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Molecular Design, Characterization, and Application of Multiinformation Dyes (MIDs) for Optical Chemical Sensings. 3. Application of MIDs for λ_{max}-Tunable Ion-Selective Optodes

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By utilizing “multiinformation dyes (MIDs)”, which have plural spectral change characteristics such as an absorption maximum wavelength (λ_{max}) shift based on a polarity change and an absorbance change due to protonation, novel λ_{max}-tunable ion-selective optodes were proposed and prepared by employing MIDs with membrane solvents having different polarities. For controlling the detecting λ_{max} of the optode, the novel polar membrane solvent [2-[[6-(2-nitrophenoxy)hexyl]oxy]methyl]isobutane-1,3-diol was designed and synthesized, which was used together with a typical membrane solvent nitrophenyl octyl ether. By mixing these two membrane solvents, the λ_{max} position of the optode detection wavelength can be shifted and controlled and was successfully applied to a λ_{max}-tunable Li$^+$-selective optode based on a highly Li$^+$-selective ionophore TTD14C4. The λ_{max} tuning technique is useful for preparing an optode system using a low-cost light source such as a light-emitting diode or a popular laser.

Since the early stage in the development of ion-selective optodes,[1−3] the methodology has been widely recognized as a useful ion-sensing tool and has grown as an active research area in chemical sensors. Many kinds of ionic species have been measured using the methodology of optodes, and these studies have recently been compiled by Bakker et al.[4] The direction of the recent developments of novel ion-selective optodes has been focused on sensing devices such as waveguide devices,[5−7] fiber-optic devices,[8] sensing plate devices,[9,10] flow analytical devices,[11−13] and so on. In the development of ion-selective optodes, a lipophilic pH indicator dye plays an important role in detecting a signal transduction process. Subsequently, many kinds of lipophilic pH indicator dyes have been synthesized and utilized for ion-selective optodes.[14−19] In all cases, the detecting information is a simple absorbance change relating to the pH indicator dye.

Recently, we proposed a molecular design concept for the dyes called “multiinformation dyes (MIDs)” for application to multidimensional optical chemical sensing.[20] Using MIDs of our developed merocyanine type, the simultaneous sensing of pH and water content was demonstrated.[21] The MIDs used in the present investigation exhibit two kinds of spectral changes, which are a λ_{max} shift based on a polarity change and an absorbance change based on protonation of the dye molecule. We think that employing MIDs rather than a simple lipophilic pH indicator dye can lead to the development of a unique ion-selective optode.

Because the MID has plural spectral change properties, we here report the design of a novel unique λ_{max}-tunable ion-selective optode as one of the applications of MIDs. Basically, the λ_{max} tuning was performed by varying the polarity of the membrane solvent. In the present investigation, the binary membrane solvent mixture of 2-nitrophenyl octyl ether (NPOE) and the newly synthesized membrane solvent [2-[[6-(2-nitrophenoxy)hexyl]oxy]-methyl]isobutane-1,3-diol (NPOE-OH) was used to continuously

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(1) Suzuki, K.; Tohda, K.; Tanda, Y.; Ohzora, H.; Nishihama, S.; Inoue, H.; Shirai, T. *Anal. Chem.* **1989**, *61*, 382.

(2) Suzuki, K.; Ohzora, H.; Tohda, K.; Miyazaki, K.; Watanabe, K.; Inoue, H.; Shirai, T. *Anal. Chim. Acta* **1990**, *237*, 155.

(3) Morf, W. E.; Seiler, K.; Rusterholz, B.; Simon, W. *Anal. Chem.* **1990**, *62*, 738.

(4) Bakker, E.; Buhlmann, P.; Pretsch, E. *Chem. Rev.* **1997**, *97*, 3083.

(5) Hisamoto, H.; Kim, K.-H.; Manabe, Y.; Sasaki, K.; Minamitani, H.; Suzuki, K. *Anal. Chim. Acta* **1997**, *342*, 31.

(6) Dohner, R. E.; Spichiger, U. E.; Simon, W. *Chimia* **1992**, *46*, 215.

(7) Freiner, D.; Kunz, R. E.; Citterio, D.; Spichiger, U. E.; Gale, M. T. *Sens. Actuators B* **1995**, *29*, 277.

(8) Shortreed, M. R.; Bakker, E.; Kopelman, R. *Anal. Chem.* **1996**, *68*, 2656.

(9) Hisamoto, H.; Miyashita, N.; Watanabe, K.; Nakagawa, E.; Yamamoto, N.; Suzuki, K. *Sens. Actuators B* **1995**, *29*, 378.

(10) Hisamoto, H.; Sato, S.; Sato, K.; Siswanta, D.; Suzuki, K. *Anal. Sci.* **1998**, *14*, 127.

(11) Hisamoto, H.; Watanabe, K.; Nakagawa, E.; Siswanta, D.; Shichi, Y.; Suzuki, K. *Anal. Chim. Acta* **1994**, *299*, 179.

(12) Hisamoto, H.; Watanabe, K.; Oka, H.; Nakagawa, E.; Spichiger, U. E.; Suzuki, K. *Anal. Sci.* **1994**, *10*, 615.

(13) Hisamoto, H.; Nakagawa, E.; Nagatsuka, K.; Abe, Y.; Sato, S.; Siswanta, D.; Suzuki, K. *Anal. Chem.* **1995**, *67*, 1315.

(14) Bakker, E.; Lerchi, M.; Rosatzin, T.; Rusterholz, B.; Simon, W. *Anal. Chim. Acta* **1993**, *278*, 211.

(15) Tan, S. S. S.; Hauser, P. C.; Wang, K.; Fluri, K.; Seiler, K.; Rusterholz, B.; Suter, G.; Krttli, M.; Spichiger, U. E.; Simon, W. *Anal. Chim. Acta* **1991**, *255*, 35.

(16) He, H.; Li, H.; Mohr, G.; Kovacs, M.; Werner, T.; Wolfbeis, O. S. *Anal. Chem.* **1993**, *65*, 123.

(17) Wang, E.; Zhu, L.; Ma, L.; Patel, H. *Anal. Chim. Acta* **1997**, *357*, 85.

(18) Lehmann, F.; Mohr, G. J.; Czerney, P.; Grummt, U. W. *Dyes Pigments* **1995**, *29*, 85.

(19) Citterio, D.; Rasonyi, S.; Spichiger, U. E. *Fresenius J. Anal. Chem.*, **1996**, *354*, 836.

(20) Hisamoto, H.; Tohma, H.; Yamada, T.; Yamauchi, K.; Siswanta, D.; Yoshioka, N.; Suzuki, K. *Anal. Chim. Acta* **1998**, *373*, 271.

(21) Hisamoto, H.; Manabe, Y.; Yanai, H.; Tohma, H.; Yamada, T.; Suzuki, K. *Anal. Chem.* **1998**, *70*, 1255.

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vary the polarity. The optodes were prepared as a poly(vinyl chloride) (PVC)-less liquid membrane-type sensing plate which is similar to that recently reported by our group.[10] A plasticized PVC membrane has been widely utilized as the membrane matrix for preparing an optode membrane. However, for preparing a λ_{max}-tunable ion-selective optode, a PVC-less liquid membrane is more adaptable than a plasticized PVC membrane. In most cases, a plasticized PVC membrane contains ~30 wt % PVC. Therefore, when a plasticized PVC membrane is used, the extent of polarity variation of the optode membrane prepared by mixing two membrane solvents is limited by the PVC contained in the membrane phase. Furthermore, as reported previously, the response time of an optode membrane prepared with a PVC-less liquid membrane is faster than that with a plasticized PVC membrane, because of the fast diffusion of an optically relevant chemical species in the membrane phase due to its low viscosity. Thus, here we prepare a λ_{max}-tunable ion-selective optode as a liquid membrane-type sensing plate. Preliminary results clarified that the λ_{max} tuning in the range from 649 to 589 nm and from 568 to 540 nm was possible for the optode using KD-M11 dye and KD-M9 dye, respectively, in an NPOE/NPOE-OH optode membrane system. This system was then applied to the neutral ionophore-based lithium ion-selective optode, achieving the λ_{max} tuning in the range from 621 to 589 nm using KD-M11 dye and TTD14C4 as a neutral lithium ionophore which was formerly developed by our research group.[22]

From a theoretical point of view, varying the polarity (hydrogen bond donor ability) of the membrane solvent influences the equilibrium constant in the theoretical response equation for the optode.[9] Varying the mixing ratio of the binary membrane solvent mixture also affects the equilibrium constant of an ion-pair extraction system concerning the measurable range of an optode. The ion extraction equilibrium constant for the optode membrane using NPOE was increased by adding NPOE-OH. In an extreme situation (NPOE-OH 100%), the equilibrium constant was ~3 orders of magnitude larger than that in the lithium ion-selective optode based on NPOE. This fact suggests that the measurable range of the optode can be lowered upon addition of NPOE-OH in NPOE. Correlation between the mixing ratio of the two membrane solvents and the position of λ_{max} and the equilibrium constants was examined in detail.

The λ_{max} tuning technique is useful for preparing an optode system using a low-cost light source such as a light-emitting diode (LED) or a popular inexpensive laser.

EXPERIMENTAL SECTION

Reagents. Chemical structures of the membrane components are shown in Figure 1. MIDs (1-(dodecyl)-4-[(3′-bromo-5′-methoxy-4′-oxocyclohexa-2′,5′-dienylidene)ethylidene]-1,4-dihydropyridine (KD-M9) and 1-(dodecyl)-4-[(3′,5′-dibromo-4′-oxocyclohexa-2′,5′-dienylidene)ethylidene]-1,4-dihydroquinoline (KD-M11)) were synthesized according to the previous report.[20] A lithium ionophore ((TTD14C4)), sodium tetrakis[3,5-bis(trifluoromethyl)]phenyl borate (NaTFPB), and NPOE were purchased from Dojindo Laboratories, (Kumamoto, Japan). The cellulose dialysis membranes of 20-μm thickness were purchased from Sanko Chemical Industry Co., Ltd. (Tokyo, Japan). Reagents of the highest grade commercially available were used for the preparation of the aqueous test electrolytes. The distilled and deionized water used had a resistivity of more than 1.5×10^7 Ω·cm at 25 °C. For the investigation of fundamental characteristics, 0.1 M tetramethylammonium cation solutions were prepared in the respective pH ranges. The preparation of buffer solutions was as follows; tetramethylammonium chloride (TMACl, 0.1 M) solution containing a buffer component (0.01 M) and tetramethylammonium hydroxide (TMAOH, 0.1 M) solution containing the same buffer component (0.01 M) were mixed and used. The buffer components used in the respective pH range were as follows: pH 2−5, citrate; pH 5−10, 2-(*N*-morpholino)ethanesulfonic acid (MES); pH 10−13, boric acid. Lithium ion solutions were prepared using 0.02 M magnesium acetate buffer solution, pH 5.0.

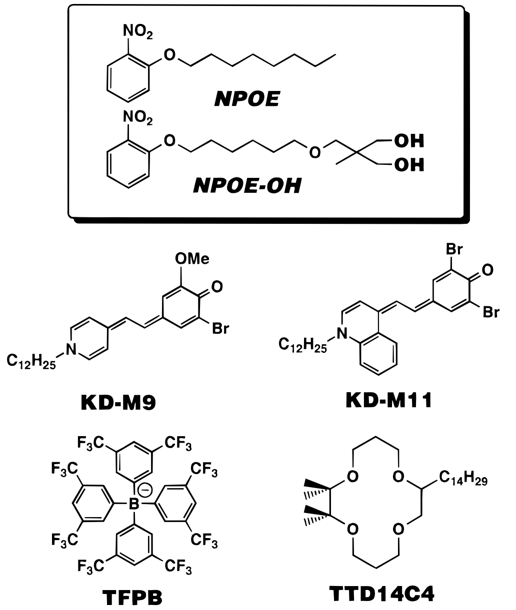

Figure 1. Chemical structures of membrane components.

Synthesis of the Membrane Solvent (NPOE-OH). The novel membrane solvent NPOE-OH was synthesized as follows. *o*-Nitrophenol (1 g, 7 mmol) was dissolved in 20 mL of *N*,*N*-dimethylformamide (DMF), and sodium hydride (NaH: 0.34 g, 8.4 mmol) was added slowly under room temperature. To this solution, 1,6-dibromohexane (5.2 g, 21 mmol) was added and the mixture stirred for 1.5 h at 60 °C. After the reaction period, a small amount of methanol was added to the solution to quench the excess NaH, and DMF was evaporated. The resulting residue was extracted three times with chloroform. After the organic phase was dried using Na_2SO_4 and evaporation, the obtained residue was purified by silica gel column chromatography with hexane−chloroform (1:1) as the eluent to yield 2-nitro-1-[(6-bromohexyl)-oxy]benzene (yield: 2.0 g, 94%). Trimethylolethane (2.38 g, 19.8 mmol) was dissolved in 30 mL of DMF, and NaH (0.79 g, 19.8 mmol) was added. 2-Nitro-1-[(6-bromohexyl)oxy]benzene (2.0 g, 6.6 mmol) was added to this solution and the mixture stirred for 1.5 h at 60 °C. After the reaction, a small amount of methanol was added to the solution, and DMF was evaporated. The resulting residue was extracted three times with toluene. After the organic phase was dried using Na_2SO_4 and evaporation, the obtained

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[22] Suzuki, K.; Yamada, H.; Sato, K.; Watanabe, K.; Hisamoto, H.; Tobe, Y.; Kobiro, K. *Anal. Chem.* **1993**, *65*, 3404.

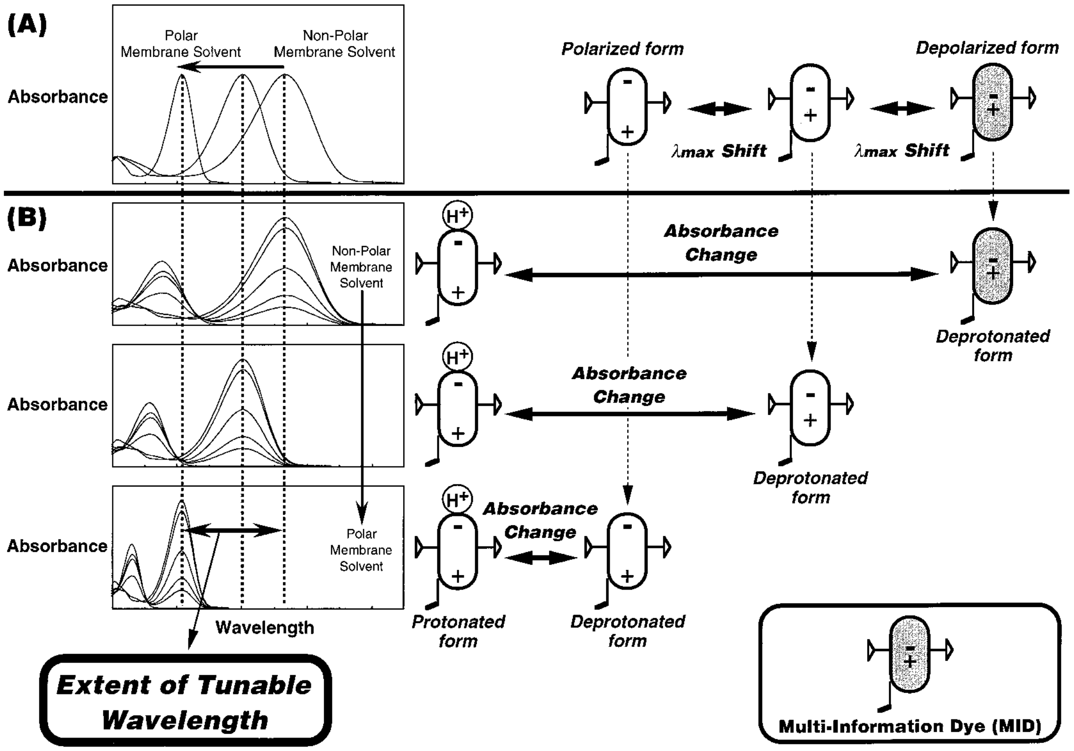

Figure 2. Schematic illustration of the concept for developing a λ_{max}-tunable ion-selective optode employing MID. (A) Shift in λ_{max} position of the optode membranes upon changing the polarities of membrane solvents and subsequent structural changes in MID. (B) Absorbance changes upon protonation of the MID in the respective polarities of the membrane solvents and subsequent structural changes in MID.

residue was purified by silica gel column chromatography with hexane−ethyl acetate (1:3) as the eluent to yield the final product, NPOE-OH (yield: 1.8 g, 80%): ^{1}H NMR (300 MHz) $\delta = 0.82$ (s, CH_3, 3H), 1.38−1.66 (m, CH_2, 6H), 1.78−1.87 (m, CH_2, 2H), 2.61−2.65 (t, OH, 2H), 3.42−3.46 (m, CH_2OH, 4H), 3.58 (m, CH_2O, 2H), 3.70 (m, CH_2O, 2H), 4.10 (t, $J = 6.24$ Hz, CH_2OAr, 2H), 7.01 (t, $J = 7.70$ Hz, ArH, 1H), 7.07 (d, $J = 7.70$ Hz, ArH, 1H), 7.51 (t, $J = 7.89$ Hz, ArH, 1H), 7.81 (d, $J = 8.07$ Hz, ArH, 1H), ($CDCl_3$). Anal. Calcd for $C_{17}H_{27}NO_6$ (341.40): C, 59.81; H, 7.97; N, 4.10. Found: C, 59.75; H, 8.10; N, 4.02.

Preparation of Chemical Sensing Plates. The detailed experimental procedure for the preparation of the chemical sensing plate has been reported elsewhere.[10] The outline for the preparation of sensing plates is as follows. The organic liquid containing the membrane solvent, lipophilic anionic additive, and MID were mixed in a small glass vial. For a fundamental investigation, an ionophore-less organic liquid was prepared with 0.056 M MID (KD-M9 or KD-M11) and 0.056 M TFPB in the membrane solvents (NPOE, NPOE-OH, or their mixtures). Variation in the mixing ratio of the two membrane solvents was carried out by varying the weight of NPOE-OH in NPOE, and the mixture was represented as weight percent. Lithium ion-sensing liquid membranes were prepared with 0.056 M KD-M11, 0.056 M TFPB, and 0.056 M TTD14C4 in the membrane solvents (NPOE or NPOE-OH). A small droplet (~0.01 g) of the prepared organic liquid was coated on both sides of octadecyl group-modified frosted glass plates (25×8 mm^2) as thin as possible (approximately 3−5 μm thick), in which a small pick was used for coating the liquid. The glass plate coated with an ion-sensing thin organic liquid layer was further covered with the dialysis membrane of 20-μm thickness, and the edge was tightly closed with a plastic fastener to prevent the leaching out of the membrane components (see ref 10).

Absorbance Measurements. The absorbance measurements for the sensing plate were carried out with the same system reported previously.[10] The double-beam spectrophotometer (U-2000; Hitachi Co., Ltd., Tokyo, Japan) and a normal conventional glass vessel (~4-mL-capacity standard optical cell) were used. The sensing plate was immersed in the glass vessel filled with the sample solution while its absorbance was monitored. The reference cell (glass vessel) of the spectrophotometer was filled with the same sample solution in order to compensate for the background absorbance in the measurement spectrum. For the expression of absorbance value, all absorbance is indicated in absorbance units (au) except "normalized absorbance", which indicates the relative portion of the deprotonated dyes. In each measurement, sensing plates were initially immersed in 0.01 M HCl solution to remove sodium cation, which is a countercation of TFPB, in the membrane phase.

RESULTS AND DISCUSSION

Basic Characteristics of the λ_{max}-Tunable Optode Based on MIDs. The concept for demonstrating the novel λ_{max}-tunable optode is schematically illustrated in Figure 2, which indicates that the control of the λ_{max} position (λ_{max} value in wavelength) as the optode detection wavelength can be varied by varying the polarity of the membrane solvent dissolving the dye. Figure 2B illustrates the absorbance changes upon protonation of the dye, which is basically the same as the response mechanism for the previously reported ion-selective optodes.[2,11,23−25] However, by

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(23) Watanabe, K.; Nakagawa, E.; Yamada, H.; Hisamoto, H.; Suzuki, K. *Anal. Chem.* **1993**, *65*, 2704.

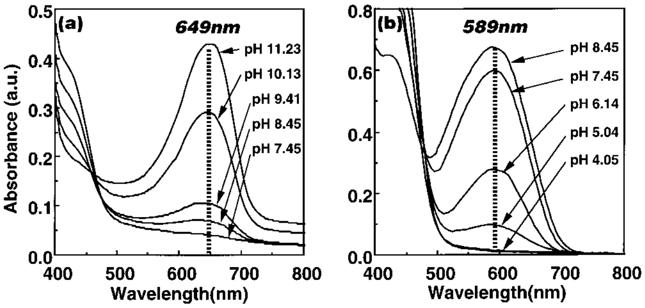

Figure 3. Typical absorption spectra of the KD-M11-based membranes upon extraction of tetramethylammonium cations: (a) NPOE-based membrane; (b) NPOE-OH-based membrane

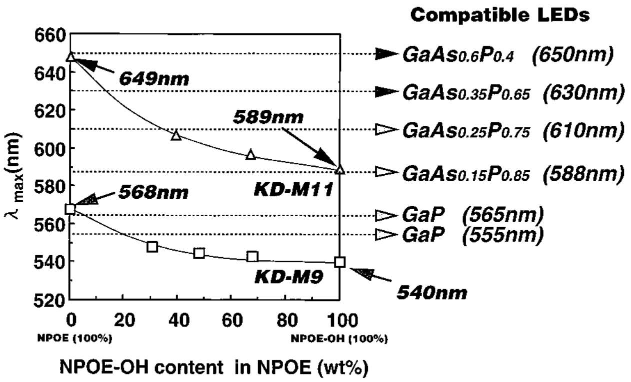

Figure 4. Variation in the λ_{max} values of optode membranes with varying mixing ratios of the membrane solvents. Here compatible LEDs are also shown (see ref 28).

employing the MID as the sensing component, the detecting λ_{max} position can be controlled by varying the polarity of the membrane solvent of the optode membrane as shown in Figure 2A. Thus by choosing different polarities of the membrane solvents, λ_{max} tuning in the optode response can be achieved and the ion concentration can be measured at the most suitable wavelength by adjusting the λ_{max} position as shown in Figure 2B. For practical application of the optodes, an LED or an easily handled inexpensive laser was most frequently utilized as the light source. However, in most cases, wavelength matching between a light source and a dye utilized for the optode were not always optimized. LED compatibility of dyes for optodes has been investigated by Wolfbeis et al.[26,27] However, in their approaches, several kinds of dyes were synthesized for choosing a dye having the appropriate maximum absorption wavelength for LEDs. Based on our concept, the detecting λ_{max} of an optode can be controlled by a single indicator dye, in which the wavelength can be continuously and accurately controlled by varying the mixing ratio of the binary membrane solvents. Thus, our present concept can solve the problem and is useful for the development of ion-selective optodes having optimum sensitivity. In this case, the polarity of the membrane solvent for the optode plays an important role. Preliminary investigations concerning the fundamental spectral characteristics of MIDs based on merocyanine dyes revealed that the λ_{max} positions of MIDs synthesized here were strongly affected by hydrogen-bonding donor solvents such as methanol or ethanol.[20] Thus, we have synthesized a membrane solvent, NPOE-OH, possessing hydroxyl groups which function as a hydrogen-bonding donor. This novel membrane solvent has a skeleton similar to that of NPOE, which is one of the typical membrane solvents for the plasticized PVC membrane. By mixing NPOE-OH and NPOE, the hydrogen bond donor ability of the optode membrane can be controlled. The λ_{max}-tunable optodes were then prepared using NPOE-OH, NPOE, or their mixtures.

To clarify the fundamental spectral characteristics of KD-M11, preliminary investigations were performed using an ionophoreless optode membrane based on KD-M11. In this case, the TMA cation was selected as the extractant (detecting analyte) due to its relatively low surface-charge density which forms the ion-pair complex with TFPB. Panels a and b of Figure 3 show the typical absorption spectra of the optode membranes based on KD-M11 with two different membrane solvents of NPOE and NPOE-OH, respectively. In this experiment, the concentrations of TMA cation were kept constant (0.1 M) and the pH values were varied. In both cases, the absorption peaks increasingly appeared upon increasing the pH in the water phase, and no obvious λ_{max} shifts were observed. By using different membrane solvents (NPOE or NPOE-OH), the λ_{max} positions were varied from 649 (NPOE) to 589 nm (NPOE-OH). These results indicate that the hydroxyl groups in the NPOE-OH molecule effectively interact with the quinoid carbonyl of KD-M11, and a hypsochromic shift subsequently occurred. As shown in Figure 3, the amounts of the extractant in the membrane phase did not affect the λ_{max} positions at the optode detecting wavelength. Consequently, the λ_{max} positions in the absorption spectra for the optode detection are mainly governed by the hydrogen bond donor ability of the membrane solvent. These results suggested that the λ_{max} positions for the optodes can be varied from 649 to 589 nm by varying the mixing ratio of NPOE and NPOE-OH. The correlation between the mixing ratio of these two membrane solvents and the λ_{max} positions for the optode membranes were then investigated. Figure 4 shows the λ_{max} positions for the optode membranes as a function of the mixing ratio of NPOE and NPOE-OH. As expected, the λ_{max} positions of the optode membranes were continuously varied upon varying the mixing ratio of NPOE and NPOE-OH. The results obtained with KD-M9-based membranes are also shown in Figure 4. The KD-M9-based optode membranes have λ_{max} values in a lower wavelength region compared with those of KD-M11-based membranes. Thus, by choosing the appropriate MID, a wide range of tunable detecting wavelength could be covered. Figure 4 also shows the emission wavelengths of compatible LEDs in the region from 550 to 650 nm.[28] The KD-M11- and KD-M9-based optode membranes have appropriate λ_{max} tuning ranges for matching the wavelength of several LED light sources. The membrane solvent NPOE-OH can be homogeneously mixed with NPOE. Thus by using the "wavelength matching map" as shown in Figure 4, λ_{max} positions for the optode can be continuously and accurately controlled to the desired detecting wavelength by mixing these two solvents.

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(24) Seiler, K.; Simon, W. *Anal. Chim. Acta* **1992**, *266*, 73.
(25) Bakker, E.; Simon, W. *Anal. Chem.* **1992**, *64*, 1805.
(26) Klimant, I.; Belser, P.; Wolfbeis, O. S. *Talanta* **1994**, *41*, 985.
(27) Mohr, G. J.; Wolfbeis, O. S. *Anal. Chim. Acta* **1994**, *292*, 41.

(28) Bass, M., Ed. *Handbook of Optics*, 2nd ed.; Vol.1, *Fundamentals, Techniques, and Design*; McGraw-Hill: New York, 1995; p 12-1.

As described in the introduction, varying the polarities of the membrane solvent affects the ion-pair extraction equilibrium between the organic phase as the optode membrane phase and the water phase as the sample solution phase. This equilibrium correlates with the detection limit of the optode. The variation of the equilibrium constants by varying the mixing ratio of the two different membrane solvents was evaluated with the following theoretical response scheme. The ion-pair extraction equilibrium can be expressed by the following

$$\mathrm{AHR_o} + i^+_\mathrm{w} \Leftrightarrow \mathrm{A_o} + \mathrm{R}i_\mathrm{o} + \mathrm{H}^+_\mathrm{w} \tag{1}$$

where i^+ represents the cation to be extracted (sensed) and H^+ represents a proton. A, R*i*, and AHR represent the deprotonated MID, the ion pair of a lipophilic anionic additive and a cation to be extracted (sensed), and the ion pair of a protonated MID and a lipophilic anionic additive, respectively. Subscripts o and w denote the organic phase and the water phase, respectively. In this case, the equilibrium constant, *K*, can be expressed by

$$K = [\mathrm{R}i]_\mathrm{o}[\mathrm{A}]_\mathrm{o}a_{\mathrm{H}^+}/[\mathrm{AHR}]_\mathrm{o}a_{i^+} \tag{2}$$

where *a* denotes the activities of the respective chemical species. Based on the mass action law, the total activity of the dye ($[\mathrm{A}]^{\mathrm{tot}}$) and that of the lipophilic anionic additive ($[\mathrm{R}]^{\mathrm{tot}}$) can be expressed by the following.

$$[\mathrm{A}]^{\mathrm{tot}} = [\mathrm{A}]_\mathrm{o} + [\mathrm{AHR}]_\mathrm{o} \tag{3}$$

$$[\mathrm{R}]^{\mathrm{tot}} = [\mathrm{Ri}]_\mathrm{o} + [\mathrm{AHR}]_\mathrm{o} \tag{4}$$

Based on eqs 3 and 4, eq 2 can be reexpressed as the following equation.

$$K = \frac{[\mathrm{A}]_\mathrm{o}([\mathrm{R}]^{\mathrm{tot}} - [\mathrm{A}]^{\mathrm{tot}} + [\mathrm{A}]_\mathrm{o})a_{\mathrm{H}^+}}{([\mathrm{A}]^{\mathrm{tot}} - [\mathrm{A}]_\mathrm{o})\mathrm{a}_{i^+}} \tag{5}$$

Under our experimental conditions, the total concentrations of the dye and the lipophilic anionic additive were the same. Thus, eq 5 can be simply expressed as the

$$K = \frac{([\mathrm{A}]_\mathrm{o})^2 a_{\mathrm{H}^+}}{([\mathrm{A}]^{\mathrm{tot}} - [\mathrm{A}]_\mathrm{o})\mathrm{a}_{i^+}} \tag{6}$$

Using eq 6, *K* values can be determined for the respective experimental conditions. Figure 5 shows four typical response curves of the optodes for the respective experimental conditions as a function of pH of the water phase using KD-M9 or KD-M11 as the dye and NPOE or NPOE-OH as the membrane solvent. All curves shown in Figure 5 were the theoretical response curves based on eq 6 by varying the *K* values in which the vertical values in the figure were defined as the relative portion of the deprotonated dye; i.e., the normalized absorbance indicates $[\mathrm{A}]_\mathrm{o}/[\mathrm{A}]^{\mathrm{tot}}$. In all cases, good correlation was observed between the experimental data plots and theoretical response curves. The curves in Figure 6 show logarithmic *K* values as a function of the mixing ratio of the two membrane solvents of NPOE and NPOE-OH in which the *K* values were determined by the theoretical curve fitting. The difference in the two curves using KD-M11 and KD-M9 is attributed to the difference in the $\mathrm{p}K_\mathrm{a}$ values of these dyes. By substituting the membrane solvent of NPOE into NPOE-OH, the *K* value increases ~3 orders of magnitude. This fact indicates that the measurable range of the optode can be lowered upon addition of NPOE-OH in NPOE, and in an extreme situation (NPOE-OH 100%), the measurable range can be lowered ~3 orders of magnitude. Thus, for preparing the $\lambda_{\max}$-tunable ion-selective optode, variation in the measurable range has to be taken into account to design the optode so that it has an appropriate response range.

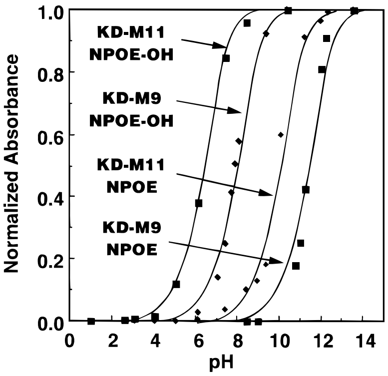

Figure 5. Typical response curves of different optode membranes as a function of pH value in the water phase. All response curves were calculated by the theoretical response equation based on eq 6. Concentrations of cationic species (tetramethylammonium cation) in the water phase were kept constant at 0.1 M (see Experimental Section).

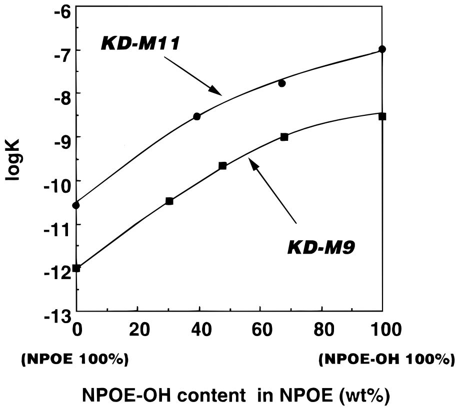

Figure 6. Variation in the logarithmic equilibrium constant (log *K*) values of optode membranes with varying mixing ratios of the membrane solvents.

Application of the $\lambda_{\max}$-Tunable Sensing System to Neutral Ionophore-Based Ion-Selective Optodes. The above-described fundamental studies were applied to a neutral ionophore-based ion-selective optode having a $\lambda_{\max}$-tunable characteristic in the detection wavelength. Panels a and b of Figure 7 show the typical absorption spectra as the response of the lithium ion-selective optodes based on KD-M11 and a highly lithium ion-selective ionophore TTD14C4 using NPOE and NPOE-OH, respectively. A typical spectrum for the optodes for the sample solution of 1 M lithium ion at pH 7.0 is also shown in Figure 7a in order to determine the $\lambda_{\max}$ value accurately. The $\lambda_{\max}$ values were changed

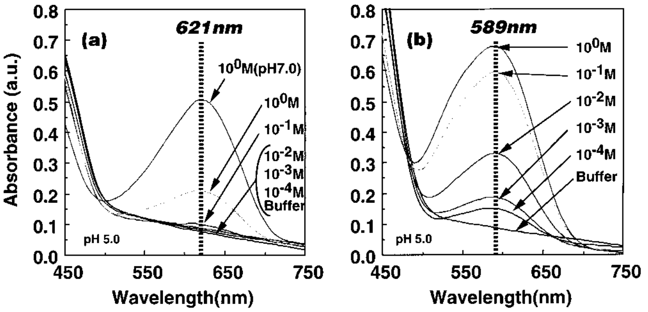

Figure 7. Typical absorption spectra of the lithium ion-selective optode membranes based on KD-M11 and TTD14C4 at pH 5.0: (a) NPOE-based membrane; (b) NPOE-OH-based membrane.

from 621 to 589 nm by substituting the membrane solvent of NPOE into NPOE-OH. In this case, the λ_{max} value using NPOE-OH and TTD14C4 was almost unchanged compared with that in the case where the TMA cation was extracted using an NPOE-OH-based optode membrane without the ionophore. When NPOE was used as the membrane solvent, the λ_{max} value was shifted 28 nm to a lower wavelength region. This result is attributed to the difference in polarity between the TMA cation and the TTD14C4–lithium ion complex in the membrane phase, because the lithium ion is the smallest cation of the alkali metal cations and has a high surface charge density compared with that of TMA. The TTD14C4–lithium ion complex affects the polarity of a relatively low polarity solvent such as NPOE. This fact indicates that the cation–ionophore complex structure in the optode membrane should be taken into consideration, when we prepare the λ_{max}-tunable ion-selective optode.

Comparing the response curves shown in Figure 7, differences in the response concentration range were observed. Figure 8 shows the response curves of the optodes based on KD-M11 and TTD14C4 for lithium ion using different membrane solvents (NPOE or NPOE-OH) at pH 5.0. By substituting the membrane solvent NPOE into NPOE-OH, the optode responds to a lower concentration of lithium ion as shown in Figure 8. In this case, the response curve was shifted 3 orders of magnitude in maximum to a lower concentration region. This value was quite comparable to that of the results for *K* values discussed earlier in this section based on the curves shown in Figure 6. Thus the response range of a λ_{max}-tunable ion-selective optode can be determined using the log *K* graphs as shown in Figure 6.

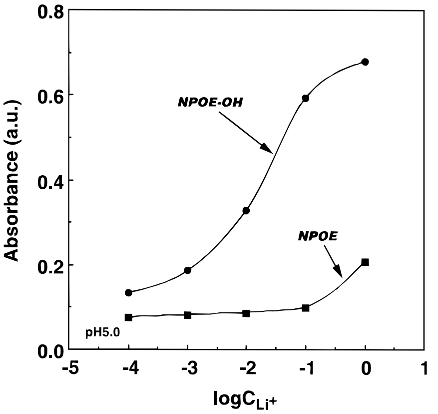

Figure 8. Response curves of the lithium ion-selective optode membranes based on KD-M11 and TTD14C4 at pH 5.0 using different membrane solvents.

CONCLUSIONS

In this report, two kinds of MIDs (KD-M9 and KD-M11) were utilized for the development of a novel λ_{max}-tunable ion-selective optode as one applicational example of MIDs. By employing a binary membrane solvent mixture, the detecting λ_{max} positions of the optode were successfully controlled with a single indicator dye. This technique is practically useful for the wavelength matching between a light source and an optode membrane, so that the optode has optimum sensitivity.

We here demonstrate the preparation of the lithium optode. Other ion-selective optodes could be prepared with the similar optode membrane components by substituting a suitable ionophore.

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