Journal of Inclusion Phenomena and Macrocyclic Chemistry (2020) 98:1–9
https://doi.org/10.1007/s10847-020-01004-y

REVIEW ARTICLE

The use of porphyrins in potentiometric sensors as ionophores

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Received: 18 March 2020 / Accepted: 4 June 2020 / Published online: 27 July 2020

Abstract

Porphyrins are a group of macrocyclic compounds which are widely used in many applications in the literature due to their multiple functions. One of their application areas is in the development of sensors which transform changes in physical and chemical parameters into electrical signals. Novel chemical sensors selective and sensitive for many anions and cations have been fabricated with the advancements in the technology. Real sample applications of these sensors can be successfully performed. In recent years, potentiometric methods have drawn researchers' attention and they have been highly studied because of their superiority over other analytical devices. Ionophores which are used in the development of potentiometric sensors and ion-selective electrodes are the most important components of these systems. Therefore, porphyrin molecules, which have favorable chemical structures, can be directly used as an active component (ionophore) in the structure of potentiometric sensors. In this review, we investigated porphyrin derivatives used as ionophore in the design of potentiometric sensors and we focused on newly developed potentiometric sensors based on porphyrin.

Keywords Porphyrins · Potentiometry · Ionophore · Sensor

Introduction

Porphyrins are important macrocyclic compounds which are composed of four pyrrole rings connected via four methine bridges (–CH=). Research on porphyrins has started with the studies in which the isolation of porphyrins from natural compounds were reported and then continue with studies that showed the synthesis of porphyrins in the laboratory conditions. The synthesis of a porphyrin was firstly carried out by Rothemund in 1935. The reaction schema of the synthesized porphyrin by Rothemund are given Fig. 1 [1]. Until today, many novel porphyrin derivates have been synthesized with the growing number of synthesis methods and derivatization reactions.

In addition to their essential roles in the metabolism of living organisms, porphyrins find a wide range of applications in the design of various sensors due to the fact that they are tetradentate ligands which provide suitable space for metals [2–4]. Furthermore, they are known to have great electrocatalytic activity; because, they contain the conjugated two-dimensional π system and have different electrochemical characteristics [5]. Porphyrins have been also used in many areas such as biology, photophysics, photochemistry, photovoltaics, optics and industry [6]. Additionally, the derivatives of porphyrins have been extensively studied by researchers, since these compounds are commonly used in biological systems and materials chemistry.

Potentiometry is an electrochemical analysis method which involves the measurement of potential in an electrode system composed of reference and indicator electrodes. In this method, while the reference electrode has a constant electrode potential at a given temperature (generally room temperature), the potential of the indicator electrode changes depending on the analyte concentration [7]. Potentiometric ion sensors and ion-selective electrodes (ISEs) measure the

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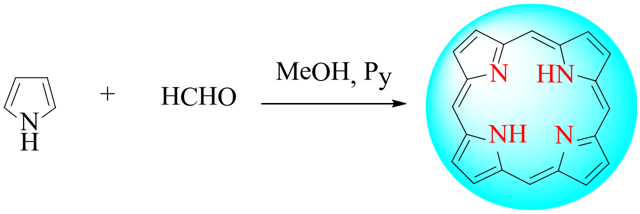


Fig. 1 Porphyrin synthesis schema [1]

potential difference between these two electrodes at the same conditions.

Sensor technology has become an area of interest for many researchers and found itself a wide range of applications. Especially, chemists have developed many sensors by using different methods for the analysis of anions and cations, and successfully performed their applications [8]. A potentiometric sensor was first developed by Cremer in 1906 [9]. Afterwards, these sensors have been used in the analysis of various samples such as environmental, industrial and pharmaceutical samples [10]. Potentiometric ion-selective electrodes or sensors have many important advantages such as the ease of preparation, short response time, high selectivity, wide linear working range, low detection limit, quite high sensitivity and low cost [11–15].

The main component of ion-selective electrodes (ISEs) used in potentiometric analyses is an ionophore that specifically interacts with a target ion (analyte) and it largely determines the ion selectivity of ISEs. Porphyrins offers a wide range of interaction mechanisms for analyte binding including van der Waals forces, hydrogen bonds, π–π interactions, π-cation, and the coordination to the central metal ion [16–18]. Porphyrins have various chemical properties such as rich redox chemistry, delocalized aromatic π-system and synthetic flexibility, which make these molecules favorable structures to be used as ionophores in the design of potentiometric sensors [19].

Porphyrin based chemical sensors have shown significant sensitivity to many different ions. Porphyrins are quite attractive materials to use in such sensors because of their high sensitivity and reversibility [20]. In addition, the high conjugation of porphyrins and distinctive capability towards different anion and cations results in various promising applications, especially in the field of potentiometric sensors. Another feature of porphyrins is that they can be sensitive to different ions through appropriate molecular exchange. Because of all these features, porphyrins are among the most suitable molecular platforms for the design of sensors and they have been widely used as ionophores in potentiometric ISEs.

In this review, we aim to provide an overview of the current progress on the use of porphyrins as ionophores in the design of potentiometric sensors. Considering the favorable chemical structures of porphyrins to be used as ionophores as mentioned above, they improve various performance parameters of potentiometric sensors and thus, lead to the development of superior analytical techniques. Here, we cover current research conducted in this topic and provide numerous examples of applications of these porphyrin-based sensors. In addition, we mention several chemical characteristics of these novel potentiometric sensors to make it possible to compare them to the alternative approaches.

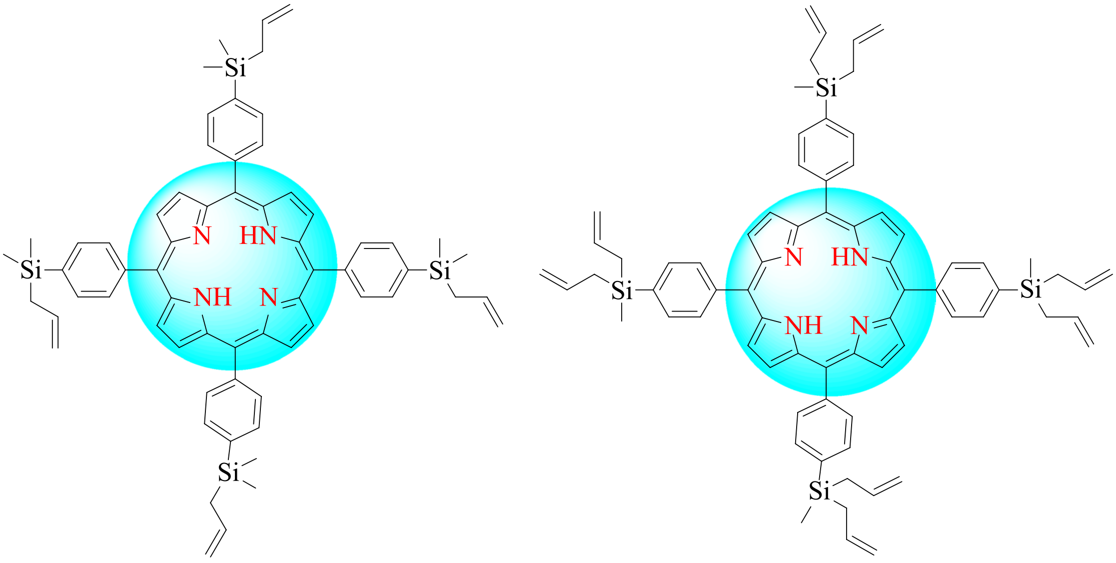
The use of porphyrins as ionophores in the design of potentiometric sensors

Gupta et al. reported the development of a copper-selective sensor using two different porphyrin derivatives (**1**, **2** shown in Fig. 2) as ionophores [21]. They showed a poly(vinyl chloride) PVC membrane structure where porphyrin derivate **2** was used as an ionophore. This copper-selective sensor worked in the linear range of 4.4×10^{-6} to 1.0×10^{-1} mol L^{-1}, it was not effected by the changes in pH between 2.8 and 7.9, and exhibited very fast response time (8 s). In addition, the developed sensor has been applied for the analysis of copper in vegetable leaves and water samples from swimming pools, and results were given in comparison to atomic absorption spectroscopy (AAS).

In another study by Gupta et al., they used 3,7,12,17-tetramethyl-8,13-divinyl 2,18-porphine dipropionic acid **(3)** (Fig. 3) as an ionophore in the structure of the developed sensor. This newly developed sensor was zinc-selective and worked in the linear range of 1.3×10^{-5} to 1.0×10^{-1} mol L^{-1}. This sensor showed a Nernstian behaviour (30 mV/decade) and was not effected by the changes in pH between 3.0 and 7.4. Also, they reported that this sensor has a response time of 10 s and a good stability [22].

Isildak and Özbek have developed all-solid-state contact PVC membrane silver(I)-selective sensor using 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine **(4)** (Fig. 3) as an ionophore [19]. They reported that this sensor worked in the linear concentration range of 1.0×10^{-1} to 1.0×10^{-6} mol L^{-1}. The developed sensor had a fast response time (< 8 s) and it was not affected by the changes in pH across a wide range (4.0–10.0). Additionally, this newly developed sensor was successfully applied to the determination of silver ions in the water samples using the method of standard addition.

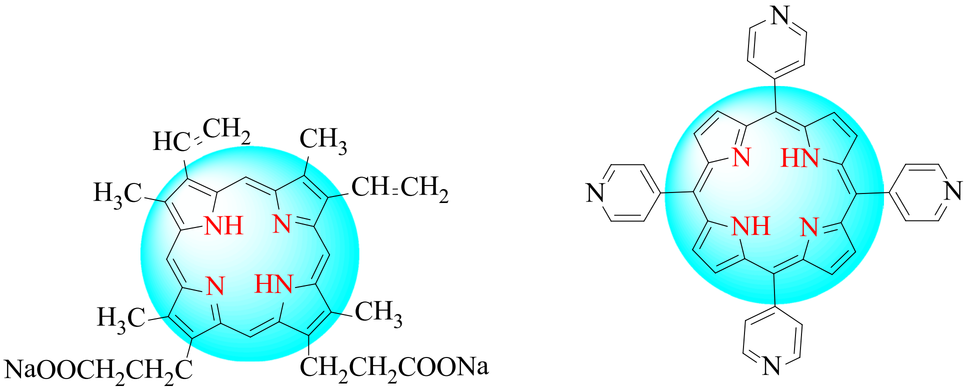
A study on iron(III)-selective potentiometric sensor using a porphyrin derivative (5-(4-arboxyphenyl)-10,15,20-tris(4-phenoxyphenyl)-porphyrin) **(5)** (Fig. 4) was performed by Vlassici et al. [23]. In this study, the developed sensor worked in the linear concentration range of 1.0×10^{-7} to 1.0×10^{-1} mol L^{-1}. This iron(III)-selective sensor which had a response



1 **2**

Fig. 2 Porphyrins **1** and **2** used as ionophores

Fig. 3 Porphyrins **3** and **4** used as ionophores



3 **4**

time of 20 s was successfully used in the determination of iron ions in tap water and lithium-ion batteries. The same group has also developed a copper(II)-selective PVC membrane sensor using another porphyrin derivative molecule (5,10,15,20-tetrakis(4-allyloxyphenyl) porphyrin) **(6)** (Fig. 4) [24]. This sensor had a working range of 1.0×10^{-7} to 1.0×10^{-1} mol L^{-1} and exhibited a close-Nernstian behaviour (28.4 ± 0.4 mV/decade). The authors also stated that this potentiometric sensor had a good selectivity and sensitivity; and a short response time (10 s).

Another study on iron(III)-selective potentiometric sensor has been performed by Fakhari et al. using 5,10,15,20-tetrakis(pentaflourophenyl)-21*H*,23*H*-porphyrin **(7)** (Fig. 4) molecule as an ionophore [25]. The reported sensor had a working range of 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1} and a response time of 10 s.

Farahani and Aghaie used a newly synthesized tetra phenyl porphyrin (TPP) **(8)** (Fig. 4) molecule as an ionophore in the design of iron(II)-selective sensor [26]. In this study, they reported that this newly developed sensor worked in the linear range of 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and had a detection limit of 9.0×10^{-7} mol L^{-1}. Additionally, the developed sensor had a response time of less than 12 s and worked in the pH range of 3.0–5.0. Another work, where TPP **(8)** molecule was used as an ionophore in the structure of a silver(I)-selective sensor, was performed by Ardakani et al. [27]. This sensor worked in a wide concentration range (1.0×10^{-6} to 1.0×10^{-4} mol L^{-1}). This sensor had a response time of less than 10 s and a pH working range of

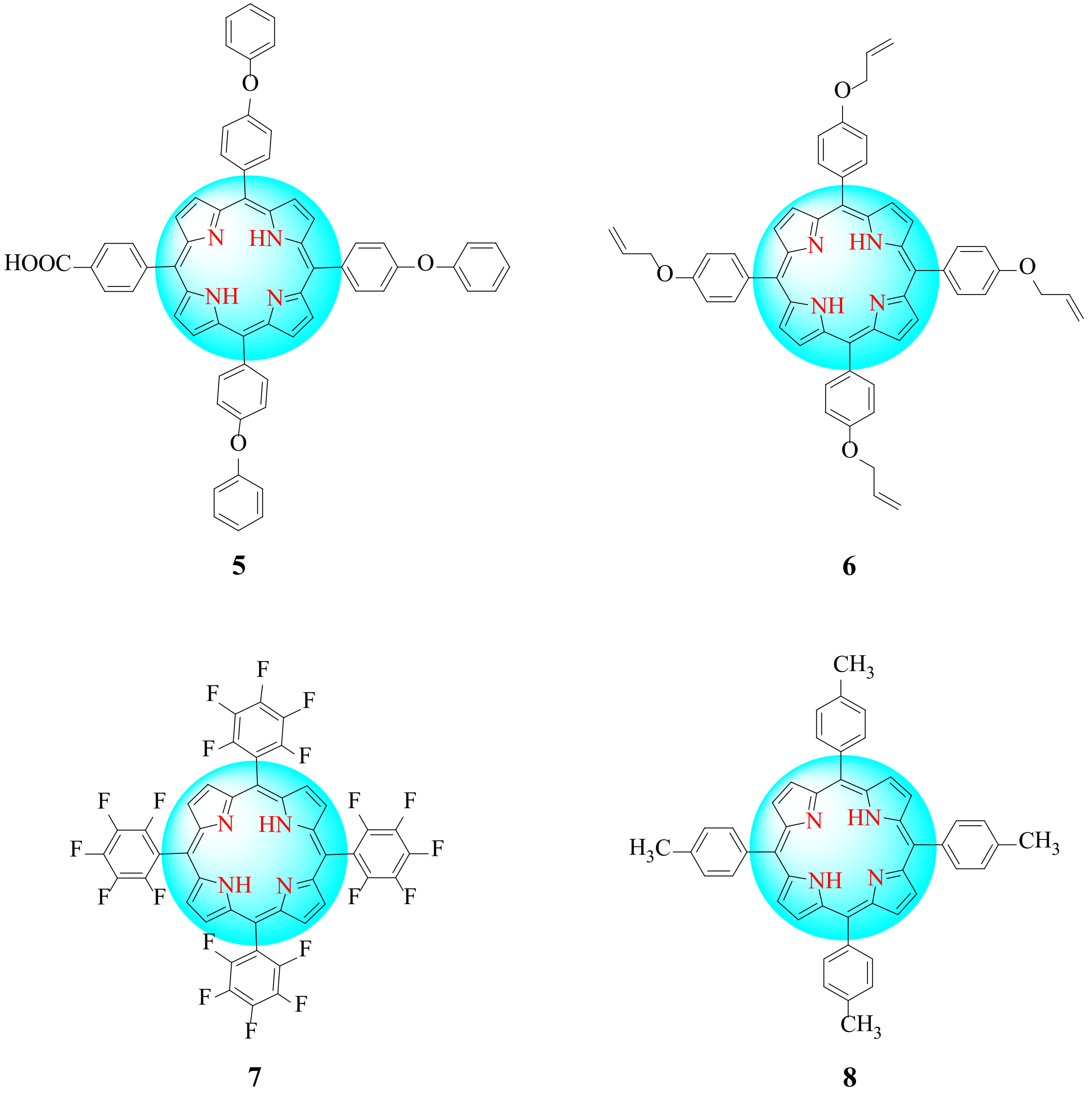
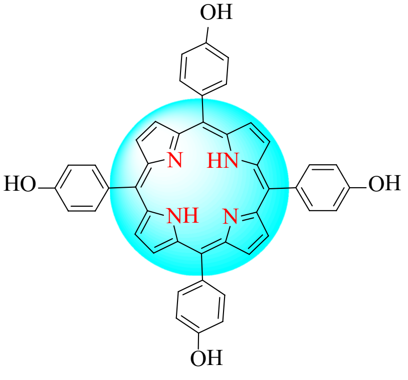


Fig. 4 Porphyrins **5**, **6**, **7** and **8** used as ionophores

3.0–9.0. Also, it was reported that the fabricated sensor had been successfully used in the direct potentiometric determination of silver ions in different real samples.

Rajabi et al. performed the synthesis of 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin **(9)** (Fig. 5) molecule and used it as an ionophore to prepare a copper carbon paste electrode [28]. The fabricated potentiometric electrode had a wide concentration range of 4.0×10^{-9} to 1.0×10^{-1} mol L^{-1} against copper ions and a very low detection limit (2.0×10^{-9} mol L^{-1}). In addition, the reported electrode exhibited a very fast response time of 5 s and was successfully applied to the potentiometric determination of Cu^{2+} ions in water samples.

Anion-selective potentiometric sensors developed with the use of porphyrin derivatives have also been reported in the literature. In a study by Sun et al., the design of an iodide selective potentiometric sensor was reported [29]. This sensor was fabricated by using tetraphenyl porphinetetrasulfonic



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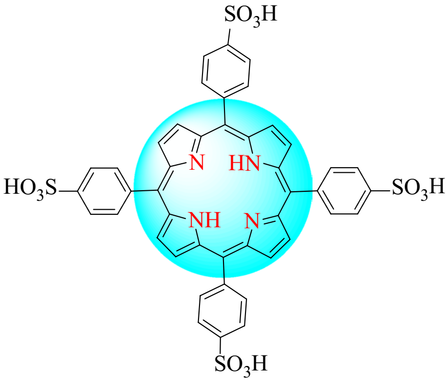

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Fig. 5 Porphyrins **9** and **10** used as ionophores

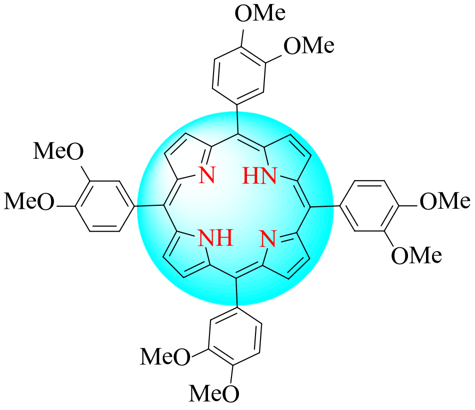
acid **(10)** (Fig. 5). The developed sensor worked in a concentration range of 1.6×10^{-6} to 1.0×10^{-1} mol L^{-1} and exhibited a Nernstian (59.0 mV/decade) behavior. The sensor showed a pH working range of 1.0–7.0.

Vlassici et al. developed lead(II), copper(II), and silver(I) selective sensors by using 5,10,15,20-tetrakis(3,4-dimetoxyphenyl) porphyrin **(11)** and 5,10,15,20-tetrakis (3-hydroxyphenyl) porphyrin **(12)** (Fig. 6) molecules as ionophores in the structure of sensors [30]. The linear working ranges of the developed sensors were between concentration range of 1.6×10^{-6} to 1.0×10^{-1} mol L^{-1} and their pH working ranges were between 5.0 and 10.0. In this study, they reported that these newly developed metal sensors had a lifetime of 4 months, and that successful real sample applications of these sensors were carried out. Additionaly, the data of real sample analyses were compared with the data from AAS. The obtained results showed that the analysis values was compatible with each other.

Another sensor developed by Fakhari et al. was a zinc(II)-selective sensor prepared by using tetra(2-aminophenyl) porphyrin **(13)** (Fig. 7) molecule as an ionophore [31]. This sensor was reported to have a working concentration range of 5.0×10^{-5} to 1.0×10^{-1} mol L^{-1} and pH working range of 3.0–9.0. The response time of the sensor was approximately 10 s. It had a lifetime of 8 months and was successfully used in the determination of zinc ions in different samples including pharmaceutical samples.

Vlassici et al. [32] prepared iodide and bromide ion-selective sensors using Pt(II) 5,10,15,20-tetra(4-methoxy phenyl)-porphyrin **(14)** (Fig. 7) molecule as an ionophore. These novel sensors worked in a concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} and had a low detection limit and a short response time. Furthermore, they reported the use of these anionic sensors in the analysis of drug and other synthetic samples.

Two PVC membrane nickel(II)-selective sensors were developed by Singh and Bhatnagar using 4,4′,4″,4‴-21*H*,23*H*-porphine–5,10,15,20-tetrayl) tetrakis (benzoic acid) (TBAP) **(15)** or 2,3,7,8,12,13,17,18-octamethyl-21*H*,23*H*-porphine (OMP) **(16)** (Fig. 7) molecules as ionophores [33]. The developed sensor by using TBAP had a linear working range of 2.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and the other sensor developed using OMP had a linear working range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}. These



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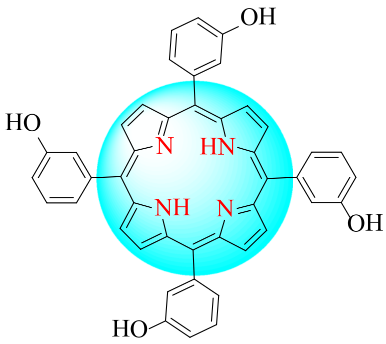

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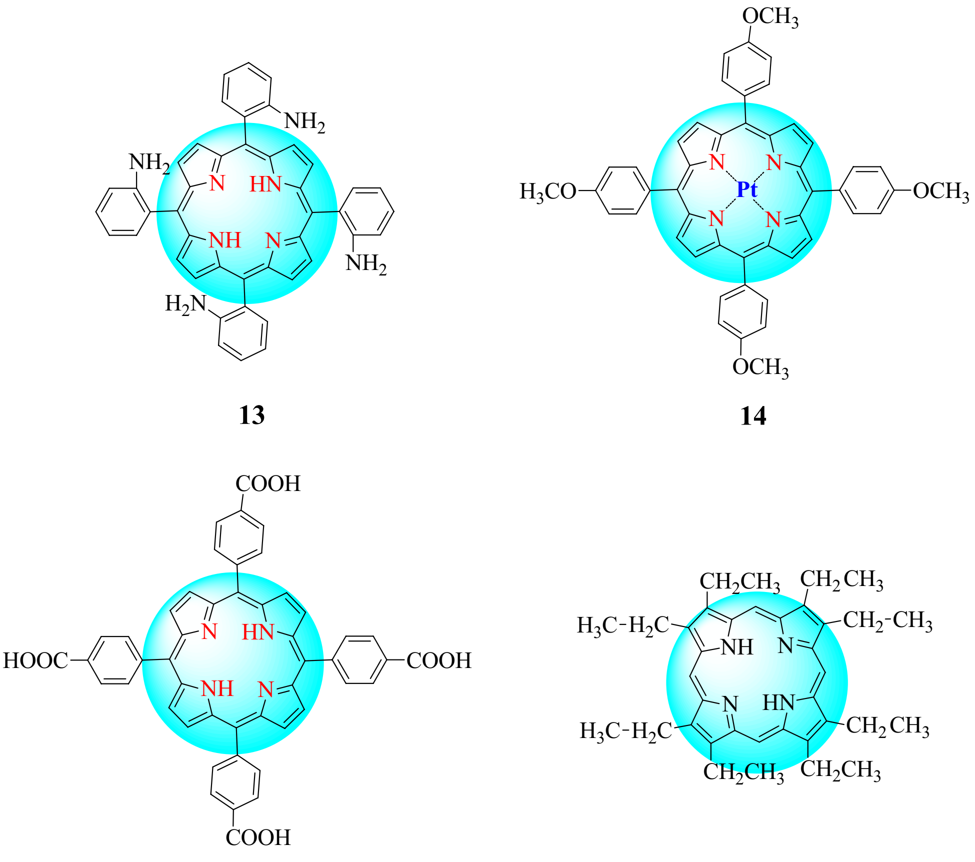
Fig. 6 Porphyrins **11** and **12** used as ionophores

Fig. 7 Porphyrins **13**, **14**, **15** and **16** used as ionophores



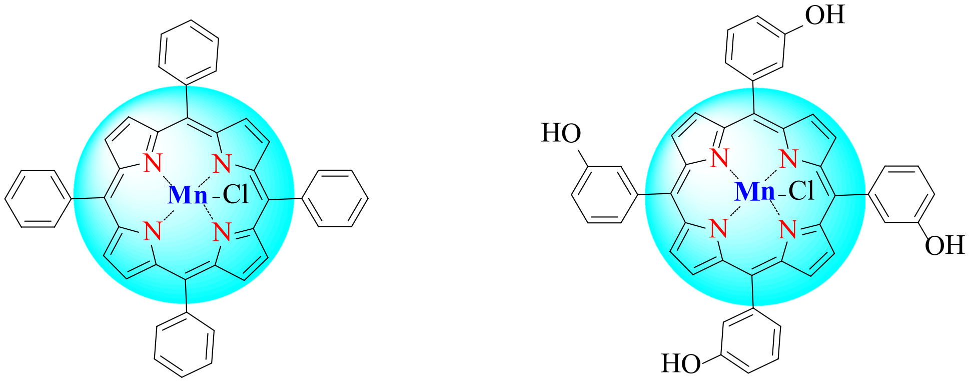
13 **14**

15 **16**

Ni^{2+}-selective sensors was not effected by the changes in pH between 2.0 and 7.0 and had response time of 10–15 s. In addition, the authors reported that these sensors were successfully used in the determination of Ni^{2+} ions in the waste water from electroplating industry.

Many studies conducted with the use of sensors based on porphyrins in drug determinations have been reported in the literature. In a study, Vlassici et al. developed a diclofenac (non-steroidal drug)-selective sensor using manganese(III) tetraphenylporphyrin chloride **(17)** and manganese(III)-tetrakis(3-hydroxyphenyl)porphyrin chloride **(18)** (Fig. 8) molecules as ionophores [34]. They showed that the developed sensor had a linear working range of 3.0×10^{-6} to 1.0×10^{-2} mol L^{-1} and detection limit of 1.5×10^{-6} mol L^{-1}. The sensor showed a good selectivity. In addition, the developed sensor was used in the determination of diclofenac in

Fig. 8 Porphyrins 17 and 18 used as ionophores



17 **18**

pharmaceutical samples. They compared the results from the sensor and HPLC method and found a good agreement between these two methods.

Some potentiometric performance characteristics such as linear working range, pH range, response time, slope and life time of the reported sensors based on porphyrins in literature are given in Table 1.

In this review, we mentioned many studies where porphyrin derivatives were used as ionophores in potentiometric sensors. We touched upon several chemical characteristics of these novel potentiometric sensors including working concentration and pH ranges, response time, lifetime and performance metrics (selectivity and sensitivity). We highlighted numerous areas of applications where these potentiometric sensors based on porphyrins might be superior to the alternatives, from water analysis to drug assays. The reports covered in this article on the use of porphyrin derivatives as ionophores point us to the fact that porphyrins have high potential to be used in new approaches in the design of potentiometric sensors in the future. The synthesis of novel porphyrin derivatives will certainly lead to the development of new ion-selective electrodes which have higher performance and applicability compared to existing ISEs. Besides their utilization in this area, many other applications of porphyrins in various scientific fields are present in the literature ranging from energy conversion technologies to photomedicine [35, 36]. Considering their highly favorable chemical structures, we expect to see more research focused on porphyrin-based applications in the coming years, both in chemical sensors field and in many other research areas.

Conclusion

Until today, amperometric [37, 38], voltammetric [39], photo-electrochemical [40], fluorescence [41], optical [42, 43], impedimetric [44, 45] and potentiometric [19, 21–34] sensors have been developed using porphyrin derivatives. The use of porphyrin derivatives as sensor materials has been an area of interest for many researchers due to their multiple functions and advantages. Many porphyrin derivatives still continue to be synthesized and used in various sensor studies. This review covers novel sensors which were developed using porphyrin derivatives as ionophores and prepared with potentiometric methods, and the application areas of these sensors. Porphyrin derivative molecules can bind to ions due to their structure with suitable cavities and therefore, they are considered as very attractive molecules in the development of potentiometric sensors. The ion selective properties of porphyrin-based sensors may be significantly related to the structure of the porphyrin derivative used in the design. Porphyrins used as ionophores in potentiometric based sensors have been demonstrated to be excellent sensor

Table 1 Potentiometric performance characteristics of the reported sensors based on porphyrins in literature

Ionophore	Ion	Concentration range (mol L^{-1})	Limit of detection (mol L^{-1})	pH working range	Response time (s)	Slope (mV/decade)	Life time (month)	References
1	Cu^{2+}	4.4×10^{-6} to 1.0×10^{-1}	2.8×10^{-7}	2.8–7.9	~ 8	29.3	~ 4	[21]
3	Zn^{2+}	1.3×10^{-5} to 1.0×10^{-1}	–	3.0–7.4	10	30.0	2	[22]
4	Ag^{+}	1.0×10^{-5} to 1.0×10^{-1}	1.9×10^{-7}	4.0–10.0	8	–	–	[19]
5	Fe^{3+}	1.0×10^{-7} to 1.0×10^{-1}	8.6×10^{-8}	2.0–3.8	20	21.6	–	[23]
6	Cu^{2+}	1.0×10^{-7} to 1.0×10^{-1}	9.8×10^{-8}	2.0–8.0	10	28.4 ± 0.4	1.5	[24]
7	Fe^{3+}	1.0×10^{-6} to 1.0×10^{-4}	6.3×10^{-7}	3.0–4.0	~ 10	25.0 ± 0.5	2	[25]
8	Fe^{2+}	1.0×10^{-6} to 1.0×10^{-2}	9.6×10^{-7}	3.0–5.0	< 12	29.4 ± 0.6	2	[26]
8	Ag^{+}	1.0×10^{-7} to 1.0×10^{-1}	1.0×10^{-7}	3.0–9.0	< 10	59.2 ± 1.0	3	[27]
9	Cu^{2+}	4.0×10^{-9} to 2.0×10^{-1}	1.0×10^{-9}	1.0–13.0	~ 5	30.1 ± 0.2	2	[28]
10	I^{-}	1.6×10^{-6} to 1.0×10^{-2}	1.0×10^{-6}	1.0–7.0	< 15	59.0	–	[29]
11	Cu^{2+}	2.5×10^{-6} to 1.0×10^{-1}	2.0×10^{-6}	5.0–10.0	–	27.8 ± 1.5	4	[30]
12	Ag^{+}	8.0×10^{-6} to 1.0×10^{-1}	7.0×10^{-6}	5.0–10.0	–	64.5 ± 1.8	4	[30]
12	Pb^{2+}	5.0×10^{-6} to 1.0×10^{-1}	3.0×10^{-6}	5.0–9.0	–	25.8 ± 1.0	4	[30]
13	Zn^{2+}	5.0×10^{-5} to 1.0×10^{-1}	3.0×10^{-5}	3.0–6.0	~ 10	26.5	8	[31]
14	Br^{-}	1.0×10^{-5} to 1.0×10^{-1}	8.0×10^{-6}	6.0–12.0	80	64.4 ± 0.4	1	[32]
14	I^{-}	1.0×10^{-5} to 1.0×10^{-1}	9.0×10^{-6}	3.0–12.0	60	52.3 ± 0.2	1	[32]
15	Ni^{2+}	2.0×10^{-6} to 1.0×10^{-1}	–	2.0–7.0	15	29.6	6	[33]
16	Ni^{2+}	1.0×10^{-5} to 1.0×10^{-1}	–	2.0–7.0	10	29	6	[33]
17–18	Diclofenac	3.0×10^{-6} to 1.0×10^{-1}	1.5×10^{-6}	5.5–11.5	–	-59.7	–	[34]

materials for real sample analysis such as food, pharmaceutical, medical and environmental monitoring.

Improvements in various parameters of potentiometric ion-selective electrodes or sensors will be of high importance in order to enhance their performance and expand their application areas. For instance; decreasing response time, increasing selectivity and sensitivity, lowering the production cost, increasing working ranges and simplifying the preparation procedures can be considered as main areas open for improvement in the design of potentiometric sensors. Studies covered in this review showed that the use of porphyrin derivatives as ionophores might provide solutions to these issues in the potentiometric sensor field. We believe that future research on porphyrins will result in the development of ISEs which outperfom current approaches.

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