Mesomorphic Effect of Discotic-type Liquid-crystalline Compounds as Neutral Carriers on Potentiometric Ion-sensing Membranes

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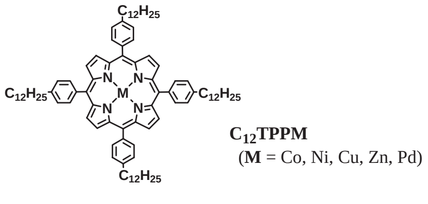
Mesomorphic porphyrin, 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin ($C_{12}TPPH_2$) and the cobalt complex $C_{12}TPPCo$ were used as neutral carriers of ion-selective electrodes (ISEs) to investigate the mesomorphic effect in potentiometric cation- and anion-sensing membranes. The selectivity coefficiency of a potentiometric cation-sensing membrane incorporating $C_{12}TPPH_2$ was drastically affected by heat-induced phase transitions of ionophoric liquid-crystalline compound. This paper is the first report that proved the heat-induced phase transition of ionophoric liquid-crystalline compound in the potentiometric ion-sensing membrane. It is noteworthy that selectivity sequence of the potentiometric cation-sensing membrane is remarkable changed by the mesomorphic effect. Furthermore, mesomorphic effect on a potentiometric anion-sensing membrane incorporating $C_{12}TPPCo$ was also demonstrated.

Mesomorphic phase transitions of liquid-crystalline compounds arise from the minor change of the molecular orientation.[1] Recently, the application of the molecular orientation of liquid-crystalline compounds has entered the research limelight in the field of ion or molecular recognition.[2] Potentiometric liquid membrane electrodes are quick and simple device.[3] However, the application of mesomorphic effects to ion-selective electrodes (ISEs) is quite limited.[4,5] In these electrodes, liquid-crystalline compounds were utilized as cation-selective neutral carriers of potentiometric liquid membranes. The potentiometric liquid membrane is composed of an ionophore, PVC as a polymer, a membrane solvent, and an additional salt. An ionophore, which discriminates ions, is dissolved or dispersed in a potentiometric liquid membrane. A most attractive ionophore is a neutral carrier that shows an excellent ion-sensing behavior.[6] The content of an ionophore is only about 1–7 wt %.[7] Therefore, non-ionophoric liquid-crystalline 4-*n*-alkyl-4′-cyanobiphenyls have been utilized as membrane solvents to achieve mesomorphic effects of ionophoric liquid-crystalline compounds on potentiometric cation-sensing membranes.[4,5]

The rod-like (calamitic) and the discotic molecules have been reported as thermotropic liquid-crystalline compounds.[1] The discotic-type molecules tidily stack to form columnar arrays. The discotic-type ionophoric liquid-crystalline compounds would be more suitable for the formation of the complex with the ion than the rod-like ionophoric liquid-crystalline compounds, because the sandwich-structure complexes would be easily formed with the ion.[8] Moreover, the mechanism of mesomorphic effects on the ion-sensing by the discotic-type ionophoric liquid-crystalline compounds would be easy to be defined. Therefore, we focused our attention on the porphyrin derivatives, 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin ($C_{12}TPPH_2$) and their metal complexes $C_{12}TPPM$ (Scheme 1), as ionophoric liquid-crystalline compounds for ISEs. Ionophoric liquid-crystalline compounds require instrumentally appropriate phase-transition temperatures for ISEs. Interestingly, these discotic-type mesomorphic porphyrin derivatives show lower and higher mesophases between the crystal and the isotropic phases.[9] Here, we report novel mesomorphic effects of the discotic-type ionophoric liquid-crystalline compounds on potentiometric ion-sensing membranes without non-ionophoric liquid-crystalline compounds as membrane solvents.

The ion-sensing liquid membranes were composed of mesomorphic porphyrin derivatives ($C_{12}TPPH_2$ or $C_{12}TPPM$: M = Co, Ni, Cu, Zn, and Pd) (2.7 or 1.9 wt %) as neutral carriers, PVC (28.3 wt %) as a polymer, 4-nitrophenyl phenyl ether (*p*-NPPE) as a plasticizer (68.2 or 69.4 wt %). Potassium tetrakis(4-chlorophenyl)borate (KTpClPB) (0.8 wt %) was used as an anion excluder for potentiometric cation-sensing membranes.[10] EMF 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|AgCl–Ag using a pH/mV meter equipped with a double junction type Ag–AgCl reference electrode. The activity coefficients were calculated according to the Davies equation.[11] The selectivity coefficients were determined by the separate solution method (SSM)[3] in order to evaluate the mesomorphic effects of ionophoric liquid-crystalline compounds on potentiometric ion-sensing membranes.

The EMF responses of cation-sensing membranes incorporating $C_{12}TPPH_2$ as an ionophore and *p*-NPPE as a membrane solvent were investigated at 25, 40, and 60 °C, because $C_{12}TPPH_2$ has three phase transition points (31, 52, and 155 °C).[9] The slopes and linear ranges in the calibration graph are summarized in Table 1. The potentiometric membrane incorporating $C_{12}TPPH_2$ exhibited high sensitivity and fast response to Ag^+ ion. Scheme 2 illustrates that selectivity coefficients for Ag^+ ion were drastically changed over measurement temperatures. Moreover, it is noteworthy that selectivity sequence of a

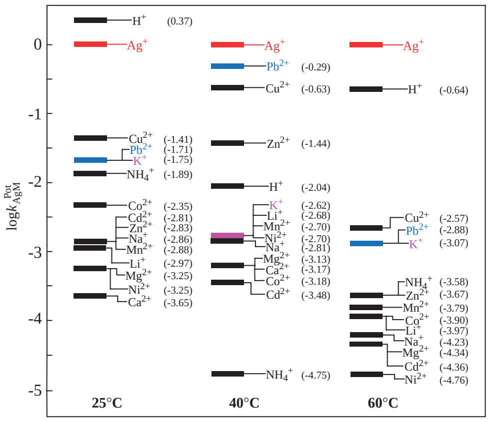


Scheme 1. Discotic-type liquid-crystalline compounds.

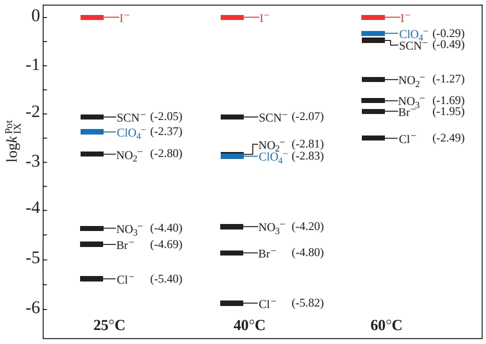
Table 1. Potential response to Ag^+ activity changes for ISEs based on $C_{12}TPPH_2$ as an ionophore

Measurement temperature/°C	Calibration graph	
	Slope/mV decade^{-1}	Linear range/log a_{Ag^+}
25	58.1 (59.2)[a]	−2.6 to −1.2
40	134.1 (62.2)[a]	−3.0 to −1.2
60	68.8 (66.1)[a]	−6.0 to −1.2

[a]The ideal Nernstian slope.



Scheme 2. Selectivity coefficients of electrode based on $C_{12}TPPH_2$.



Scheme 3. Selectivity coefficients of electrode based on $C_{12}TPPCo$.

potentiometric cation-sensing membrane is remarkably changed. Compared to selectivity coefficients with respect to K^+ ion, selectivity coefficients for Ag^+ ion with respect to Pb^{2+} ion were greatly affected. It seems that the minor change of the molecular orientation from the crystal (25 °C) to the lamellar mesophase[9b] (40 °C) caused the change of the discrimination of Pb^{2+} ion because Pb^{2+} ion is similar in ion size and chemical property to Ag^+ ion.

The potentiometric membranes incorporating $C_{12}TPPM$ (M = Ni, Cu, Zn, and Pd) as an ionophore began to respond in cation fashion as the concentration of KSCN or KI increased at 25 °C. The potentiometric membrane incorporating $C_{12}TPPCo$ as an ionophore exhibited the I^--selective anion-sensing. This membrane responded to I^--activity changes with the slopes of −73 mV decade^{-1} over the activity range from $10^{-2.1}$ to $10^{-1.1}$ M at 25 °C. Unlike $C_{12}TPPH_2$, the change of the slopes and linear ranges in the calibration graph of the potentiometric membrane incorporating $C_{12}TPPCo$ was minute between measurement temperatures (25, 40, and 60 °C). In selectivity sequences of the potentiometric anion-sensing membrane, the orders of ClO_4^- ion only were changed (Scheme 3).

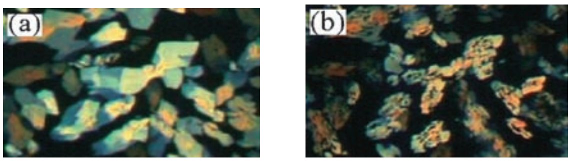


Figure 1. Polarizing microscope textures of plasticized polymeric membrane incorporating the porphyrin derivative $C_{12}TPPH_2$ at (a) 25 and (b) 40 °C.

To investigate the behavior of discotic-type ionophoric liquid-crystalline compounds in potentiometric ion-sensing membrane, the cation-sensing membrane incorporating $C_{12}TPPH_2$ was observed by a polarizing microscope under the conditions corresponding to the EMF measurements. The polarizing microscope textures were somewhat changed by heating from 25 °C (Figure 1a) to 40 °C (Figure 1b). Further, the probe light was not completely transmitted with increasing temperature from 40 to 60 °C. These texture changes show the phase transition from the crystalline phases to the isotropic liquid. It means that the heat-induced phase transitions appeared in the potentiometric ion-sensing membrane without non-ionophoric liquid-crystalline compounds as membrane solvents. The reproducibility of these texture changes in the potentiometric ion-sensing membrane was repeatedly demonstrated.

This work was supported by a Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science.

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