

Ion-sensing Behavior of Ion-selective Electrodes Based on 5,10,15,20-Tetrakis (4-*n*-Dodecylphenyl) porphyrin

Takayo Moriuchi-Kawakami,* Hiroshi Nishimura, Keiichi Fujimori, Yasuhiko Shibutani,
Takushi Sugino,*† and Yo Shimizu††

*Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology,
Omiya 5-16-1, Asahi, Osaka 535-8585*

†*Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST),
Midorigaoka 1-8-31, Ikeda, Osaka 563-8577*

††*Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST),
Midorigaoka 1-8-31, Ikeda, Osaka 563-8577*

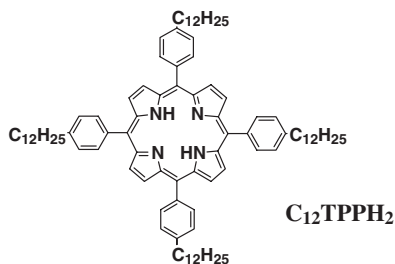
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5, 10, 15, 20-Tetrakis (4-*n*-dodecylphenyl) porphyrin ($C_{12}TPPH_2$) as a neutral carrier of ion-selective electrodes exhibited excellent cation-sensing behavior for the Ag^+ ion with high sensitivity and fast potential response.

Ion-selective electrodes (ISEs) form one of the most important groups of chemical sensors.¹ Potentiometric liquid membrane electrodes are quick and simple devices. A potentiometric liquid membrane is composed of an ionophore, a polymer, a plasticizer, and an additional salt. The content of an ionophore which really discriminates ions is about 2.5 wt %. An ionophore is dissolved or dispersed in a potentiometric liquid membrane. The original ion selectivity of an ionophore is directly reflected in the resulting ion-sensing behavior of the ISE. A most attractive ionophore for the cation-sensing is a neutral carrier which realizes excellent ion-sensing behavior. Numerous compounds such as crowns, calixarenes, and antibiotics, have been reported as neutral carriers for the cation-sensing.²

Famous metalloporphyrins have been utilized as the carriers of ISEs for anions.^{2,3} However, the porphyrin as a neutral carrier for the cation-sensing has been rarely reported.^{4,5} Here, we have proposed a porphyrin derivative as a new neutral carrier for the cation-sensing. The proposed porphyrin derivative, 5,10,15, 20-tetrakis(4-*n*-dodecylphenyl)porphyrin ($C_{12}TPPH_2$), has four *n*-dodecyl groups (Scheme 1). The ion-sensing behavior could depend somewhat on the lipophilicity of an ionophore.⁶ This paper reports the ISEs based on the porphyrin derivative $C_{12}TPPH_2$ exhibited excellent ion-sensing behavior for the Ag^+ ion.

The composition of the potentiometric liquid membranes used was $C_{12}TPPH_2$ as an ionophore (2.7 wt %), PVC as a polymer (28.3 wt %), a plasticizer (68.2 wt %) and potassium tetrakis (4-chlorophenyl)borate (KTpCIPB) as an additional salt



Scheme 1. 5,10,15,20-tetrakis (4-*n*-dodecylphenyl) porphyrin derivative.

(0.8 wt %) for the exclusion of anionic effect.⁷ $C_{12}TPPH_2$ was prepared by reported procedures.⁸ Measurements were performed on cells of the type $Ag-AgCl | 0.1 M AgNO_3 ||$ membrane $||$ sample solution $| 0.1 M CH_3COOLi || 3.3 M KCl | Ag-AgCl$ at 25 ± 0.1 °C using a pH/mV meter equipped with a double-junction type $Ag-AgCl$ reference electrode.

In this study, four ISEs **1–4** using 2-nitrophenyl octyl ether (*o*-NPOE) (electrode **1**), bis(1-butylpentyl) adipate (BBPA) (electrode **2**), 2-nitrophenyl phenyl ether (*o*-NPPE) (electrode **3**), and 4-nitrophenyl phenyl ether (*p*-NPPE) (electrode **4**) as plasticizers were proposed. *o*-NPOE, BBPA, and *o*-NPPE are liquid plasticizers, while *p*-NPPE is a solid one. Four potentiometric liquid membranes were investigated with an optical microscope and an atomic force microscope. The surfaces of the membranes using *o*-NPOE and *o*-NPPE were obviously smooth. In particular, $C_{12}TPPH_2$ as an ionophore homogeneously dissolved in the membrane using *o*-NPOE. On the other hand, the use of *p*-NPPE provided a solid-like membrane. Then $C_{12}TPPH_2$ evidently dispersed in the membrane. The membrane using BBPA was comparatively smooth, and $C_{12}TPPH_2$ was moderately dissolved. Thus, the obtained electrodes **1–4** began to respond in cation fashion as the concentration of the Ag^+ ion increased.

The ISE **1** based on porphyrin derivative $C_{12}TPPH_2$ dis-

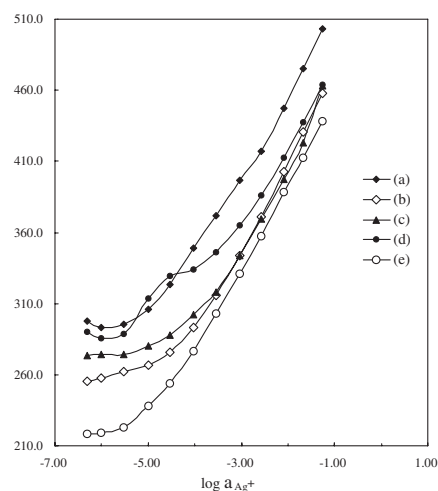
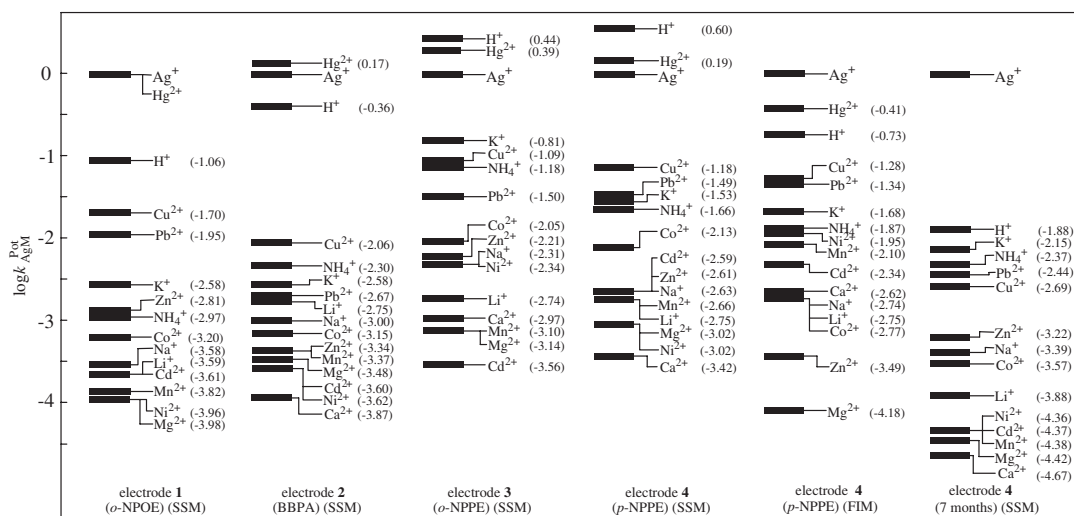


Figure 1. EMF response of electrodes **1–4** based on the porphyrin derivative $C_{12}TPPH_2$: (a) **1** using *o*-NPOE, (b) **1** using *o*-NPOE after one month, (c) **2** using BBPA, (d) **4** using *p*-NPPE, (e) **4** using *p*-NPPE after 7 months.



Scheme 2. Selectivity coefficients of electrodes 1–4 based on the porphyrin derivative $C_{12}TPPH_2$ (determined by the separate solution method (SSM), and the fixed interference method (FIM)).

played an excellent calibration curve for the Ag^+ ion over the activity range from $10^{-3.2}$ to $10^{-1.2}$ M (Figure 1a). The slope was 59.2 mV/decade. This value agreed with the theoretical Nernstian value.¹ No deterioration in the potential properties of this electrode 1 was observed, even if the conditioning time was lengthened from 24 to 48 h. After a month, the electrode 1 again exhibited the Nernstian response over the activity range from $10^{-4.0}$ to $10^{-1.2}$ M, although potential lowering was observed (Figure 1b). The electrode 2 also displayed an excellent calibration curve for the Ag^+ ion (Figure 1c). The Nernstian response was observed over the activity range from $10^{-3.7}$ to $10^{-1.2}$ M. The electrode 3 showed a poor calibration curve for the Ag^+ ion. *p*-NPPE is an isomer of *o*-NPPE. Nevertheless, the electrode 4 exhibited good calibration over the activity range from $10^{-2.5}$ to $10^{-1.2}$ M (Figure 1d). After seven months, the electrode 4 showed an excellent calibration curve over the range from $10^{-4.0}$ to $10^{-1.2}$ M (Figure 1e).

Responses of the ISEs 1–4 based on $C_{12}TPPH_2$ were measured for a series of cations M^+ or M^{2+} . All ISEs 1–4 showed response times of less than 1 min. The selectivity coefficients of the Ag^+ ion with respect to a cation M were determined by the separate solution method (SSM)¹ (Scheme 2). The selectivity coefficients of the electrode 4 were also determined by the fixed interference method (FIM).¹ The single-ion activities were calculated using the Debye–Hückel theory.⁹ Interestingly, these ISEs 1–4 provided the high degree of selectivity for the Ag^+ ion. The Hg^{2+} ion gave the serious interference. Although this disadvantage was similar to that of the commercial Ag_2S solid-state electrode for the Ag^+ ion, no responsibility for the S^{2-} ion was observed.¹⁰ The serious interference by the H^+ ion could result from the hydrogen bond. The ability of the electrode 1 for the ion discrimination lowered after a month. This was probably caused by the effusion of the ionophore from the smooth and moist membrane. On the electrode 4, the ability for the discrimination improved after seven months. Moreover, the interference of the H^+ ion considerably decreased. These advantages might be attributable to the solid-like membrane.

The optimized conformation of the parent porphyrin was calculated by the semi-empirical molecular orbital method

(PM3 level) using the SPARTAN SEMIEMPIRICALS PROGRAM (release 5.0.3). The calculation result gave the well-known rigid plane conformation for the parent porphyrin.¹¹ The transannular $NH\cdots HN$ and $N\cdots N$ distances were 2.09 and 3.02 Å. According to the ionic radius fitting the cavity of the porphyrin and the square planar coordination by the porphyrin, the target cation as a candidate seems to be the Ag^+ and Hg^{2+} ions (1.2 Å), the Pb^{2+} ion (1.3 Å), the K^+ ion (1.5 Å) or the NH_4^+ ion (1.5 Å).¹² This preference tendency almost agreed with the experimental result shown in Scheme 2. However, the high preference of the Cu^{2+} ion (0.7 Å)¹¹ was probably affected by the electronic property of the conjugated system in the porphyrin derivative.

On the other hand, $C_{12}TPPH_2$ was not exhibited the ion-sensing for the Ag^+ ion in $CH_3CN-CHCl_3$ (1:1 v/v) solution. The absorption of $C_{12}TPPH_2$ in 1×10^{-6} mol/dm³ solution was only slightly affected by the presence of the Ag^+ ion. No dependence of the absorbance on the concentration of the Ag^+ ion was detected.

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