

Supporting Information

for

Covalently Attached Ionophores to Extend the Working Range of Potentiometric pH Sensors with Poly(decyl methacrylate) Sensing Membranes

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Materials

2,2-Dimethoxy-2-phenylacetophenone (DMPA), 1,6-hexanediol dimethacrylate, magnesium sulfate, sodium chloride, lithium chloride, lithium hydroxide, tripropylamine, methacryloyl chloride, diisopropylamine, 3-pyridinepropanol, lithium aluminum hydride, dichloromethane, 4-methoxyphenol, boric acid, ammonium chloride, and triethylamine were purchased from Sigma Aldrich (St. Louis, MO, USA). Decyl methacrylate (DMA, 97%) was purchased from Pfaltz & Bauer (Waterbury, CT, USA). Chloroform-*d* was purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Potassium chloride, potassium hydroxide, basic alumina, sodium hydroxide, anhydrous ethyl ether, phosphoric acid, and tetrahydrofuran were purchased from Fisher Chemical (Lenexa, KS, USA). Nanographite powder (GS-4827, BET surface area of 250 m²/g, particle size distribution from 0.10 μm to 10 μm) and potassium tetrakis(pentafluorophenyl)borate (KTPFB) were purchased from Alfa Aesar (Tewksbury, MA, USA). Potassium hydrogen phthalate and pH 4, 7, and 10 buffer solutions were purchased from Thermo Fisher Scientific (Waltham, MA, USA). DMA, 1,6-hexanediol dimethacrylate and anhydrous inhibitor-free tetrahydrofuran (THF) were passed through basic alumina before use. All sample solutions were prepared with deionized and charcoal-treated water (18.2 MΩ/cm specific resistance) using a Milli-Q Plus reagent-grade water system (Millipore, Bedford, MA, USA).

Synthesis of 3-(pyridin-3-yl)propyl methacrylate

For the synthesis of this covalently attachable pyridine-based ionophore, a literature procedure was modified.^{1,2} A mixture of 3-(pyridin-3-yl)propanol (1 mL, 7.7 mmol, 1.00 equivalent) and triethylamine (1.9 mL, 13 mmol, 1.75 equivalents) in dichloromethane (20.0 mL, dried over molecular sieves) was stirred at 0 °C under argon for 15 min. Methacryloyl chloride (1 mL, 7.7 mmol, 1.00 equivalent) was then added dropwise over 30 min, and stirring continued for 5 h at room temperature. The reaction solution was washed twice with a saturated aqueous solution

of ammonium chloride (2×20 mL) and then with deionized water (1×20 mL). The combined aqueous layers were extracted with dichloromethane (2×20 mL), and 100 ppm 4-methoxyphenol was added to the combined dichloromethane phases to prevent polymerization. Upon drying with anhydrous sodium sulfate and filtering off of all solids, the dichloromethane was evaporated with a rotary evaporator, and the resulting product was dried overnight on the vacuum, giving a slightly brown oil (95% yield). The identity and purity of the final product was confirmed by ^1H NMR spectroscopy (Figure S1).

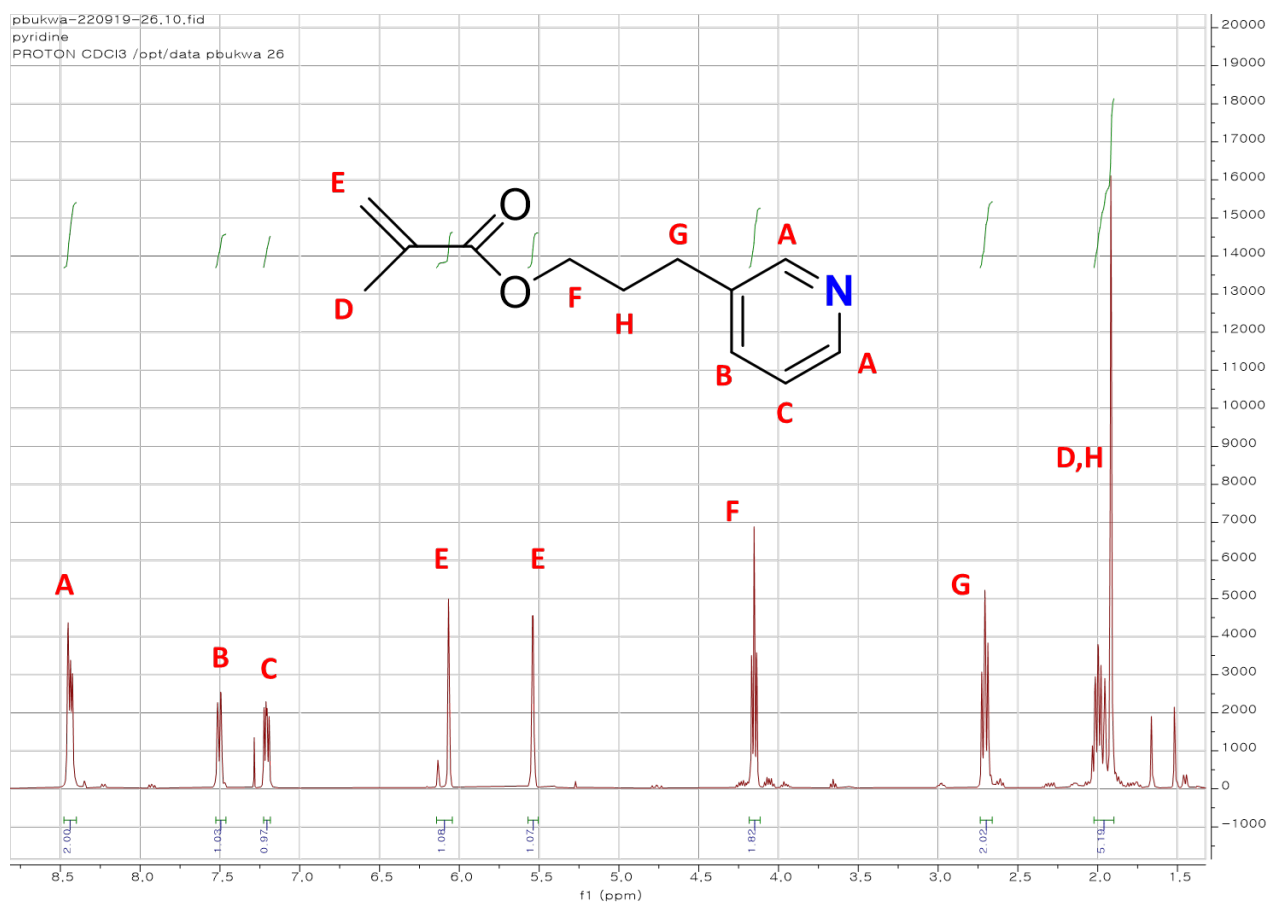


Figure S1. A covalently attachable ionophore with a pyridine group: ^1H NMR spectrum (CDCl_3) of 3-(pyridine-3-yl)propyl methacrylate.

Synthesis of 10-(diisopropylamino)decyl methacrylate^{3,4}

A solution of diisopropylamine (1.56 mL, 8.96 mmol, 2.0 equivalents) in dry dichloromethane (20 mL) was added dropwise over 20 min to a precooled solution of methyl sebacoyl chloride (1.05 g, 4.48 mmol, 1 equivalent) in dry dichloromethane (20 mL). The solution temperature was kept in the range of 10–15 °C using an ice–water bath. The reaction solution was then kept at room temperature for 4 h, followed by quenching with 2% aqueous HCl solution (30 mL). After 5 min of stirring, the dichloromethane phase was separated, the aqueous layer was extracted with additional portions of dichloromethane (2x15 mL), and 100 ppm 4-methoxyphenol was added to the combined dichloromethane phases to prevent polymerization. The dichloromethane solution was then dried over anhydrous sodium sulfate, all solids were filtered off, and the solvent was evaporated on a rotary evaporator, giving a 75% yield of a colorless oil (Figure S2).

To reduce simultaneously the amido and ester groups of the thus obtained monoamide monoester, 1.7 g (0.60 mol) of the above raw product was dissolved in 20 mL anhydrous THF, the solution was kept under a nitrogen atmosphere and cooled with an ice–water bath to maintain the temperature at 4 °C, and LiAlH₄ (0.40 g, 0.96 mol) was added. After 10 min, the temperature of the mixture was raised to 50 °C and kept there overnight. The reaction mixture was then diluted with diethyl ether, cooled to 0 °C using an ice–water bath, and quenched by slowly adding 2 mL water, followed by 2 mL 15% aqueous NaOH, and 32 mL water. After warming to room temperature and stirring for 15 min, the organic phase was separated off, 10 g anhydrous magnesium sulfate were added for drying, the suspension was stirred for 15 min, the solids were filtered off, the solvent was evaporated, and the resulting raw product was purified by flash chromatography over a silica gel column with 50% hexane/50% ethyl acetate as eluent (see Figure S3 for the ¹H NMR spectrum). The resulting product was a colorless oil (48% yield).

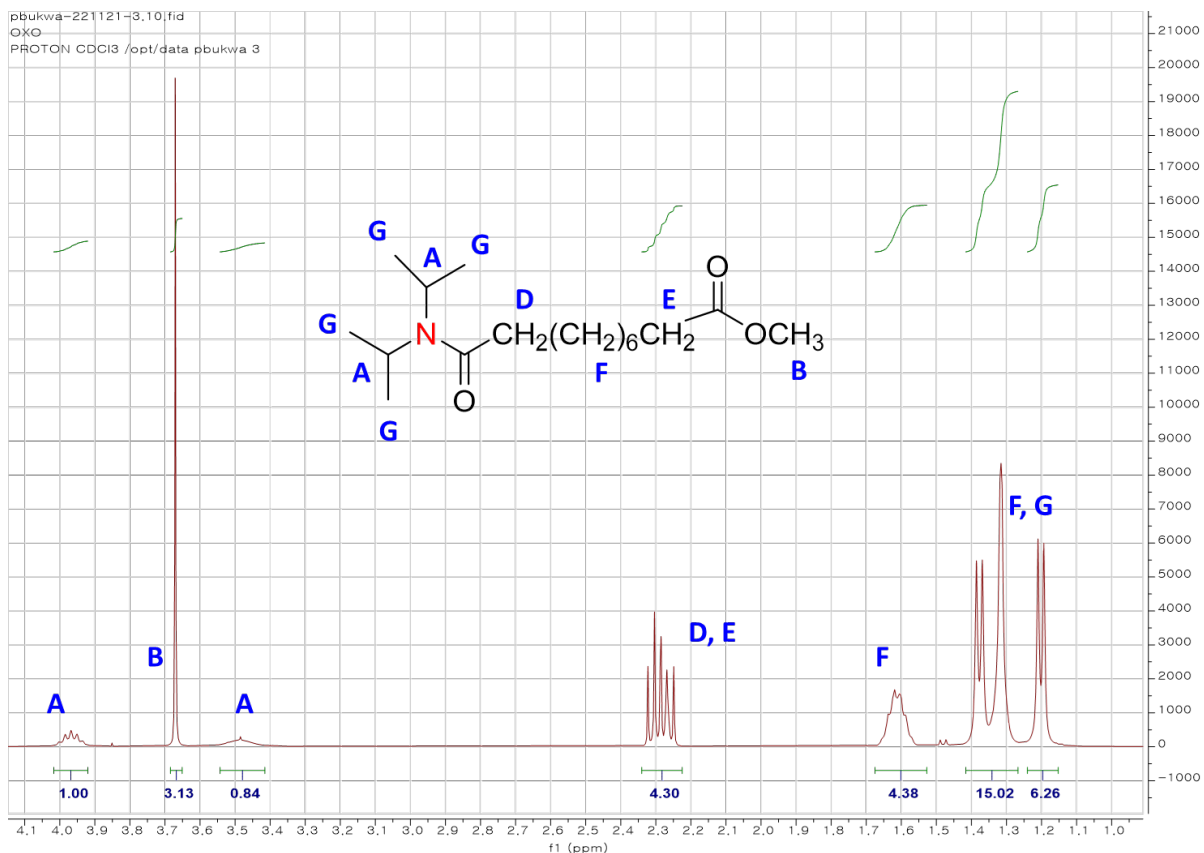


Figure S2. Synthesis of a covalently attachable ionophore with a tertiary amino group: ¹H NMR spectrum (CDCl₃) of the intermediate methyl 10-(diisopropylamino)-10-oxodecanoate.

A solution of the thus obtained amino-substituted alcohol (1.0 g, 3.9 mmol, 1.00 equivalent) and triethylamine (0.99 g, 9.75 mmol, 2.50 equivalent) in dried dichloromethane (20.0 mL) was stirred at 0 °C under argon atmosphere for 30 min. Methacryloyl chloride (0.69 g, 6.63 mmol, 1.70 equivalent) was then added dropwise during 30 min and stirring continued overnight at room temperature. The reaction solution was washed twice with a saturated aqueous ammonium chloride solution (2 × 20 mL) and then with deionized water (2 × 20 mL). The combined aqueous layers were extracted with dichloromethane (3 × 30 mL), all organic layers were combined, and 100 ppm 4-methoxyphenol was added as a polymerization inhibitor. The solution was dried over anhydrous sodium sulfate, all solids were filtered off, the solvent

was evaporated on a rotary evaporator, and the resulting product was dried on the vacuum leading to a colorless oil (70 % yield from the amino-substituted alcohol). The identity and purity of the final product was confirmed by ^1H NMR spectroscopy (Figure S4).

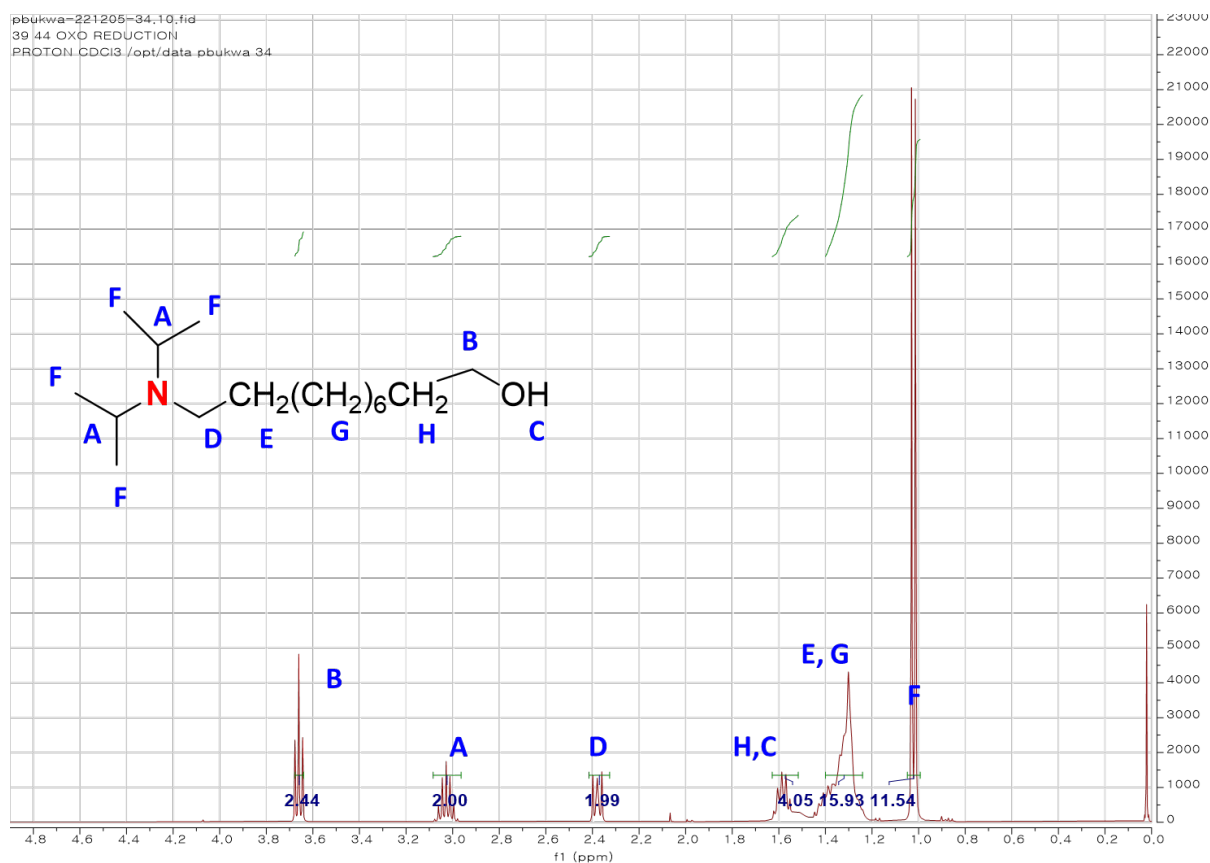


Figure S3. Synthesis of a covalently attachable ionophore with a tertiary amino group: ^1H NMR spectrum (CDCl_3) of 10-(diisopropylamino)decan-1-ol.

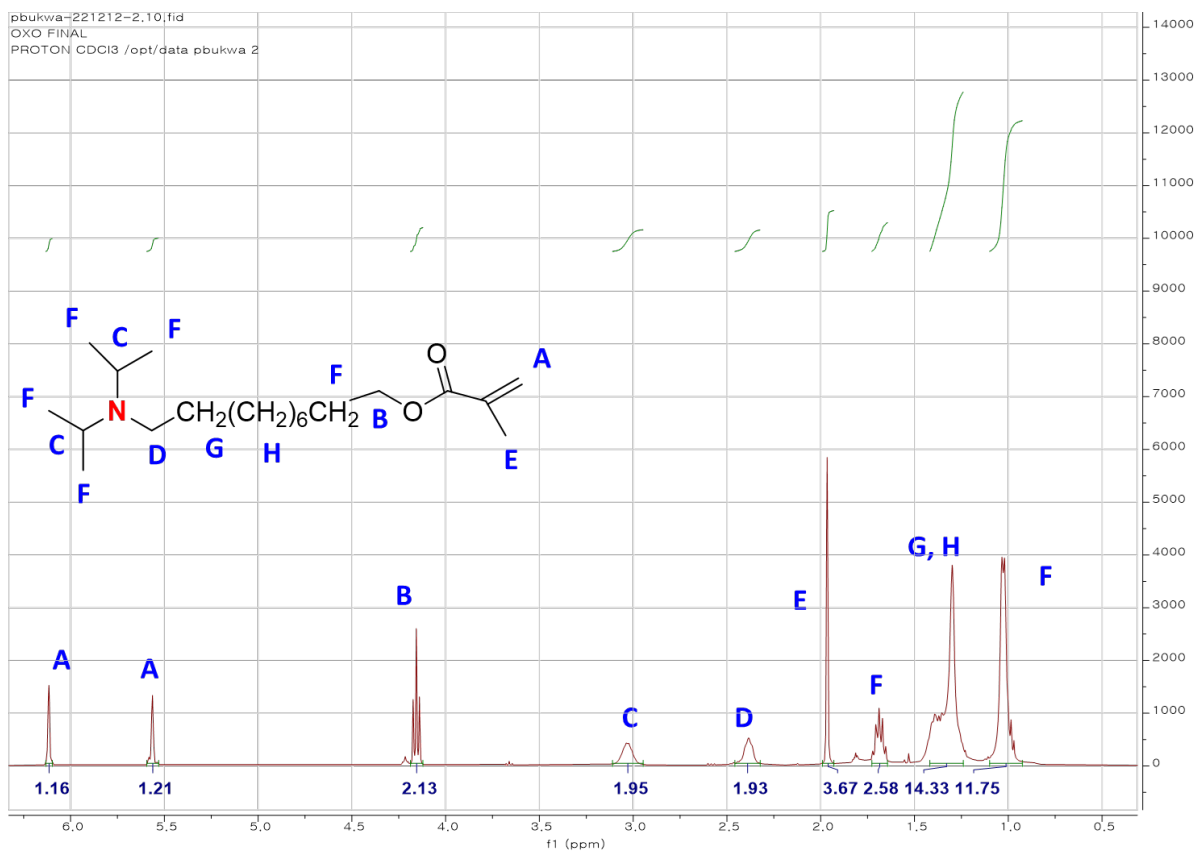


Figure S4. A covalently attachable ionophore with a tertiary amino group: ¹H NMR spectrum (CDCl₃) of 10-(diisopropylamino)decyl methacrylate.

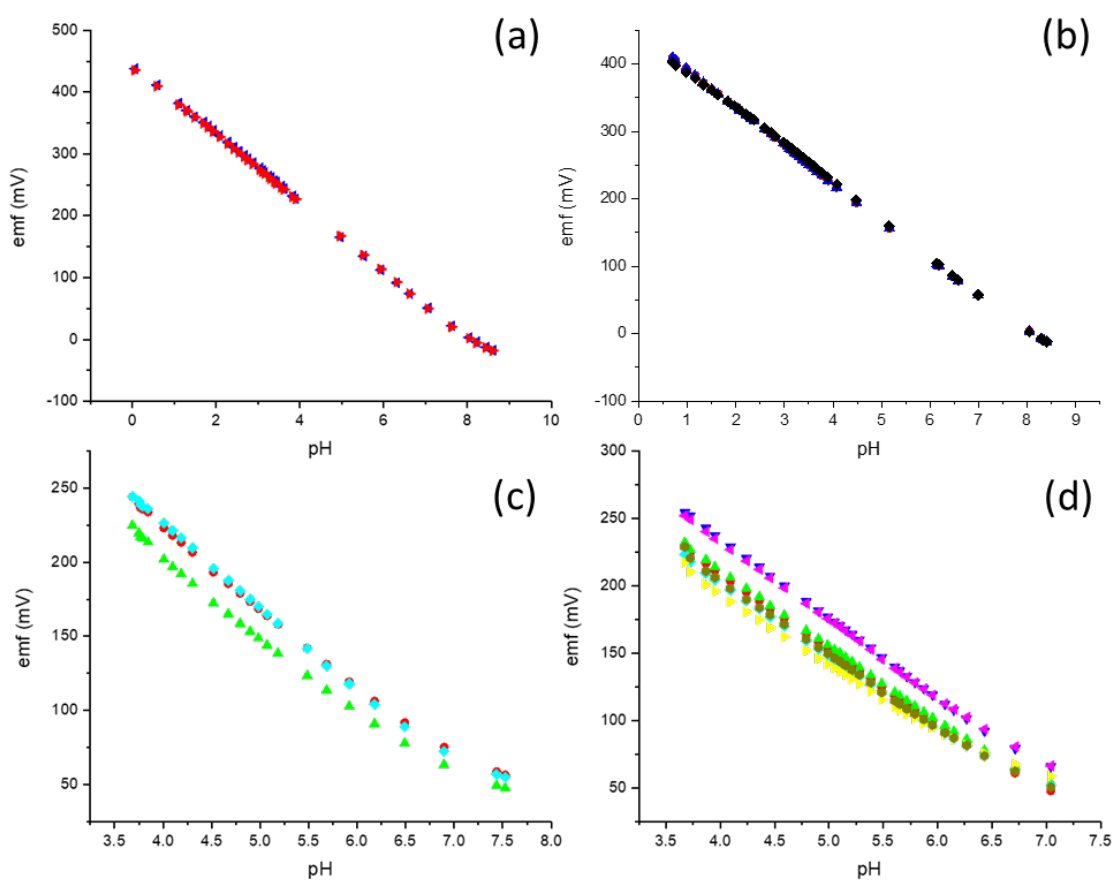


Figure S5. Upper detection limits of pH ISEs comprising the less basic ionophore from this work (**3**) in aqueous samples with backgrounds of different counter ions. (a) Nitrate: The electrodes were placed in 1.0 mM sodium borate buffer (pH=8.5) for one day. The pH was adjusted by addition of 1.0 M HNO₃. (b) Chloride: The electrodes were placed in 1.0 mM sodium borate buffer (pH=8.5) for one day. The pH was adjusted by additions of 1.0 M HCl. (c) Hydrogen phthalate: The electrodes were placed in 1.0 mM sodium borate buffer (pH=8.5). The pH was adjusted by addition of 1.0 M potassium hydrogen phthalate. (d) Hydrogen phthalate: The electrodes were placed in 1.0 mM sodium borate buffer (pH=8.5) and 10 mM potassium hydrogen phthalate for one day. The pH was adjusted by addition of 1.0 M potassium hydrogen phthalate.

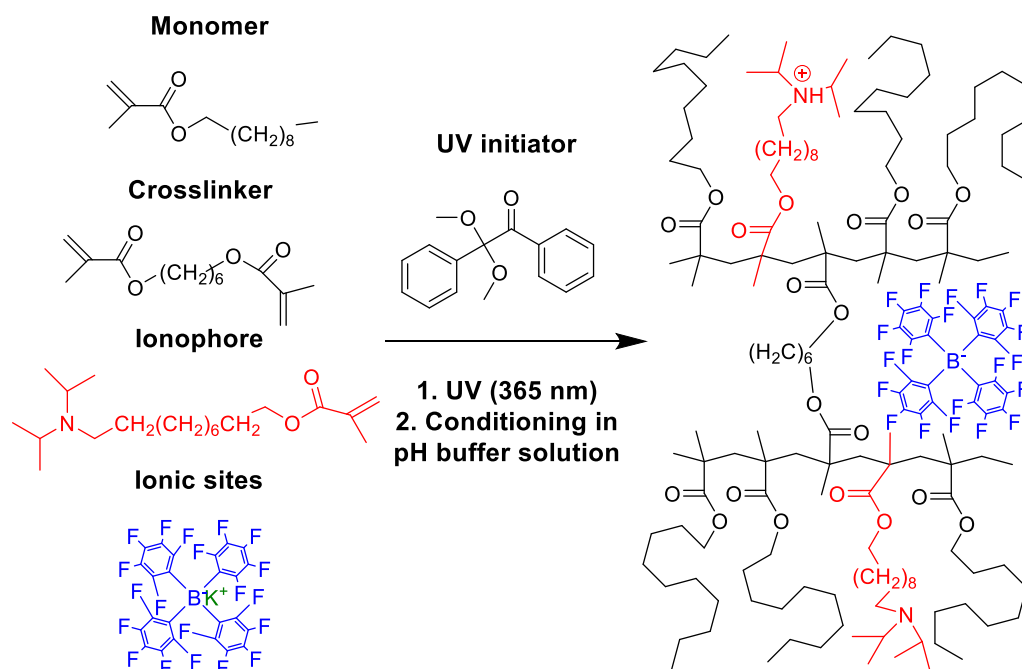


Figure S6. Photopolymerization of DMA membranes with covalent attachment of tertiary amine-based ionophore **4**. Matrix monomer: decyl methacrylate; crosslinker: hexanediol dimethacrylate; ionophore: 10-(diisopropylamino)decyl methacrylate, ionic sites monomer: potassium tetrakis(pentafluorophenyl)borate (blue); and UV-initiator: 2,2-dimethoxy-2-phenylacetophenone.

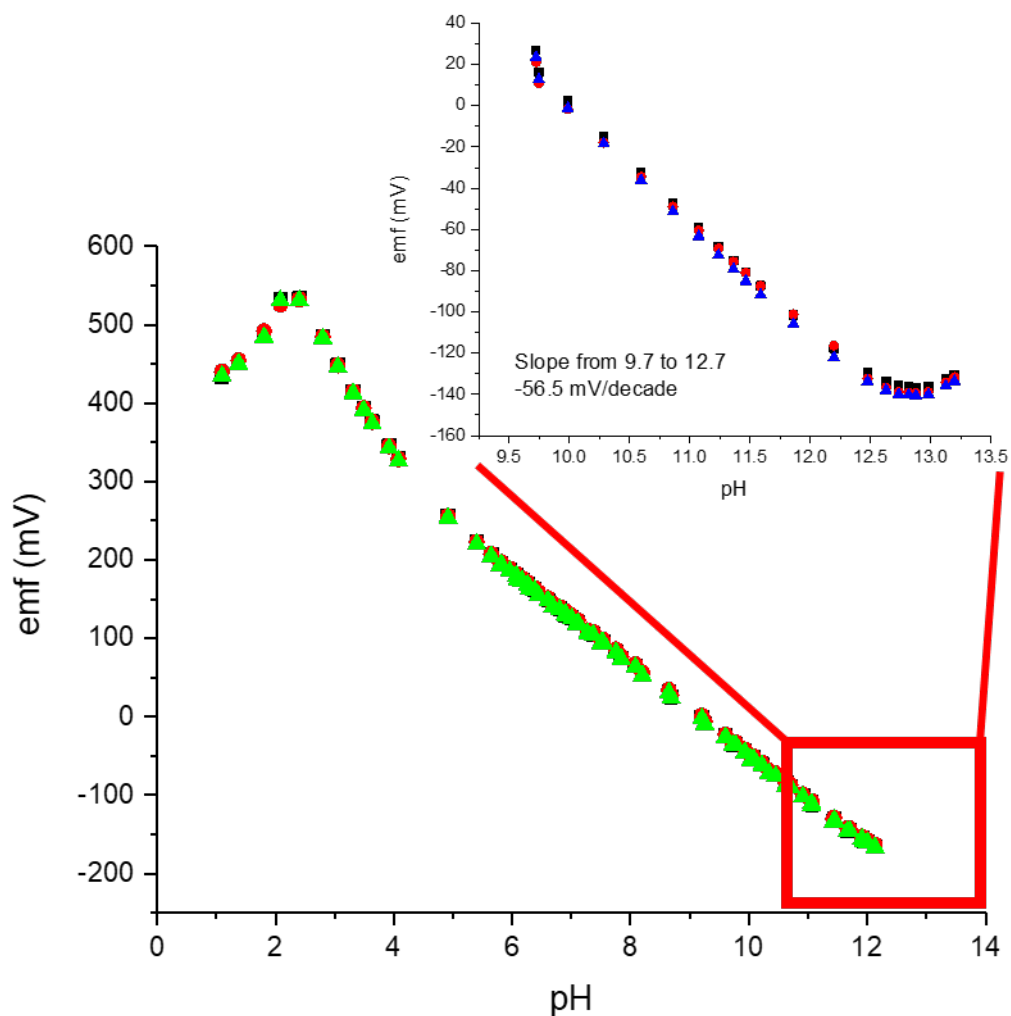


Figure S7. Working range of three identically prepared DMA-based pH ISEs based on the covalently attachable tertiary amine-based ionophore **4**: The pH was adjusted by addition of 1.0 M HCl or 1.0 M NaOH to the pH buffer, with an initial pH 7.1 of 10 mM sodium phosphate buffer background. The pH shown on the x-axis was measured using a pH glass electrode, and emf values were determined relative to a free-flowing double-junction reference electrode.

References

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