exciting new pathways for their utilization in sensing. For example modification of cationic part might allow modification of lipophilicity thus changing the polarity of the ionic liquid. This simple modification has for example led to the description of a very simple, polymer membrane based reference electrode.²⁴ It could be envisioned that other structural modification can lead to modification of physical and chemical properties of ILs thus altering and optimizing their performance for many application-specific requirements. Over the last few years, ionic liquids have been used as the ion exchange salts and plasticizers²⁵ for the preparation of ISEs and these studies demonstrate the increasing potential of RTILs to be used as sensing materials.

A very important direction of research in our group is development of simple yet robust sensors for use by non-specialists for *in situ* applications. Routine monitoring of urinary iodide (UI) is an excellent example where iodide-selective electrode can make the most significant impact. Dietary iodine insufficiency significantly impairs psycho-physiological growth and metabolism and can

result in iodine deficiency disorders (IDD) such as hypothyroidism, goitre, cretinism, mental retardation etc. Measuring UI in a representative cohort of individuals from a specific population provides a useful index of the iodine level endemic to that region.²⁶

Here we try to create a hybrid material that allows development of sensing membrane that does not need sophisticated optimization protocols. We describe a new polymerizable triazole based ionic liquid derivative that has been covalently attached to a hydrophobic self-plasticized polymer backbone for practical use in ion selective electrodes that do not require conditioning. In this study we report on the first plasticizer-free ion selective membrane based on copolymerized triazole-based ionic liquid for the detection of iodide ions. In this system copolymerized triazole moiety is the cationic part and the iodide serves as its counterion in the proposed polyionic liquid (polyIL). The response mechanism of this system can be understood in analogy to plasticizer-free polymer membrane-based ISEs based on charged ionophores where triazole moiety serves as charged ionophore to iodide.

EXPERIMENTAL

Materials

Methacryloyl chloride, 2,2'-azobis(2-methylpropionitrile) (AIBN), lauryl methacrylate (LMA), propargyl alcohol, 1-bromobutane, bis(2-ethylhexyl)sebacate (DOS), sodium ascorbate, tridodecylmethylammonium iodide (TDMAI) and poly(3-octylthiophene) (POT) were purchased from Sigma-Aldrich. Poly(vinyl chloride) (PVC), tridodecylmethylammonium chloride (TDMACl) and tetrahydrofuran (THF) were obtained from Fluka. Triethylamine was distilled from calcium hydroxide immediately prior to use and AIBN was recrystallized from cold methanol. All other reagents were of the highest commercially available purity and were used as received. Solutions of metal ions were prepared in ultra-pure water obtained from a Pico Pure 3 water system. Working solutions of different activities were prepared by serial dilutions of a 1 M stock solution. DropSens Dual Carbon Screen-printed Electrodes (C1110) were purchased from Metrohm, USA. Gel permeation chromatography (GPC) was performed on a system composed of a PerkinElmer Series 200 LC Pump, two Polargel-M 300 \times 7.5 mm columns connected in series, a Varian 356- LC refractive index (RI) detector and an Eldex CH-150 column heater. The measurements were made using THF as the eluent at a flow rate of 1.0 ml/min at 40°C. Linear PEG standards were used for molecular weight calibrations. All the compounds and polymers have been synthesized according to previously published procedures. Their purity was confirmed by comparing the ¹³C-NMR spectra to data published in the literature. Experimental details are described in the supplemental information.

Preparation of iodide-selective electrodes

For potentiometric measurements a solution of POT (10⁻³M of monomer in chloroform) was drop cast onto the top of screen-printed electrodes and left at room tempera-

ture to dry. Note that POT routinely serves in polymer membrane-based ISEs. Its role as ion-to-electron conductor and a lipophilic inner membrane layer capable of preventing formation of water layer between the membrane and solid electrode is well described in the literature.²⁷ Iodide selective electrodes were prepared by dissolving 100 mg of IL based copolymer (polyIL) in THF (0.5 ml). After its complete dissolution an aliquot (~20 mL) was drop cast onto the top of the solid contact electrodes (SCEs) and left at room temperature to dry overnight. If not otherwise stated, the electrodes were placed directly in the solution used for the potentiometric measurements without any conditioning.

Preparation of artificial urine

Artificial urine (AU) sample was prepared as proposed by Brooks with some modifications.²⁸ Supplementary Table 1 demonstrates molarities of each salt used for the preparation of AU. The appropriate amounts of NH₃ were added from a 30% ammonium hydroxide stock solution. All other salts were recrystallized, oven dried overnight at 100°C and added as solids. The salts were dissolved in one litre of ultra pure water and the pH of AU solution was adjusted to 4 with 1 M sulphuric acid.

Potentiometric measurements

Potentiometric responses of all electrodes were recorded using Lawson Labs Inc. 16-channel EMF-16 interface (3217 Phoenixville Pike Malvern, PA 19355, USA) in a stirred solution against a double-junction Ag/AgCl reference electrode with a 1 M LiOAc bridge electrolyte (Fluka). Non-conditioned ISEs were immersed in sample solution (ultra-pure water or artificial urine as indicated) followed by addition of aliquots of known concentration of KI. The pH of the solution was monitored using a glass VWR symphony 14002-780 Ag/AgCl pH electrode.

Selectivity measurements

Iodide selective electrodes were prepared and applied onto the electrodes according to the protocol described in 'Preparation of iodide-selective membranes'. Each electrode was left at room temperature to dry overnight. The following day, the iodide selective membranes were conditioned in the 0.1 M CaCl₂ solution and responses towards all ions were recorded according to separate solution method as described by Bakker.²⁹

RESULTS AND DISCUSSION

Response characteristics

1,2,3-triazole based compounds have been recently recognized as weakly coordinating metal ion ligands for sensing of biologically relevant molecules.³⁰ Therefore, these compounds have promising application prospects as sensing moieties for the fabrication of ISEs. Their ionic liquid derivatives are particularly attractive due to their chemical versatility and the ability to fine-tune their properties via salt methathesis.³¹ With the goal of finding a good candidate for selective iodide sensing, our research group examined the possibility of using 2-[[1-(butyl)-1H-1,2,3-triazole-4-yl]methoxy]ethyl 2-methy-

lacrylate (LMA) poly ionic liquids with iodide serving as a counter ion (Figure 1). Covalent attachment of the positively charged motifs to the polymer backbone prevents their diffusion into the sample and ensures that only the negatively charged ions can be exchanged between the sample and the sensing layer.

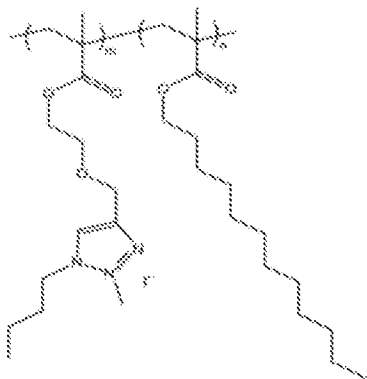


Figure 1. Structure formula of the di-block copolymer.

Most of the membranes under study exhibited good signal stability and near-Nernstian response (-56.1 ± 2.1 mV/decade) towards iodide ions within the concentration range spanning from $10^{-7.2}$ to 10^{-3} M as illustrated in Figure 2.

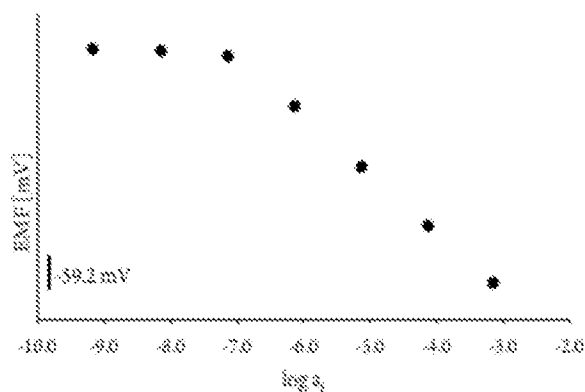


Figure 2. Response curve of I^- selective electrode made of copolymerized 1,2,3-triazole moieties and immersed directly into sample solution (conditioning step omitted).

Interestingly, the same potentiometric behavior was observed for membranes conditioned in the solution of primary ions (10^{-5} M) prior to the experiment, as well as for membranes that were immediately immersed in the sample solution. On each occasion, both lower detection limits (LDLs) and selectivity of either conditioned or non-conditioned ion selective membranes remained the same. In fact, under the same experimental conditions the responses on both conditioned and non-conditioned electrodes almost perfectly overlap each other. Such phenomenon could be attributed to the iodide-containing chemical structure of the polymer used to produce the sensing layer. Since each sensing membrane is already

"preloaded" with the anion of interest, it can be hypothesized that local equilibrium is reached as soon as the casting solvent evaporates.

These findings have remarkable implications for the development of new class of ion selective sensors where the need for long, complex and repeated conditioning is a significant burden, for example, in single-use disposable sensors for field biological and environmental applications. One could easily imagine development of sensors based on copolymerized ionic liquids where the counter ion is the charged species of interest.

However, this idea comes with a caveat; the copolymerized cation component of ionic liquid (in this case triazole moiety) may exhibit certain selectivity to counterions. For example, groups of Flood³² and Bachas³³ have utilized triazole-based ligands for halide sensing. The good indication that triazole moiety exhibits some selectivity to iodide is presented in the Figure 3. We prepared triazole-based copolymer containing NO_3^- as counter ion (Supporting Information) and recorded its response to iodide relative to iodide-containing copolymer. The nitrate-containing copolymer exhibited strong super-Nernstian response indicating the exchange of nitrate to iodide ions. Observation of the super-Nernstian response indicates strong membrane uptake of iodide ions most likely because of stronger preference of triazole moiety to iodide versus nitrate. Uptake of iodide ions creates inward ion fluxes resulting in super-Nernstian response as reported in the literature.^{34,35} Is it clear that the future development of these conditioning-free polyIL-based membranes must include the determination of the counter ion selectivity sequence.

Interestingly, Wardak has also observed super-Nernstian response slopes in the cases when free, not covalently attached ionic liquids (phosphonium- and imidazolium-based) are clearly utilized as non-specific ion exchanger.^{36,37} The origin of this super-Nernstian response is not clear and more work is needed in order to shed light on exact function of ILs in polymer membrane based ion-selective electrodes.

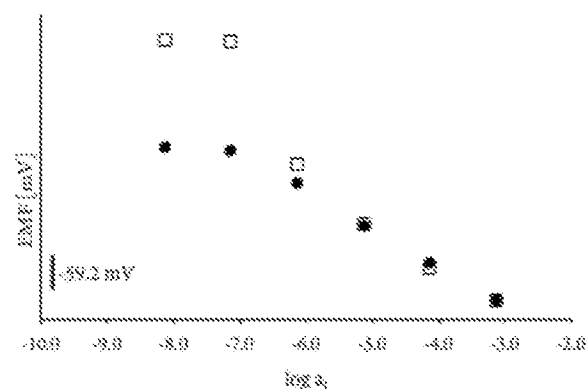


Figure 3. Closed circles: potentiometric response of I^- selective electrode made of copolymerized 1,2,3-triazole moieties and immersed directly into sample solution (conditioning step omitted). Open squares: the same copolymer containing NO_3^- as counter ion.

To further confirm the functionality of the synthesized copolymer and whether it functions as the ionophore in sensing membranes, 2 wt% of the polyIL, along with 1% TDMACl, were added to 33% PVC and 66% DOS and dissolved in minimum amount of THF. The cocktail mixture was applied according to the previously described method and the resulting membrane was used directly for the determination of iodide. Since only a small quantity of the polyIL was introduced into the membrane bulk, the addition of lipophilic salts appeared to be essential to provide the ion-exchanging properties to this membrane. On each occasion, the polyIL-based electrodes were run alongside classical iodide-selective electrodes based on [9]mercuracarborand-3 (MC-3). Both electrodes exhibited near-Nernstian behavior to iodide ions over similar concentration range as illustrated in Figure 4. MC-3 ionophore was selected in this study as it has been previously recognized as an excellent halide ion chelator.³⁸ Its impressive LOD for iodide (2×10^{-9} M or 0.25 ppb) have been achieved under optimal experimental conditions.³⁹ However, strong interference from hydroxide and some halide ions renders MC3-based ISEs unsuitable for the analysis of iodide in biological samples especially when no sample pre-treatment is desired. The herein developed sensing membrane based on polyIL displayed almost identical behavior to MC-3 based membranes even when introduced as ionophore in a traditional membrane matrix. Importantly, such sensing films required no sample optimization and could be used without any conditioning.

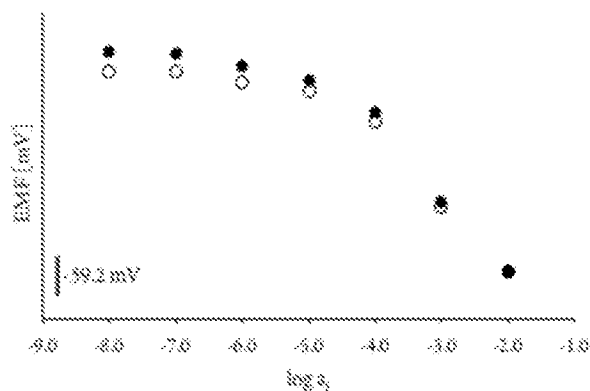


Figure 4. Response characteristics of iodide selective electrodes containing MC3 as ionophore (open circles; slope = -59.7 mV/decade), and using our newly synthesized compound (closed circles). In the case of the latter the slope was -56.1 mV/decade with $R^2 = 0.99$.

Slight differences between MC3- and polyIL-based membranes as well as the difference between this and optimal responses are indeed observed. The increase in LOD in MC3-based membrane relative to the optimal can be attributed to the elevated pH of the sample. In an attempt to mimic pH of human urine with the view of potential application of the sensor in the determination of iodide in urine (please see the discussion in the section Selectivity) we have determined the responses in sample

of pH = 6 even though the optimal response is expected at $\text{pH} \leq 3$.³⁹ On the other hand, the non-optimal response of polyIL-based membrane could be attributed to the non-optimal ionophore-ionic sites ratio. Optimization is likely possible but exceeds the scope of this paper and thus it has not been done here. Nevertheless, these experiments further demonstrate that the polyIL exhibits ion-sensing properties and constitutes an attractive alternative for development of highly sensitive and selective iodide sensors even when introduced into other more traditional polymeric matrices.

Selectivity

Selectivity is an extremely important characteristic of a chemical sensor. It quantifies the preference for the chosen analyte over the other potentially interfering ions and therefore defines the practical functionality of ISEs for sensing purposes. In this research study we focused on interfering ions that have the most significant presence in urine i.e. nitrate, sulfate, bromide, and chloride with the latter being the most important. The concentration of chloride in urine is strongly influenced by the dietary intake. Urinary chloride in a healthy individual can span from 10 to 25 mmol/L.⁴⁰ This indicates that the proposed sensor should exhibit sufficient selectivity to discriminate against Cl^- ions. Figure 5 and Table 1 show the responses of polyIL-based membrane to studied ions, and their response slopes and selectivity coefficients respectively.

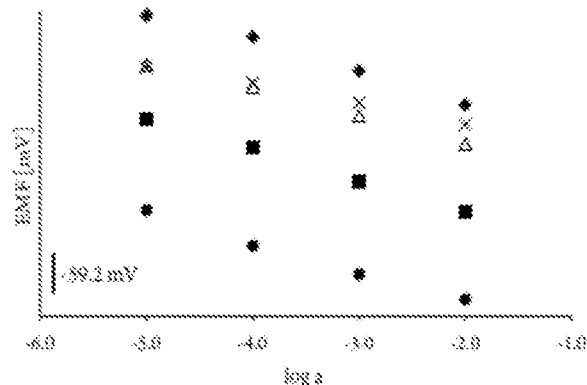


Figure 5. Potentiometric response of ionic liquid based ion selective electrodes for various anions: I^- (circles), NO_3^- (open triangles), Cl^- (diamonds), SO_4^{2-} (crosses) and Br^- (squares).

Table 1. Selectivity coefficients and experimental slopes for the copolymer based ISEs (I^- slope = -57.3 ± 0.1 mV).

Anion	Cl^-	Br^-	NO_3^-	SO_4^{2-}
$\log K^{\text{POT}}$	-4.5 ± 0.2	-2.3 ± 0.1	-3.6 ± 0.1	-5.2 ± 0.1
Slope [mV]	-53.8 ± 1.3	-55.1 ± 1.7	-48.2 ± 2.7	-29.8 ± 2.0

It is noteworthy that this electrode exhibited higher selectivity for I^- over Cl^- than any previously reported ionophore based iodide selective electrodes.^{41,42} To further explore the functionality of our polyIL we have determined selectivity coefficients of simple ion-exchange membrane based on TDMAI (results shown in Supplemental Info). Drastically smaller selectivity coefficients of TDMAI-based membranes compared to polyIL-based further indicate specificity of triazole moiety to iodide. It is also important to point out that response slopes for all interfering ions are near-Nernstian indicating the preference of the triazole-based moiety for iodide. None of the studied ions can displace iodide as the counterion to triazole-based cation. As a consequence, no outward fluxes of iodide are created thus enabling observation of near-Nernstian slopes for all ions and calculations of unbiased selectivity coefficients despite the fact that primary ion is present in the membrane prior to the their determination. This is a very important finding in terms of the robustness and practical application of polyIL-based electrodes. The presence of primary ions in the membrane does not affect the membrane performance and more importantly it significantly reduces the need for membrane preparation and optimization.

Robustness

Despite recent improvements in the sensing field producing wide range of chemical sensors that featuring selectivity and sensitivity towards many analytes of interest, their relatively poor robustness often limited practical real-life applications. For example, membrane life-time is considered important factor that defines sensor's robustness. It is relatively well understood that the lifetime of ISEs can be considered as a function of chemical stability and lipophilicity of components that are used to prepare ion selective membranes. In order to fulfill the electroneutrality requirement within the membrane, the loss of ionophore must be accompanied either by co-extraction (opposite charged species diffuse into the sample) or ion exchange (transfer of ions of the same charge into the membrane).⁴³ In this study, a plasticizer free copolymer with covalently attached ionophore was synthesized to prevent mass diffusion of such species and also to fully eliminate plasticizer exudation and therefore improve overall durability of iodide selective electrodes. Potentiometric responses of iodide selective ISEs were recorded over a period of two weeks to assess their practicality as applied chemical sensors. Each electrode was prepared on the same day using only freshly made cocktails. In addition, each electrode was only used once (during initial measurement) and then stored in the distilled water and re-used. Since, it was demonstrated that the presence of iodide ions within the membrane is sufficient enough to establish thermodynamic equilibrium, no sample pre-treatment (conditioning) was carried out. Note that the full possible response range was not recorded for these electrodes. Rather, our focus was placed on the smaller response range in order to monitor the reproducibility and robustness. The table 2 contains

the response characteristics (slope and response range) of at least four randomly selected electrodes from the larger dataset. Near-Nernstian behavior at the measured response range was observed in all cases (see Table 2). Note that no worsening of potentiometric response of freshly prepared ISEs and those stored in the distilled water for either a week or two weeks were observed. The same observations were made with the regards to their signal stability as even after two weeks of storage, no significant signal drift was measured. Retention of the slope, signal stability and measured detection limits especially in the cases of used ISEs that were stored for extensive period of time is an extremely important finding in terms of practical, *in field* application.

Table 2. Response range and slopes of selected ISEs.

Electrode Category	Fresh	1 week	2 weeks old
Measured range	$10^{-5} - 10^{-2} M$		
Slope	-53.3 ± 0.5	-50.0 ± 1.7	-58.9 ± 1.3

Determination of iodide in artificial and real urine

To further assess the utility of polyIL-based ISEs, such sensors were used to determine the activity of iodide ions in the solution of artificial urine. Note that the composition of human urine is strongly influenced by the diet, activity and overall health of an individual. Therefore, numerous ways to prepare artificial urine sample were proposed in the literature. In this study, the composition of AU was selected to resemble physiological human urine as mentioned in the experimental section. During the measurements, tested electrodes exhibited near-Nernstian behavior (63.2 mv per decade) over a large concentration range with lower detection limits found at $10^{-6.5} M$ (see Figure 6A). It is apparent that high concentration of background (interfering) ions lead to slightly increased lower detection limit compared to the one observed under no interference conditions (see Figure 2). Nevertheless, typical urinary iodide concentrations range from 0.3 μM to 6.0 μM ($10^{-6.5} M - 10^{-5.2} M$).⁴⁴ Note that proposed values of average urinary iodine levels as a guide for a region's IDD status are: $<10^{-6.8} M$ (severe); $10^{-6.8} M - 10^{-6.4} M$ (moderate); $10^{-6.4} M - 10^{-6.1} M$ (mild) and $>10^{-6.1} M$ (normal).⁴⁵ This demonstrates that the proposed sensor could be potentially applied for the quantification of iodide in human urine and therefore it could be used as an indicative test for iodide related disorders.

Encouraged by the promising results obtained using artificial urine, we have attempted the measurement of iodide in real urine. Figure 6B depicts the response of non-

conditioned polIL-based electrode obtained in a real urine sample. Iodide level in this sample was estimated as 3.16×10^{-6} M (0.40 ppm). This result was evaluated using ICPMS (experimental details given in Supplemental Info) and the iodide level of 1.35×10^{-6} M (0.17 ppm) was determined. The results obtained with the two techniques agree reasonably well which is very encouraging for further application of polyIL-based iodide selective electrodes in real-life urine samples.

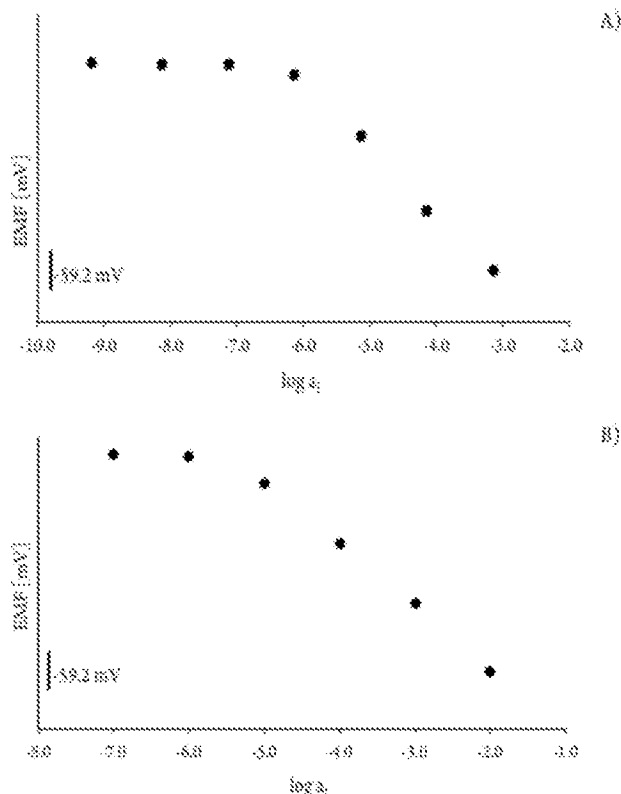


Figure 6. Potentiometric responses of the self-plasticized copolymer based ion selective membranes for the determination of iodide in artificial urine (A) and in real urine samples (B). Note that none of the electrodes were conditioned in the solution of primary ions prior to the experiment.

CONCLUSIONS

This work describes, a new simple sensor that can be used for the immediate determination of iodide ions without any sample pre-treatment. The proposed ionic liquid based self-plasticized copolymer shows high affinity for iodide ions which act as counter-ions to the triazole cationic moiety. The inherent presence of the iodide enabled demonstration of simple, one-component ISEs with high selectivity to iodide. The selectivity was sufficient for detection of iodide in biologically relevant samples. Moreover, the presence of iodide in the membrane also eliminated the need for conditioning. The non-conditioned ISEs showed excellent robustness and durability when stored for two weeks. Therefore, this study demonstrates an excellent potential of self-plasticized

copolymers as sensing materials for the development of ISEs that can be directly used for *in situ* detection of biologically relevant ions without the need for sophisticated conditioning protocols.

ASSOCIATED CONTENT

Supporting Information

Further experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*a.radu@keele.ac.uk; *SGranadosFocil@clarku.edu

Present Addresses

*Lennard-Jones Laboratories, Birchall Centre, Keele University, Keele, Staffordshire ST5 5BG, United Kingdom.

Author Contributions

All The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work has been generously supported by Royal Society (RG120118) and Marie Curie IRSES Grant (IBS Network; R6810 B475). LM gratefully acknowledges support from Keele University.

REFERENCES

- (1) Bakker, E.; Bühlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, 97 (8), 3083–3132.
- (2) Lewenstam, A.; Maj-Zurawska, M.; Hulanicki, A. *Electroanalysis* **1991**, 3 (8), 727–734.
- (3) Rocha, R. A.; Rojas, D.; Clemente, M. J.; Ruiz, A.; Devesa, V.; Vélez, D. *J. Agric. Food Chem.* **2013**, 61 (45), 10708–10713.
- (4) McGraw, C. M.; Radu, T.; Radu, A.; Diamond, D. *Electroanalysis* **2008**, 20 (3), 340–346.
- (5) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, 98 (4), 1593–1688.
- (6) Telting-Diaz, M.; Bakker, E. *Anal. Chem.* **2001**, 73 (22), 5582–5589.
- (7) Gehrig, P.; Rusterholz, B.; Simon, W. *Anal. Chim. Acta* **1990**, 233, 295–298.
- (8) Heng, L. Y.; Hall, E. A. H. *Anal. Chim. Acta* **2000**, 403 (1–2), 77–89.
- (9) Heng, L. Y.; Toth, K.; Hall, E. A. H. *Talanta* **2004**, 63 (1), 73–87.
- (10) Qin, Y.; Peper, S.; Radu, A.; Ceresa, A.; Bakker, E. *Anal. Chem.* **2003**, 75 (13), 3038–3045.
- (11) Qin, Y.; Peper, S.; Bakker, E. *Electroanalysis* **2002**, 14 (19–20), 1375–1381.
- (12) Mendecki, L.; Fayose, T.; Stockmal, K. A.; Wei, J.; Granados-Focil, S.; McGraw, C. M.; Radu, A. *Anal. Chem.* **2015**, 87 (15), 7515–7518.

- (13) Püntener, M.; Fibbioli, M.; Bakker, E.; Pretsch, E. *Electroanalysis* **2002**, *14* (19-20), 1329–1338.
- (14) Reinhoudt, D. N.; Engbersen, J. F. J.; Brzozka, Z.; van der Vlekkert, H. H.; Honig, G. W. N.; Holterman, H. A. J.; Verkerk, U. H. *Anal. Chem.* **1994**, *66* (21), 3618–3623.
- (15) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57* (9), 2600–2604.
- (16) Rosatzin, T.; Bakker, E.; Suzuki, K.; Simon, W. *Anal. Chim. Acta* **1993**, *280* (2), 197–208.
- (17) Qin, Y.; Bakker, E. *Anal. Chem.* **2003**, *75* (21), 6002–6010.
- (18) Kimura, K.; Sunagawa, T.; Yajima, S.; Miyake, S.; Yokoyama, M. *Anal. Chem.* **1998**, *70* (20), 4309–4313.
- (19) Zahran, E. M.; New, A.; Gavalas, V.; Bachas, L. G. *The Analyst* **2014**, *139* (4), 757–763.
- (20) Safavi, A.; Maleki, N.; Honarasa, F.; Tajabadi, F.; Sedaghatpour, F. *Electroanalysis* **2007**, *19* (5), 582–586.
- (21) Coll, C.; Labrador, R. H.; Mañez, R. M.; Soto, J.; Sancenón, F.; Seguí, M.-J.; Sanchez, E. *Chem. Commun.* **2005**, No. 24, 3033.
- (22) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8* (8), 621–629.
- (23) Ahrens, S.; Peritz, A.; Strassner, T. *Angew. Chem. Int. Ed.* **2009**, *48* (42), 7908–7910.
- (24) Cicmil, D.; Anastasova, S.; Kavanagh, A.; Diamond, D.; Mattinen, U.; Bobacka, J.; Lewenstam, A.; Radu, A. *Electroanalysis* **2011**, *23* (8), 1881–1890.
- (25) Shvedene, N. V.; Chernyshov, D. V.; Khrenova, M. G.; Formanovsky, A. A.; Baulin, V. E.; Pletnev, I. V. *Electroanalysis* **2006**, *18* (13-14), 1416–1421.
- (26) Dunn, J. T. *J. Clin. Endocrinol. Metab.* **1998**, *83* (10), 3398–3400.
- (27) Veder, J.-P.; De Marco, R.; Clarke, G.; Chester, R.; Nelson, A.; Prince, K.; Pretsch, E.; Bakker, E. *Anal. Chem.* **2008**, *80* (17), 6731–6740.
- (28) Brooks, T.; Keevil, C. W. *Lett. Appl. Microbiol.* **1997**, *24* (3), 203–206.
- (29) Bakker, E. *Anal. Chem.* **1997**, *69* (6), 1061–1069.
- (30) Struthers, H.; Spingler, B.; Mindt, T. L.; Schibli, R. *Chem. - Eur. J.* **2008**, *14* (20), 6173–6183.
- (31) *Arkivoc* **2009**, 2009 (12), 193.
- (32) Hua, Y.; Flood, A. H. *Chem. Soc. Rev.* **2010**, *39* (4), 1262.
- (33) Zahran, E. M.; Hua, Y.; Li, Y.; Flood, A. H.; Bachas, L. G. *Anal. Chem.* **2010**, *82* (1), 368–375.
- (34) Sokalski, T.; Zwickl, T.; Bakker, E.; Pretsch, E. *Anal. Chem.* **1999**, *71* (6), 1204–1209.
- (35) Ceresa, A.; Bakker, E.; Hattendorf, B.; Günther, D.; Pretsch, E. *Anal. Chem.* **2001**, *73* (2), 343–351.
- (36) Wardak, C. *Electroanalysis* **2014**, *26* (4), 864–872.
- (37) Wardak, C. *Sens. Actuators B Chem.* **2015**, *209*, 131–137.
- (38) Badr, I. H.; Diaz, M.; Hawthorne, M. F.; Bachas, L. G. *Anal. Chem.* **1999**, *71* (7), 1371–1377.
- (39) Malon, A.; Radu, A.; Qin, W.; Qin, Y.; Ceresa, A.; Maj-Zurawska, M.; Bakker, E.; Pretsch, E. *Anal. Chem.* **2003**, *75* (15), 3865–3871.
- (40) Zhang, W. *Front. Biosci.* **2005**, *10* (1-3), 88.
- (41) Shahrokhian, S.; Taghani, A.; Moattar, F. *Electroanalysis* **2002**, *14* (23), 1621–1628.
- (42) Jalali, F.; Rajabi, M. J.; Bahrami, G.; Shamsipur, M. *Anal. Sci. Int. J. Jpn. Soc. Anal. Chem.* **2005**, *21* (12), 1533–1535.
- (43) Bühlmann, P.; Umezawa, Y.; Rondinini, S.; Vertova, A.; Pigliucci, A.; Bertesago, L. *Anal. Chem.* **2000**, *72* (8), 1843–1852.
- (44) Toh, H. S.; Tschulik, K.; Batchelor-McAuley, C.; Compton, R. G. *The Analyst* **2014**, *139* (16), 3986.
- (45) Abraham, G. E.; Tlechas, J.; Hakala, J. *Orig. Internist* **2004**, *11* (4), 19–32.

Provisional Application for Patent Cover Sheet

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c)

Inventor(s)

Inventor 1

Remove

Given Name

Middle Name

Family Name

City

State

Country ;

Sergio

Granados-Focil

Worcester

MA

US

Inventor 2

Remove

Given Name

Middle Name

Family Name

City

State

Country ;

Aleksandar

Radu

Keele

UK

Inventor 3

Remove

Given Name

Middle Name

Family Name

City

State

Country ;

Lukasz

Mendecki

Keele

UK

All Inventors Must Be Listed – Additional Inventor Information blocks may be generated within this form by selecting the **Add** button.

Add

Title of Invention

ROBUST, AND PLASTICIZER-FREE IODIDE-SELECTIVE SENSOR

Attorney Docket Number (if applicable)

CLK16-01P

Correspondence Address

Direct all correspondence to (select one):

☒ The address corresponding to Customer Number

☐ Firm or Individual Name

Customer Number

58406

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

Yes, the invention was made by an agency of the United States Government. The U.S. Government agency name is:

Yes, the invention was under a contract with an agency of the United States Government. The name of the U.S. Government agency and Government contract number are:

Entity Status

Applicant asserts small entity status under 37 CFR 1.27 or applicant certifies micro entity status under 37 CFR 1.29

- ☒ Applicant asserts small entity status under 37 CFR 1.27
- ☐ Applicant certifies micro entity status under 37 CFR 1.29. Applicant must attach form PTO/SB/15A or B or equivalent.
- ☐ No

Warning

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

Signature

Please see 37 CFR 1.4(d) for the form of the signature.

Signature	Christopher J. Lutz/			Date (YYYY-MM-DD)	2016-04-08
First Name	Christopher J.	Last Name	Lutz	Registration Number (If appropriate)	44883

This collection of information is required by 37 CFR 1.51. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **This form can only be used when in conjunction with EFS-Web. If this form is mailed to the USPTO, it may cause delays in handling the provisional application.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that : (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.