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Facile synthesis of five 2D surface modifiers by highly selective photocyclic aromatization and efficient enhancement of oxygen permselectivities of three polymer membranes by surface modification using a small amount of the 2D surface modifiers

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ABSTRACT

A facile synthesis of novel five 2D (planar) surface modifiers having a triphenylbenzene derivatives as a 2D structure has been achieved by the highly selective photocyclic aromatization reaction. Efficient enhancement of oxygen permselectivities through the three polymer membranes has been achieved by adding a small amount (<5.0 wt%) of the 2D surface modifiers. Among the five 2D surface modifiers, a modifier compound having oligoethylene oxide groups showed the best performance for the enhancement. These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated. In some of the surface-modified blend membranes, their plots in the P_{O_2}-α graph were over or close to the upper boundary line by Robeson in 1991. Since all the membranes containing the 2D surface modifiers showed better permselectivities than the corresponding substrate membranes, it is very promising for the future.

1. Introduction

Permselective membranes separating gases such as oxygen and nitrogen have many practical uses to solve environmental and energy problems. So, many studies have been reported on such membranes in the form of not only organic polymers but also inorganic compounds [1–24]. The requirements for oxygen permselective membranes are (1) a high permeability coefficient (P_{O_2}: $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$), (2) a high separation factor ($\alpha = P_{O_2}/P_{N_2}$), and (3) good membrane forming ability (high mechanical strength). However, it has proven difficult to realize all three requirements at the same time in almost all membrane materials reported. For example, membranes having higher P_{O_2} values had lower α values, and membranes having higher α values had lower P_{O_2} values, that is, P_{O_2} and α showed a tradeoff relationship [1–24]. Also membranes having higher P_{O_2} values tended to be too flexible and those having higher α values tended to be too brittle.

To solve the above problems, that is, to obtain materials that simultaneously satisfy the above three requirements, we reported surface modifications of conventional polymer membranes having enough mechanical strength by solvent casting of a mixture of small amounts of surface active polymers and the conventional base polymers [25–27]. It was an effective method to enhance α with a small decrease in P_{O_2}, while resulting in no change to the good membrane forming abilities of the base polymers. Although similar reports have been made for nanofiltration of aqueous solution [28–30], to the best of our knowledge, there have been no reports except for our group [25–27] on such methods of surface modifications of membranes for enhancing gas separation selectivities. However, the extent of enhancement of α was not enough.

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In this study, to improve the effectiveness of the surface modifiers, five kinds of 2D(=a planar structure) surface modifiers were designed (Chart 1). They have a π-conjugated planar (2D) part, hydroxyl groups, and hydrophilic or hydrophobic groups.

We have reported recently a novel polymer reaction called SCAT (highly selective photocyclic aromatization reaction) (Scheme 1) [31]. It quantitatively gives 1,3,5-triphenylbenzene derivatives having six hydroxyl groups and any kinds of three substituents by a simple procedure (using only light irradiation) in high conversions and selectivity. In addition the reaction has good tolerance for many kinds of functional groups. These advantages of SCAT are very useful for the synthesis of 2D surface modifiers having different kinds of functional groups and therefore we selected SCAT as the synthetic route in this study. In this article, a facile synthesis of the 2D surface modifiers by the SCAT reaction and enhancement of α by surface modification using the 2D surface modifiers are reported.

2. Experimental

2.1. Material

All the solvents except for tetrahydrofuran(THF) used for monomer synthesis and polymerization were distilled as usual. Dry THF (99.5% purity) purchased from Kanto chemistry was used. The polymerization initiator, $[Rh(nbd)Cl]_2$ (nbd = 2,5-norbornatiene) purchased from Aldrich Chemistry was used as received. Poly(vinyl alchohol)(PVA) purchased from Wako Pure Chemistry Industries, Ltd. was used as received. 1-Phenyl-2-*p*-(trimethylsilyl)phenylacetylene (DPA) [32] and *p*-(trimethylsilyl)phenylacetylene(SPA) [33] were synthesized and polymerized according to the literature.

2.2. Synthesis of new 2D surface modifiers(***T-R***)(Chart 2)(Scheme 2)

2.2.1. Synthesis of the monomers (***M-R***) (Scheme 3)

2.2.1.1. Synthesis of ***M-EO***, ***M-Do*** and ***M-S3*** (Scheme 3)

*2.2.1.1.1. Synthesis of 3,5-bis(hydroxymethyl)-4-{2-(1,4,7-trioxa octyl)phenylmethyl}oxy-1-phenylacetylene (**M-EO**) (Scheme 3).* According to the synthetic route shown in Scheme 3, **M-EO** was synthesized via compounds **1-7** in 8.1% as a total yield. All the following reaction procedures were conducted under dry nitrogen.

*2.2.1.1.2. 4-Bromo-2,6-bis(hydroxymethyl)-1-phenol (**1**) (Scheme 3) [34].* According to the literature, **1** was prepared. Yield: 56.8% (114 g). ^1H NMR (DMSO-d_6, TMS): $\delta = 8.16$ (s, 1H, PhO*H*), 7.29(s, 2H, (Ph*H*)$_2$), 5.31(t, 2H, *J* = 5.0 Hz, (CH$_2$O*H*)$_2$), 4.51(d, 4H, *J* = 5.0 Hz, (C*H*$_2$OH)$_2$).

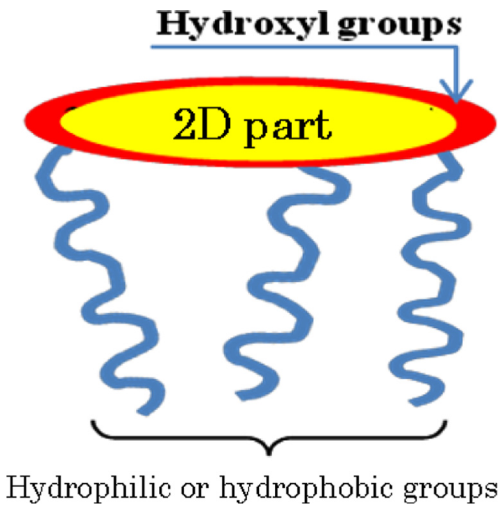


Chart 1. Molecular design of the 2D surface modifier.

*2.2.1.1.3. 2,6-Bis(acetoxymethyl)-4-bromo-1-phenyl acetate (**2**) (Scheme 3).* To a pyridine solution (50 mL) of **1** (10.0 g, 42.9 mmol), acetic anhydride (30.0 mL, 317 mmol) was added dropwise at 0 °C. The solution was stirred for 1.5 h at room temperature and ethyl acetate (100 mL) was added to the mixture. The mixture was washed with a saturated aqueous solution of $CuSO_4 \cdot 5H_2O$ to remove pyridine and extracted with CH_2CL_2. The organic layer was dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **2** as a white solid. Yield: 78.4% (12.1 g). Rf = 0.30 (ethyl acetate/hexane = 1/2 (v/v)). ^1H NMR (DMSO-d_6, TMS): $\delta = 7.56$ (s, 2H, ((Ph*H*)$_2$)), 4.97(s, 4H, Ph(C*H*$_2$O)$_2$), 2.34(s, 3H, PhOCOC*H*$_3$), 2.09(s, 6H, Ph(CH$_2$OCOC*H*$_3$)$_2$).

*2.2.1.1.4. 2,6-Bis(acetoxymethyl)-4-(trimethylsilylethynyl)-1-phenyl acetate (**3**) (Scheme 3).* A mixture of **2** (11.8 mg, 32.9 mmol), triphenylphosphine (610 mg, 2.33 mmol), copper iodide (752 mg, 3.95 mmol) and trimethylsilylacetylene (6.50 mL, 45.7 mmol) in triethylamine (130 mL) was refluxed for 24 h. After the mixture was filtered, the solvent was removed by evaporation and the crude product was purified by silica-gel column chromatography to give **3** as a brown liquid. Yield: 95.6% (11.8 g). Rf = 0.30 (ethyl acetate/hexane = 1/3 (v/v)). ^1H NMR ($CDCl_3$, TMS): $\delta = 7.53$ (s, 2H, (Ph*H*)$_2$), 4.98 (s, 4H, Ph(C*H*$_2$OAc)$_2$), 2.32(s, 3H, PhOCOC*H*$_3$), 2.06(s, 6H, Ph(CH$_2$OCOC*H*$_3$)$_2$), 0.22(s, 9H, Si(C*H*$_3$)$_3$).

*2.2.1.1.5. 2,6-Bis(acetoxymethyl)-4-ethynyl phenol (**4**) (Scheme 3).* To a mixture of lithium hydride (3.00 g, 79.1 mmol) and THF (120 mL), a THF solution (15 mL) of **3** (14.9 g, 39.5 mmol) was added dropwise at 0 °C. After the mixture was stirred for 2 h at room temperature, deionized water (140 mL) was added dropwise into the reaction mixture at 0 °C. The mixture was stirred for 12 h at room temperature and was treated with a 2N HCl aq. solution to precipitate aluminum salts. After the mixture was filtered, THF was removed from the solution by evaporation. The product was dissolved in ethyl acetate and the solution was washed with water and extract by CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **4** as a white solid. Yield: 70.3% (4.90 g). Rf = 0.39 (ethyl acetate/hexane = 2/3 (v/v)). ^1H NMR (DMSO-d_6, TMS): $\delta = 8.98$(s, 1H, PhO*H*), 7.27(s, 2H, (Ph*H*)$_2$), 4.52(s, 4H, *J* = 5.0 Hz, Ph(C*H*$_2$OH)$_2$), 3.91(s, 1H, *H*C≡C), 3.31(t, 2H, *J* = 5.0 Hz, (CH$_2$O*H*)$_2$).

*2.2.1.1.6. 2-(2-Methoxyethoxy)ethyl 4-methylbenzenesulfonate (**5**) (Scheme 3).* To a mixture of sodium hydride (3.50 g, 87.6 mmol) and THF (50 mL), **4** (7.80 mL, 65.7 mmol) was added dropwise at 0 °C. Then *p*-toluenesulfonyl chloride (10.4 g, 54.7 mmol) dissolved in THF (20 mL) was added dropwise at 0 °C. The solution was stirred for 9 h at room temperature and the reaction mixture was treated with a 4N HCl aq. solution until the pH read 4 and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **5** as a colorless viscous liquid. Yield: 64.3% (9.60 g). Rf = 0.39 (ethyl acetate/hexane = 1/1 (v/v)). ^1H NMR ($CDCl_3$, TMS): $\delta = 7.80$ (d, 2H, *J* = 8.5 Hz, (Ph*H*)$_2$), 7.34(d, 2H, *J* = 8.5 Hz, (Ph*H*)$_2$), 4.17(t, 2H, *J* = 4.6 Hz, OC*H*$_2$CH$_2$), 3.69(t, 2H, *J* = 4.6 Hz, OCH$_2$C*H*$_2$O), 3.57 (t, 2H, *J* = 4.3 Hz, OC*H*$_2$-CH$_2$OCH$_3$), 3.47(t, 2H, *J* = 4.3 Hz, OCH$_2$C*H*$_2$OCH$_3$), 3.35(s, 3H, OC*H*$_3$), 2.45(s, 3H, PhC*H*$_3$).

*2.2.1.1.7. 2-{2-(2-Methoxyethoxy)ethoxy}-1-phenylmethynol (**6**) (Scheme 3).* To a mixture of 2-hydroxybenzyl alcohol (5.00 mg, 40.3 mmol), potassium carbonate (11.1 g, 80.6 mmol), and 18-crown-6 (5.35 mg, 20.1 mmol) in dry acetone (200 mL), **5** (12.1 g, 44.3 mmol) dissolved in dry acetone(10 mL) was added dropwise at

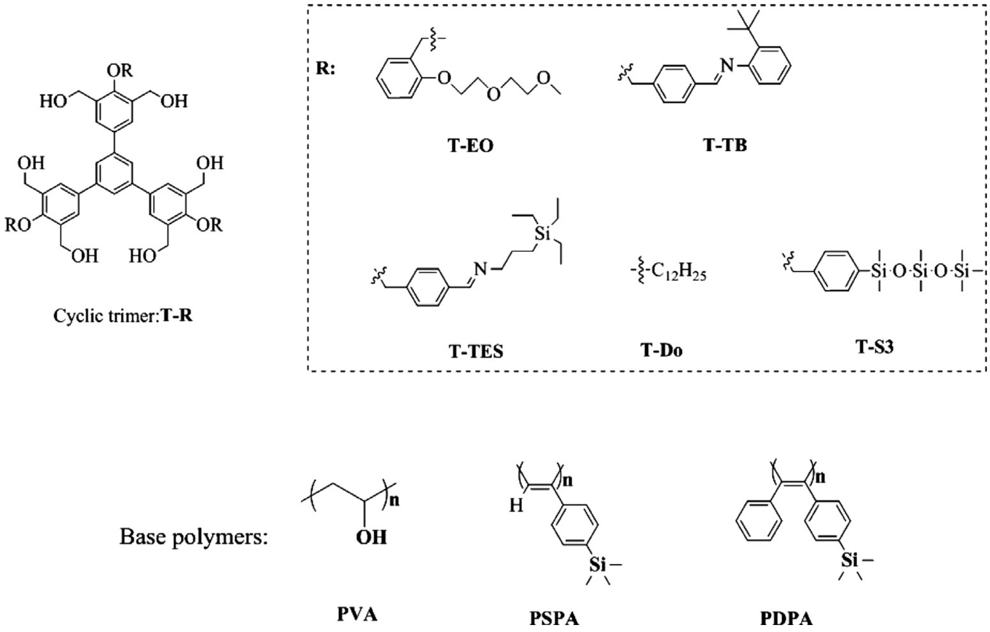
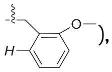
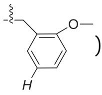
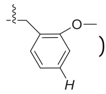
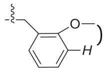
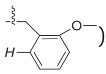
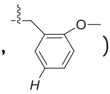
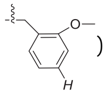
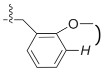
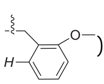
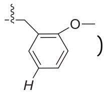
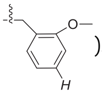
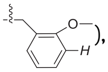
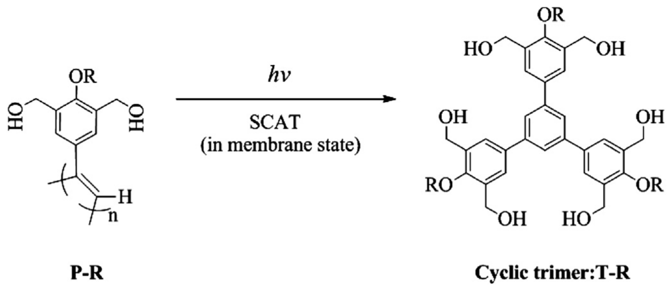


Chart 2. Chemical structures of the 2D surface modifiers.

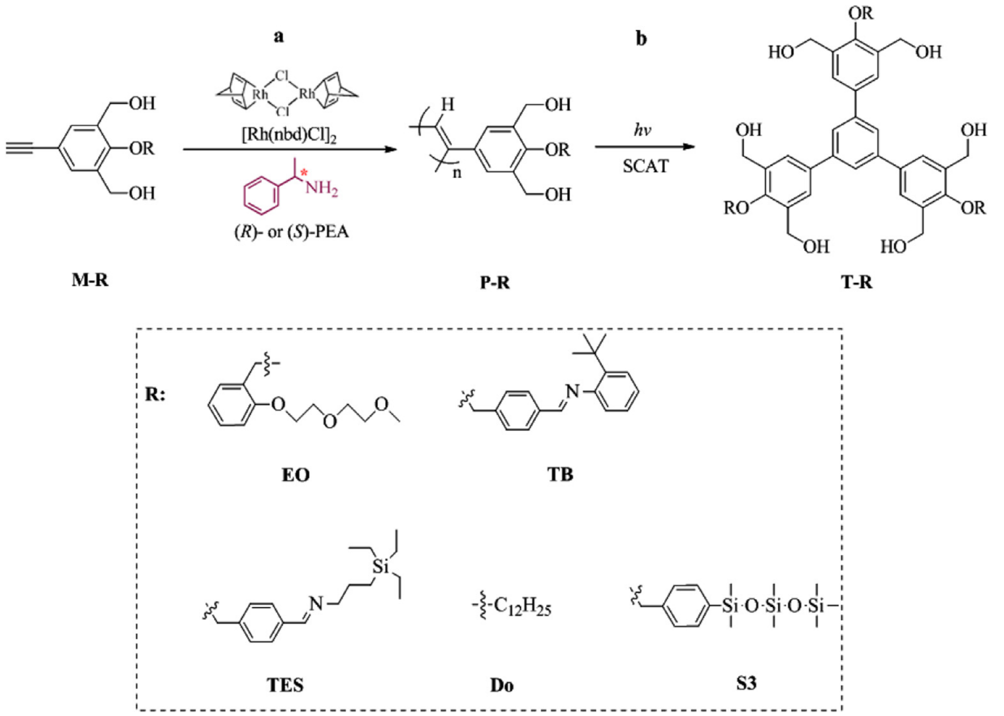
0 °C. This solution was refluxed for 48h and allowed to stand for 2 h at 25 °C. After the mixture was filtered, deionized water was added to the resulting solution and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with a 2N HCl aq. solution and dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **6** as a colorless viscous liquid. Yield: 66.2% (6.00 g). Rf = 0.31 (ethyl acetate/hexane = 1/1 (v/v)). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 7.35$(d, 1H, $J = 7.6$ Hz, ), 7.24(dd, $J = 7.6$ Hz, $J = 8.4$ Hz, 1H, ), 7.02(dd, 1H, $J = 8.4$ Hz, $J = 8.0$ Hz, ), 6.90(d, 1H, $J = 8.0$ Hz, ),4.65(d, 2H, $J = 5.0$ Hz, $PhCH_2OH$), 4.18(t, 2H, $J = 4.6$ Hz, $PhOCH_2CH_2$), 3.83(t, 2H, $J = 4.6$ Hz, $PhOCH_2CH_2O$), 3.67(t, 2H, $J = 4.3$ Hz, $OCH_2CH_2OCH_3$), 3.54(t, 2H, $J = 4.3$ Hz, $OCH_2CH_2OCH_3$), 3.36(s, 3H, OCH_3), 3.33(t, 1H, $J = 5.0$ Hz, CH_2OH).

*2.2.1.1.8. 1-(1,4,7-Trioxaoctyl)-2-(bromomethyl)benzene (**7**) (Scheme 3).* To a solution of **6** (5.71 g, 25.2 mmol) dissolved in CH_2Cl_2 (200 mL), triphenylphosphine (10.0 g, 38.2 mmol) dissolved in CBr_4 (14.2 g, 42.9 mmol) were added dropwise at 0 °C. This solution was stirred at 0 °C for 1 h and a saturated $NaCO_3$ aq. solution was added to quench the reaction. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was washed with a saturated $NaCO_3$ aq. solution and dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **7** as a colorless viscous liquid. Yield: 86.5% (6.30 g). Rf = 0.50 (ethyl acetate/hexane = 3/1 (v/v)). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 7.40$(d, 1H, $J = 7.6$ Hz, ), 7.28(dd, $J = 7.6$ Hz, $J = 8.4$ Hz, 1H, ), 7.01(dd, 1H, $J = 8.4$ Hz, $J = 8.0$ Hz, ), 6.95(d, 1H, $J = 8.0$ Hz, ), 4.57(s, 2H, $PhCH_2Br$), 4.15(t, 2H, $J = 4.6$ Hz, $PhOCH_2CH_2$), 3.86(t, 2H, $J = 4.6$ Hz, $PhOCH_2CH_2O$), 3.72(t, 2H, $J = 4.6$ Hz, $OCH_2CH_2OCH_3$), 3.53(t, 2H, $J = 4.6$ Hz, $OCH_2CH_2OCH_3$), 3.37(s, 3H, OCH_3).

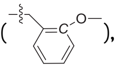
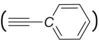
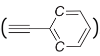
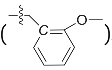
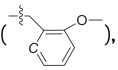
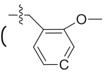
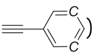
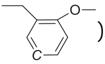
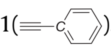
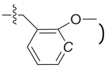
*2.2.1.1.9. 3,5-Bis(hydroxymethyl)-4-{2′-(1,4,7-trioxaoctyl)benzyloxy}-1-phenylacetylene (**M-EO**) (Scheme 3) [35].* To a mixture of **4** (1.10 g, 6.17 mmol), potassium carbonate (1.71 g, 12.3 mmol), and 18-crown-6 (1.79 g, 6.79 mmol) in dry acetone (33 mL), **7** (1.96 g, 6.79 mmol) was added dropwise at 0 °C. This solution was refluxed for 40 h and then allowed to stand for 2 h at 25 °C. After the mixture was filtered, deionized water was added to the resulting solution and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with a 2N HCl aq. solution and dried over anhydrous $MgSO_4$ for 1 h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **M-EO** as a white solid. Yield: 65.0% (1.50 g). Rf = 0.17 (ethyl acetate/hexane = 1/1 (v/v)). ^{1}H NMR ($CDCl_3$, TMS):$\delta = 7.53$(s, 2H, $C{\equiv}C(PhH)_2$), 7.44(d, 1H, $J = 7.6$ Hz, ), 7.34(dd, $J = 7.6$ Hz, $J = 8.4$ Hz, 1H, ), 7.00(dd, 1H, $J = 8.4$ Hz, $J = 8.0$ Hz, ), 6.91(d, 1H, $J = 8.0$ Hz, ), 5.01(s, 2H, $PhOCH_2Ph$), 4.75(d, 4H, $J = 6.0$ Hz,



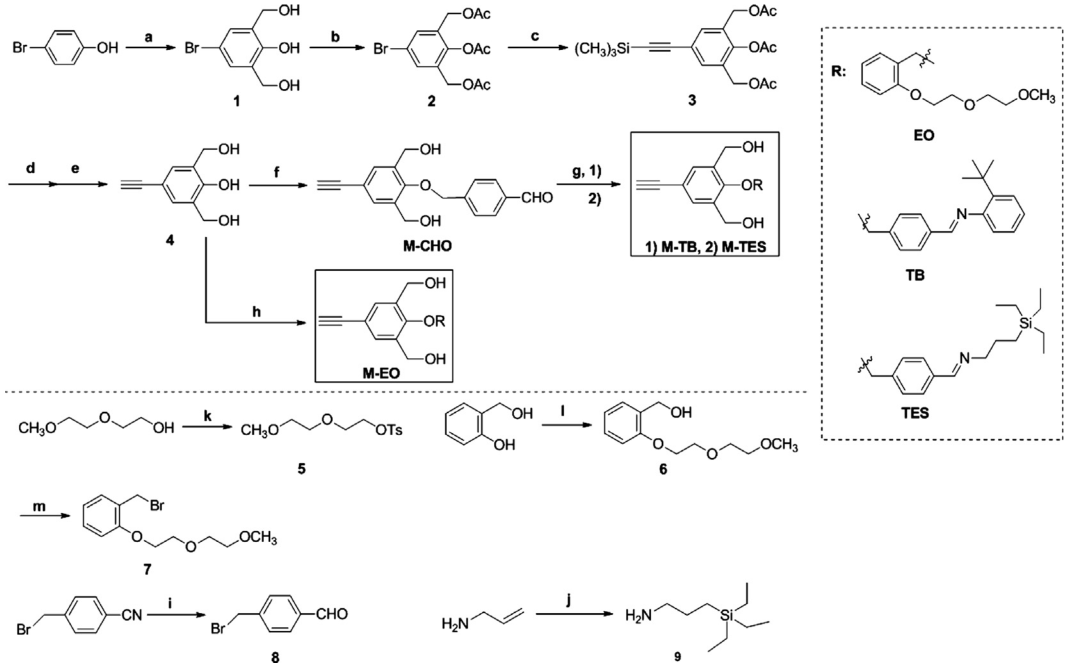
Scheme 1. Highly selective photocyclic aromatization (SCAT).



Scheme 2. Synthesis of the 2D surface modifiers by a) helix-sense-selective polymerization (HSSP) and b) highly selective photocyclic aromatization (SCAT).

$\mathrm{Ph(C}\mathit{H}_2\mathrm{OH)_2}$), 4.19(t, 2H, $J = 4.4$ Hz, $\mathrm{PhOC}\mathit{H}_2\mathrm{CH_2}$), 3.86(t, 2H, $J = 4.4$ Hz, $\mathrm{PhOCH_2C}\mathit{H}_2\mathrm{O}$), 3.71(t, 2H, $J = 4.4$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2OCH_3}$), 3.58(t, 2H, $J = 4.4$ Hz, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{OCH_3}$), 3.36(s, 3H, $\mathrm{OC}\mathit{H}_3$), 3.03(s, 1H, $\mathit{H}\mathrm{C{\equiv}C}$), 2.82(t, 2H, $J = 6.0$ Hz, $\mathrm{Ph(CH_2O}\mathit{H})_2$). ^{13}C NMR ($CDCl_3$, TMS): δ = 157.24(), 155.94(), 135.06(), 133.16(), 131.56(), 130.54(), 125.14, () 121.26(), 118.41(), 111.82(), 83.30($\mathrm{HC{\equiv}}\mathit{C}$), 76.91($\mathrm{H}\mathit{C}\mathrm{{\equiv}C}$), 72.57($\mathrm{Ph\text{-}}\mathit{C}\mathrm{H_2O\text{-}}$), 60.75($\mathrm{\text{-}}\mathit{C}\mathrm{H_2OH}$), 60.75($\mathrm{\text{-}O}\mathit{C}\mathrm{H_2CH_2}$), 67.38($\mathrm{\text{-}OCH_2}\mathit{C}\mathrm{H_2}$), 66.85($\mathrm{O}\mathit{C}\mathrm{H_2CH_2OCH_3}$), 68.97($\mathrm{OCH_2}\mathit{C}\mathrm{H_2OCH_3}$), 56.7($\mathrm{OCH_2CH_2O}\mathit{C}\mathrm{H_3}$). Anal. Cacld for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78; O, 24.84; Found: C, 68.41; H, 6.83; O, 24.76.

*2.2.1.1.10. Synthesis of 3,5-bis(hydroxymethyl)-4-dodecyloxy-1-phenylacetylene (**M-Do**) (Scheme 3) [34].* **M-Do** was synthesized according to our previous paper [30]. ^{1}H NMR ($CDCl_3$, TMS): δ = 7.48(s, 2H, $\mathrm{(Ph}\mathit{H})_2$), 4.70(d, 4H, $J = 5.9$ Hz, $\mathrm{(C}\mathit{H}_2\mathrm{OH)_2}$), 3.88(t, 2H, $J = 6.6$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2}$), 3.04(s, 1H, $\mathrm{C{\equiv}C}\mathit{H}$), 2.11(t, 2H, $J = 5.9$ Hz, $\mathrm{(CH_2O}\mathit{H})_2$), 1.79(quint, 2H, $J = 6.6$ Hz, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.50–1.20(m,



Scheme 3. Synthesis of the monomers(**M-R**) as a material of the 2D surface modifiers.

18H, $OC_2H_4(CH_2)_9CH_3$), 0.89(t, 3H, CH_2CH_3). IR (KBr): 3600–3100(OH), 3308(HC≡C), 3000–2800(CH), 2116(C≡C), 1200–1000(CO) cm^{-1}. Anal. Cacld for $C_{22}H_{34}O_3$: C, 76.70; H, 9.36; O, 13.94; Found: C, 76.65; H, 9.76; O, 13.68.

*2.2.1.1.11. Synthesis of 3,5-bis(hydroxymethyl)-4-{4′-(1-heptamethyltrisiloxanyl)benzyloxy}- 1-phenylacetylene (**M-S3**) (Scheme 3) [36].* **M-S3** was synthesized according to our previous paper [32]. ^{1}H NMR ($CDCl_3$, TMS): δ = 7.59 (d, 2H, J = 8.0 Hz, $PhOCH_2(PhH)_2$), 7.50(s, 2H, C≡C(Ph*H*)$_2$), 7.40(d, 2H, J = 8.0 Hz, Si(Ph*H*)$_2$), 4.96(s, 2H, $PhOCH_2$), 4.67(d, 4H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 3.03(s, 1H, C≡C*H*), 1.96(t, 2H, J = 6.0 Hz, $(PhCH_2OH)_2$), 0.33(s, 6H, $PhSi(CH_3)_2$), 0.06(s, 9H, $Si(CH_3)_3$), 0.03(s, 6H, $OSi(CH_3)_2O$). IR (KBr): 3600–3100(OH), 3312(HC≡C), 2109(C≡C), 1258(SiC) cm^{-1}. Anal. Cacld for $C_{24}H_{36}O_5Si_3$: C, 58.97; H, 7.42; Found: C, 58.96; H, 7.49.

*2.2.1.2. Synthesis of **M-TB** and **M-TES** (Scheme 3).* According to the synthetic route as shown in Scheme 3, **M-TB** and **M-TES** were synthesized via compounds **1-4, M-CHO, 8-9** in 12.0% as a total yield. All the following reaction procedures were conducted under dry nitrogen.

*2.2.1.2.1. Synthesis of 3,5-bis(hydroxymethyl)-4-{4′-(2′′-tert-butyl-1-iminomethyl)benzyloxy}-1-phenylacetylene (**M-TB**) (Scheme 3) [37].* 4-Bromomethylbenzaldehyde(**8**) (Scheme 3)

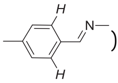
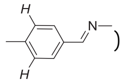
4-bromomethylbenzonitrile (14.0 g, 71.4 mmol) was dissolved in dry CH_2Cl_2 (260 mL) and the solution was stirred at 0 °C for 20min. 1.0 M diisobutylaluminium hydride hexane solution (DIBAL) (70 mL, 70 mmol) was added dropwise to the solution at 0 °C. The solution was stirred for 15 min at 0 °C and then DIBAL solution (35 mL) was added dropwise again. The mixture was stirred for 15 min at 0 °C and for 30 min at 25 °C. This reaction mixture was washed with 50% H_2SO_4 (150 mL) aq. solution to precipitate the aluminum salt. After the mixture was filtered, deionized water was added to the solution and the aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ for 1 h. This mixture was filtered and concentrated to give **8** as a white solid. Yield: 56.3% (8.00 g). ^{1}H NMR ($CDCl_3$, TMS): δ = 10.0 (s, 1H, PhC*H*O), 7.85 (d, 2H, J = 8.0 Hz, $BrCH_2(PhH)_2$), 7.54 (d, 2H, J = 8.0 Hz, $(HPh)_2CHO$), 4.50 (s, 2H, $BrCH_2Ph$).

*2.2.1.2.2. 3,5-Bis(hydroxymethyl) -4-(4′-formylbenzyloxy)phenyl-acetylene (**M-CHO**) (Scheme 3).* A mixture of **4** (3.79 g, 21.3 mmol), **8** (4.23 g, 21.3 mmol) and K_2CO_3 (8.80 g, 63.9 mmol) in DMF (107 mL) was stirred for 50 h at 70 °C. After the mixture was filtered, the solvent was evaporated. The residue was washed with water and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ for 1h. After filtration and concentration, the crude product was purified by silica-gel column chromatography to give **M-CHO** as a white solid. Rf = 0.70 ($CHCl_3$/MeOH = 95/5 (v/v)). ^{1}H NMR ($CDCl_3$, TMS): δ = 10.0 (s, 1H, PhC*H*O), 7.94 (d, 2H, J = 8.0 Hz, $(HPh)_2CHO$), 7.63 (d, 2H, J = 8.0 Hz, $OCH_2(PhH)_2$), 7.54 (s, 2H, HC≡C(Ph*H*)$_2$), 5.08 (s, 2H, $PhOCH_2Ph$), 4.69 (d, 4H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 3.07 (s, 1H, *H*C≡C), 1.74 (t, 2H, J = 6.0 Hz, $Ph(CH_2OH)_2$).

*2.2.1.2.3. 3,5-Bis(hydroxymethyl)-4-{4′-(2″-tert-butyl-1-iminomethyl)benzyloxy}-1-phenyl-acetylene (**M-TB**) (Scheme 3).* A mixture of **M-CHO** (200 mg, 0.670 mmol), 2-*tert*-butylaniline (0.21 mL, 1.4 mmol) and Al_2O_3 (700 mg) in dry THF (7 mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed by evaporation to yield a white solid. The crude product was purified by recrystallization from chloroform/hexane(=10/90 (v/v)) to give **M-TB** as a white solid. Yield: 70.0% (200 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 8.36(s, 1H, PhC*H* = N), 7.90-6.81(m, 10H, Ph*H*), 5.01(s, 2H, $PhOCH_2Ph$), 4.62(d, 4H, $Ph(CH_2OH)_2$), 3.38(s, 1H, *H*C≡C),1.43(s, 9H, $PhC(CH_3)_3$). IR (KBr): 3326 (OH), 3232 (HC≡C), 1646 (C=N) cm^{-1}. Anal. Cacld for $C_{28}H_{29}O_3N$: C, 78.66; H, 6.84; N, 3.28; Found: C, 77.68; H, 6.81; N, 3.28.

*2.2.1.2.4. Synthesis of 3,5-bis(hydroxymethyl)-4-[4′-{3-(triethylsilyl)propyliminomethyl}benzyloxy]-1-phenyl-acetylene (**M-TES**) (Scheme 3) [38].* 3-(Triethylsilyl)propylamine (**9**) (Scheme 3)

$H_2PtCl_6 \cdot 6H_2O$ (26 mg, 50 μmol) and toluene (15 mL) were added to a flask and the mixture was stirred at 80 °C until $H_2PtCl_6 \cdot 6H_2O$ was dissolved completely. Triethylsilane (8.00 mL, 50.2 mmol) and allylamine (4.20 mL, 55.2 mmol) were added dropwise to the solution at 40 °C separately and this reaction solution was stirred at 85 °C for 120 h. The solvent was removed by evaporation and the crude product was purified by vacuum distillation at 54 °C (250 Pa) to give **9** as a colorless liquid. Yield: 67.7% (5.89 g). ^{1}H NMR ($CDCl_3$, TMS): δ = 2.65 (t, 2H, J = 7.0 Hz, NH_2CH_2), 1.42 (m, 2H, $NH_2CH_2CH_2CH_2$), 1.27(br, 2H, CH_2NH_2), 0.92 (t, 9H, J = 8.0 Hz, $Si(CH_2CH_3)_3$), 0.59 (t, 2H, J = 8.0 Hz, $NCH_2CH_2CH_2Si$), 0.49 (q, 6H, J = 8.0 Hz, $Si(CH_2CH_3)_3$).

*2.2.1.2.5. 3,5-Bis(hydroxymethyl)-4-[4′-{3-(triethylsilyl)propyliminomethyl}benzyloxy]-1-phenylac -etylene (**M-TES**) (Scheme 3).* A mixture of **M-CHO** (500 mg, 1.68 mmol), **9** (586 mg, 3.36 mmol) and Al_2O_3 (10.0 g) in dry THF (16 mL) was stirred for 3 days at room temperature. After the mixture was filtered, the solvent was removed by evaporation to yield a white solid. The crude product was purified by recrystallization in chloroform/hexane(=5/95 (v/v)) to give **M-TES** as a white solid. Yield: 56.5% (428 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 8.27 (s, 1H, PhC*H* = N), 7.76 (d, 2H, J = 8 Hz, ), 7.50 (s, 2H, C≡CPh*H*), 7.45 (d, 2H, J = 8 Hz, ), 4.99 (s, 2H, $PhOCH_2Ph$), 4.65 (d, 4H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 3.59 (t, 2H, J = 7.0 Hz, NCH_2CH_2), 3.04 (s, 1H, *H*C≡C), 1.90 (t, 2H, J = 6.0 Hz, $Ph(CH_2OH)_2$), 1.68 (m, 2H, $NCH_2CH_2CH_2$), 0.91 (t, 9H, J = 8.0 Hz, $Si(CH_2CH_3)_3$), 0.53 (t, 2H, J = 8.0 Hz, $NCH_2CH_2CH_2Si$), 0.49 (q, 6H, J = 8.0 Hz, $Si(CH_2CH_3)_3$). IR (KBr): 3322 (OH), 3233 (HC≡C), 1643 (C=N) cm^{-1}. Anal. Cacld for $C_{27}H_{37}O_3NSi$: C, 71.80; H, 8.26; N, 3.10; Found: C, 71.74; H, 8.17; N, 3.10.

2.2.2. Synthesis of the polymers (**P-R**) by helix-sense-selective polymerization (HSSP) of **M-R** (Scheme 2a) [34]

*2.2.2.1. Synthesis of **P-EO** by HSSP of **M-EO** (Scheme 2a).* A solution of $[Rh(nbd)Cl]_2$ (1.37 mg, 2.98 μmol) and (*S*)- or (*R*)-phenylethylamine (PEA) (153 μL, 1.20 mmol) in $CHCl_3$ (1.0 mL) was added to a solution of **M-EO** (100 mg, 260 μmol) in $CHCl_3$ (1.6 mL). The reaction solution was stirred at room temperature for 12 h. The crude polymer was purified by reprecipitation of the $CHCl_3$ solution into a large amount of (hexane/ethyl acetate = 2/3 (v/v)) and dried *in vacuo* to give **P-EO** as a brownish red polymer in 55% yield. ***Mw*** = 2.6×10^5. ^{1}H NMR ($CDCl_3$/DMSO-d_6 = 3/2(v/v)): δ = 7.28(s, 1H, $HPhOCH_2CH_2O$), 7.16(m, 1H, $HPhOCH_2CH_2O$), 6.81(m, 4H, HC=CPh*H* and $HPhOCH_2CH_2O$), 5.88(br, cis proton in the main chain), 4.57–4.37 (m, 6H, $PhOCH_2Ph$ and $Ph(CH_2OH)_2$), 3.97–3.49 (m, 10H, $OCH_2CH_2OCH_2CH_2OCH_3$ and $Ph(CH_2OH)_2$), 3.36(s, 3H, OCH_3).

*2.2.2.2. Synthesis of **P-TB** by HSSP of **M-TB** (Scheme 2a).* A solution of $[Rh(nbd)Cl]_2$ (0.80 mg, 1.76 μmol) and (*S*)- or (*R*)-PEA (28.2 μL, 220 μmol) in dry THF (0.44 mL) was added to a dry THF (0.44 mL) solution of **M-TB** (37.0 mg, 88.0 μmol). The reaction solution was stirred at room temperature for 24 h. The crude polymer was purified by reprecipitation of the THF solution into a large amount of methanol and the formed solid was dried *in vacuo* to give **P-TB** as a red solid in 57% yield. ***Mw*** = 7.9×10^7. ^{1}H NMR (CCl_4/DMSO-d_6 = 5/1(v/v), TMS): δ = 7.56–6.81(br, 10H, Ph*H*), 5.93(br, cis proton in the main chain), 4.79(br, 2H, $PhOCH_2Ph$), 4.37(br, 4H, $Ph(CH_2OH)_2$), 1.51(br, 9H, $C(CH_3)_3$). IR (KBr): 3600–3100(OH), 3000–2800(CH), 1645 (C=N) cm^{-1}.

*2.2.2.3. Synthesis of **P-TES** by HSSP of **M-TES** (Scheme 2a).* The HSSP of **M-TES** was carried out similarly to that of **M-TB** to give **P-TES** *as* an orange solid in 98% yield. ***Mw*** = 3.0×10^5. ^1H NMR(CCl_4/DMSO-d_6 = 5/1(v/v)): δ = 8.15 (br, 1H, PhC*H* = N), 7.58–6.92 (br, 6H, Ph*H*), 5.91 (br, cis proton in the main chain), 4.75 (br, 2H, PhOCH_2Ph), 4.35 (br, 4H, Ph($CH_2OH)_2$), 3.53 (br, 2H, NCH_2CH_2), 1.65 (br, 2H, N$CH_2CH_2CH_2$), 0.88 (br, 9H, Si($CH_2CH_3)_3$), 0.51 (br, 2H, N$CH_2CH_2CH_2$Si), 0.47 (br, 6H, Si($CH_2CH_3)_3$). IR (KBr): 3375 (OH), 1645 (C=N) cm^{-1}.

*2.2.2.4. Synthesis of **P-Do** by HSSP of **M-Do** (Scheme 2a) [34].* **P-Do** was synthesized from **M-Do** according to our previous paper in 36.5% yield. ***Mw*** = 2.5×10^6.^1H NMR ($CDCl_3$/DMSO-d_6 = 55/45(v/v), TMS): δ = 6.77(s, 2H, (Ph*H*$)_2$), 5.76(br, cis proton in the main chain), 4.61(s, 2H, PhOCH_2), 4.32(s, 4H, Ph($CH_2OH)_2$), 3.55(br, 2H, Ph($CH_2OH)_2$), 1.29–1.64(m, 20H, $OCH_2CH_2(CH_2)_9CH_3$), 0.89(b, 3H, CH_2CH_3). IR(KBr): 3700–3100(OH), 3000–2800(CH), 1200–1000(CO) cm^{-1}.

*2.2.2.5. Synthesis of **P-S3** by HSSP of **M-S3** (Scheme 2a) [35].* **P-S3** was synthesized from **M-S3** according to our previous paper in 89% yield. ***Mw*** = 4.0×10^7. ^1H NMR (DMSO-d_6/CCl_4 = 1/5, TMS): δ = 7.54–7.34(br, 6H, Ph*H*), 5.89(br, cis proton in the main chain), 4.75(br, 2H, PhOCH_2Ph), 4.38(br, 4H, (CH_2OH)2), 0.34–0.04(br, 21H, (–Si($CH_3)_3$) and (–SiO($CH_3)_2$–$)_2$). IR(KBr): 3600–3100(OH), 1256(SiC), 1051 (SiO) cm^{-1}.

*2.2.3. Synthesis of the 2D surface modifiers(**T-R**) by highly selective photocyclic aromatization (SCAT) of **P-R** (Scheme 2b) [31]*

The **P-R** membranes (thickness around 20 μm) were irradiated under nitrogen at 25 °C by visible light (400–500 nm, 2.54 mW/cm^2) for 2–4 weeks. The conversions and selectivities were determined by GPC detected by UV. Visible light (400–500 nm) irradiation was carried out by using a 300 W of Xe lamp (Asahi Spectra, MAX-302 with vis mirror module) through a cutoff filter (Asahi Spectra, LUX400 ($\lambda > 400$ nm), XF541 ($\lambda < 510$ nm), and XF546 ($\lambda < 610$ nm)).

*2.2.3.1. Synthesis of **T-EO** by SCAT of **P-EO** (Scheme 2b).* SCAT of **P-EO** (Mw = 2.6×10^5) membrane gave a brownish red membrane in 100% conversion and 83.2% selectivity. The crude product was purified by silica-gel column chromatography to give a brownish red powder in 78.4% yield.

*2.2.3.2. Synthesis of **T-TB** by SCAT of **P-TB** (Scheme 2b).* SCAT of **P-TB** (Mw = 7.9×10^7) membrane gave a brown membrane in 100% conversion and 65.8% selectivity. The crude product was purified by Al_2O_3 chromatography to give a brown powder in 61.2% yield.

*2.2.3.3. Synthesis of **T-TES** by SCAT of **P-TES** (Scheme 2b).* SCAT of **P-TES** (Mw = 3.0×10^5) membrane gave a faint orange membrane in 100% conversion and 79.5% selectivity. The crude product was purified by Al_2O_3 chromatography to give a slightly orange powder in 75.2% yield.

*2.2.3.4. Synthesis of **T-Do** by SCAT of **P-Do** (Scheme 2b).* SCAT of **P-Do** (Mw = 2.5×10^6) membrane gave a brown membrane in 100% conversion and 100% selectivity. The crude product was purified by silica-gel column chromatography to give a brown powder in 91.1% yield.

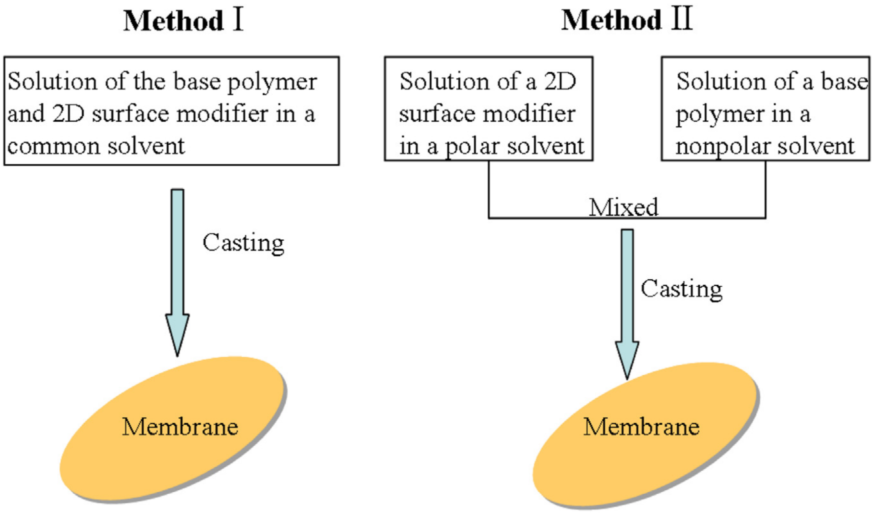
*2.2.3.5. Synthesis of **T-S3** by SCAT of **P-S3** (Scheme 2b).* SCAT of **P-S3** (Mw = 4.0×10^7) membrane gave a brownish red membrane in 100% conversion and 95% selectivity. The crude product was purified by silica-gel column chromatography to give a brownish red powder in 90.7% yield.

2.3. Membrane preparation

The surface-modified membranes were prepared from the binary solution of the mixture consisting of small amounts (less than 5.0 wt%) of one of the 2D surface modifiers and one of the base polymers (see Chart 2) by two kinds of solvent casting methods (Method I and Method II) as shown in Scheme 4.

2.3.1. PVA-based membranes by Method I

A dimethyl sulfoxide(DMSO) solution(1.0 mL) of poly(vinyl alcohol)(PVA) (40 mg) and 0.060–10.0 wt% of one of the 2D surface modifiers was cast on a poly(tetrafluoroethylene) sheet. The solvent(DMSO) was evaporated in a reduced pressure (1.33×10^{-3} MPa) for 12 h and then by heating at 50 °C at this pressure for 24 h. The resulting membranes were allowed to stand for 8 h at 25 °C. Finally, the membranes were detached from the poly(tetrafluoroethylene) sheet and were annealed *in vacuo* at 30 °C for 24 h.



Scheme 4.

2.3.2. *PSPA-based and PDPA-based membranes by two methods (Methods I and II)*

Method I (conventional method): A toluene solution (1.0 mL) of the base polymer (35 mg) and 0.060–5.0 wt% of the 2D surface modifier was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24 h at room temperature, the membrane was detached from the poly(tetrafluoroethylene) sheet and dried *in vacuo* for 24 h at room temperature.

Method II (newly developed method): A toluene solution(1.0 mL) of the base polymer (50 mg) and chloroform solution(0.50 mL) of the 2D surface modifier (0.175 mg) were first blended together (In the case of T-EO, methanol was used instead of chloroform.). And then the mixed solution was cast on a poly(tetrafluoroethylene) sheet. After the solvent was evaporated for 24 h at room temperature, the membrane was detached from the sheet and dried *in vacuo* for 24 h at room temperature.

2.4. *Measurement of oxygen permselectivities*

Oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}: cm^3 (STP)·cm/cm^2·s·cmHg) of mixed gases of oxygen and nitrogen (O_2/N_2 = 20/80 (v/v)) were measured by gas chromatographic method using YANACO GTR-10. The *P*, the oxygen separation factors (α), the diffusion coefficients (*D*) and the solubility coefficients (*S*) were calculated by the following equations:

$$P = \frac{Q \times l}{A \times \Delta P \times t}$$

$$\alpha = P_{O_2}/P_{N_2}$$

$$D = l^2/6T$$

$$S = P/D$$

where Q, *l*, A, Δp, *t*, and *T* are the amount of the permeated gas, the thickness of the membrane, the permeation area of the membrane, the pressure difference across the membrane, the permeation time and the time lag, respectively. The A and *l* of the membranes were 0.38–1.77 cm^2 and 25–120 μm, respectively. Disc-type membranes were used. The Δp was 1 atm and the measurement temperature was 25 °C.

2.5. *Characterization of membranes*

ATR-FTIR(using ATR PR0450-S) and FT-IR spectra were recorded on a JASCO FTIR-4200 spectrometer, contact angles of distilled water droplets on the air-side surface of the membranes were measured at 25 °C with a DM301, Kyowa Interface Science Co., Ltd.

2.6. *Apparatus*

NMR spectra were recorded on a JEOL GSX 270 at 400 MHz for ^{1}H NMR and ^{13}C NMR. Average molecular weight (***Mw***) was estimated by gel permeation chromatography (tetrahydrofuran as an eluent, polystyrene calibration) using JASCO Liquid Chromatography instruments with PU 2080, DG 2080 53, CO 2060, UV 2070, CD 2095 and two polystyrene gel columns (Shodex KF 807L).

3. Results and discussion

3.1. *Molecular design and synthesis of new 2D surface modifiers*

In this study, five kinds of 2D surface modifiers (Chart 2) were synthesized and used. All the compounds have a 1,3,5-trisubstituted benzene as a hydrophobic planar (2D) part, six hydroxyl groups, and three hydrophilic(**T-EO**) or hydrophobic(**T-TB**, **T-TES**, **TDo**, and **T-Si**) groups. All the 2D surface modifiers were synthesized by SCAT(Scheme 1) [27], which is our original method, of the corresponding polyphenylacetylenes according to Scheme 2. As a typical example, the 3D chemical structures of **T-EO** are shown in Chart 3. It has 1,3,5-trisubstituted benzene as a hydrophobic 2D part and three hydrophilic arms of an oligoethylene oxide which can function as an anchor segment in hydrophilic base polymer membranes such as poly(vinyl alcohol)(PVA). Chart 4 indicates an example of an ideal 2D supramolecular structure of six **T-EO** molecules on a membrane surface. It has some molecular-size pores which can recognize and separate gas molecules such as oxygen and nitrogen.

In order to separate gas molecules more effectively, thinnest membranes without any defects are desired. In addition, no distribution of the additives inside the base membrane is thought to be better because such additives may change the original good performance of the base membranes. Therefore, the minimum amount of the 2D surface modifier (**T-EO**) needed for such a thinnest surface layer was calculated. As shown in Chart 5, the result of calculation showed very little amount (=6.0 × 10^{-3} wt%) of **T-EO** is enough for making the ideal thin layer. Therefore we added small amounts of the additives in this study.

3.2. *New preparation method (Method II) of surface-modified membranes*

The surface-modified membranes were prepared from the solution of the mixture consisting of small amounts (less than 5.0 wt

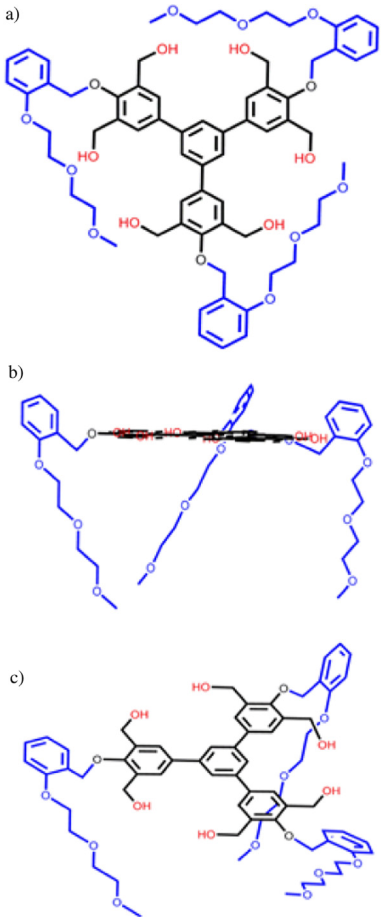


Chart 3. 3D molecular structure of **T-EO**.

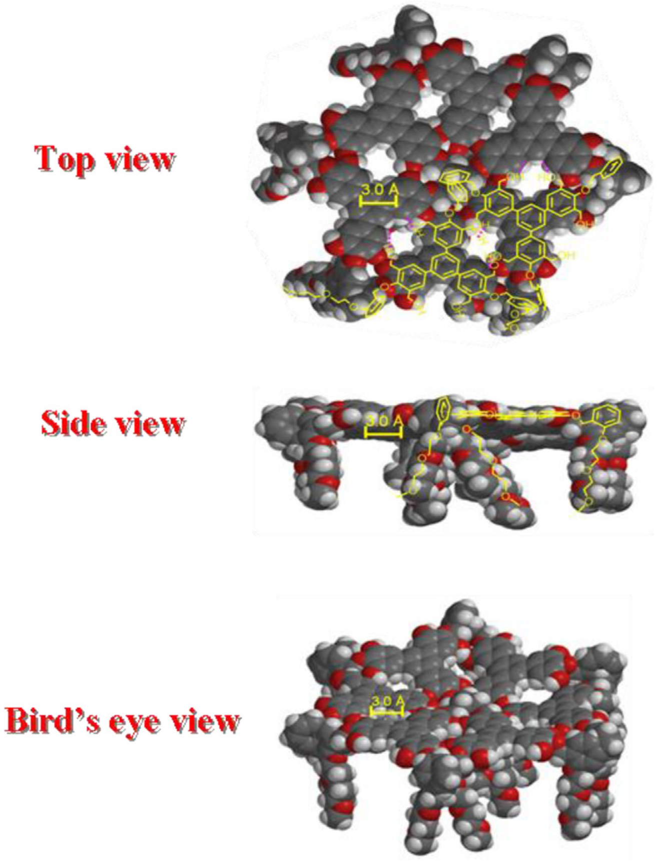


Chart 4. Possible 2D supramolecular structure of **T-EO** on the blend membrane surface.

%) of one of the 2D surface modifiers and one of the base polymers (see Chart 2) by two kinds of solvent casting methods as shown in Scheme 4. In Method I (a conventional method), a solution of the base polymer and 0.060–5.0 wt.-% of the 2D surface modifiers in a common solvent was cast on a poly(tetrafluoroethylene) sheet. In Method II (a new method), one solution of the base polymer in a non-polar solvent having a higher boiling point and another solution of 0.060–5.0 wt.-% of the 2D surface modifiers in a polar solvent having a lower boiling point were prepared and then the two solutions were mixed and the binary solution was cast on a poly(tetrafluoroethylene) sheet. Because hydrophobic compounds tend to be concentrated at the surface when it was blended with a hydrophilic base polymer and the solution was cast in the air, in the case of this combination, i.e., a more hydrophobic additive and a more hydrophilic base polymer, the resulting membrane prepared by Method I (conventional method, see Scheme 4) forms more hydrophobic surface. Therefore, the combination of **T-EO** and PVA, i.e., a hydrophobic additive and a hydrophilic base polymer is suitable for Method I. As a fact, **T-EO** was accumulated at the surface of PVA judging from change in the contact angles (Table 1, nos. 1–6). However, in the case of the opposite combination, i.e., a more hydrophilic additive and a more hydrophobic base polymer like **T-EO** and poly(*p*-trimethylsilylphenylacetylene) (PSPA) were not suitable for Method I (Table 1, nos. 12–14). To overcome the problem, a new method, i.e., Method II (see Scheme 4) was designed and carried out. Methanol and toluene were used as a good solvent for **T-EO** and PSPA, respectively. As shown in Table 1, nos. 15–17, **T-EO** was successfully accumulated on the surface of PSPA membranes. Because the boiling point of methanol is lower than that of toluene, **T-EO** may be concentrated and precipitated at the surface first during the evaporation of the solvent after casting. By this new method, membranes whose surfaces were covered by more hydrophilic additives could be prepared easily.

3.3. Improvements of oxygen permselectivities by surface modification using the 2D surface modifiers

*3.3.1. Three kinds of membranes modified by the 2D surface modifier having oligo(ethylene oxides) (**T-EO**)*

Fig. 1 shows the results of oxygen permselectivity of **T-EO** containing polymer membranes based on PVA, PDPA [28], or PSPA [29]. In all the blend membranes, oxygen permselectivities were higher than that of pure membranes, PVA(○), PDPA(Δ), or PSPA(□) membranes, respectively. In the case of PVA-based membranes (Fig. 1,●) when 1.0 wt% of **T-EO** was added, the permselectivity increased almost twice higher than that of the pure base polymer membrane, i.e., the PVA membrane without any drop of permeability. When 1.0 wt% of **P-EO** (the precursor polymer of **T-EO**, see Scheme 2) was added (Fig. 1, ▼), the permselectivity was not improved and the permeability decreased. Therefore the small amount of **T-EO** may form a certain surface structure which enhanced the performance effectively. In particular, in the case of PDPA-based membranes (Fig. 1, ▲), when a small amount (1.0 wt%) of **T-EO** was added, both the permselectivity and permeability increased simultaneously. In addition, the plots of **T-EO**/PDPA membranes (▲) are over the Robeson's boundary line in 1991 [4] indicating a relatively good performance. It may be because **T-EO** may form an ideal surface structure. On the other hand, in the case of PSPA-based membranes (Fig. 1, ■), when 5.0 wt% of **T-EO** was added, the permselectivity increased but permeability decreased a

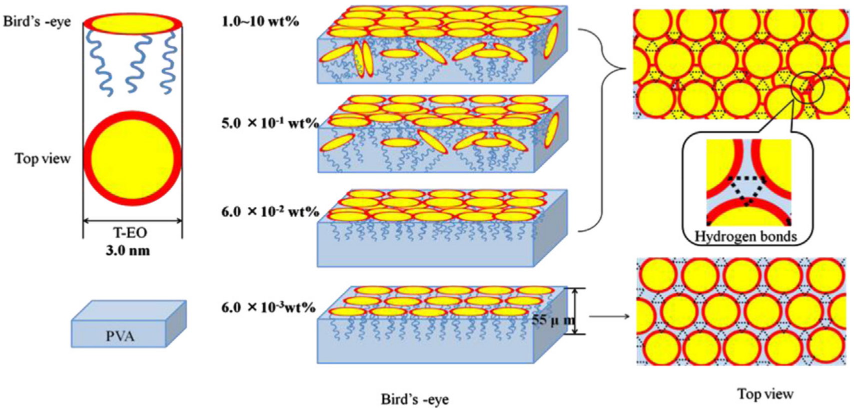


Chart 5. Possible membrane structures of **T-EO**/PVA membranes having different amount of T-EO.

Table 1
Characterization of the surfaces of **T-EO** containning polymer membranes.

No.[a]	Additives[b]	Content (wt%)	θ(°)[c]
1	None (PVA)	0.0	39.1
2	**T-EO** (Method I)[d]	0.06	40.4
3		0.50	40.1
4		1.0	40.4
5		5.0	51.5
6		10.0	53.1
7	**P-EO** (Method I)[d]	1.0	42.2
8		5.0	30.2
9		10.0	34.2
10		100(=**P-EO**)	69.5
11	None (PSPA)	0.0	106
12	**T-EO** (Method I)[d]	0.50	105
13		1.0	107
14		5.0	104
15	**T-EO** (Method II)[d]	0.50	100
16		1.0	95
17		5.0	87

[a] Nos. 2–9: Prepared by Method I using PVA as a base polymer; nos.12–14: Prepared by Method I using PSPA as a base polymer; nos.15–17: Prepared by Method II using PSPA as a base polymer.

[b] For the code, see Chart 2.

[c] Advancing contact angles for water droplets on the air surface of the blend membranes.

[d] Method I: Casting a solution of the base polymer and 2D surface modifier in a common solvent; Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.

little. It may be because **T-EO** was present not only at the surface but also inside the membranes (See Chart 5).

3.3.2. *Poly(p-trimethylsilyldiphenylacetylene)(PDPA)-based membranes modified by the four kinds of 2D surface modifiers*

Fig. 2 shows oxygen permselectivity of PDPA-based polymer membranes modified by the four kinds of 2D surface modifiers. In all the blend membranes, oxygen permselectivities were higher than that of the pure PDPA membrane(○) although the permeability decreased except for **T-EO**(●). In particular, **T-TB**(■) enhanced the permselectivity most effectively among the four additives (**T-EO**(●), **T-TB**(■), **T-Do**(▼), and **T-S3**(◆)). Since the plots of **T-EO**/PDPA membranes(●) are over the Robeson's boundary line in 1991 [4], they are relatively good.

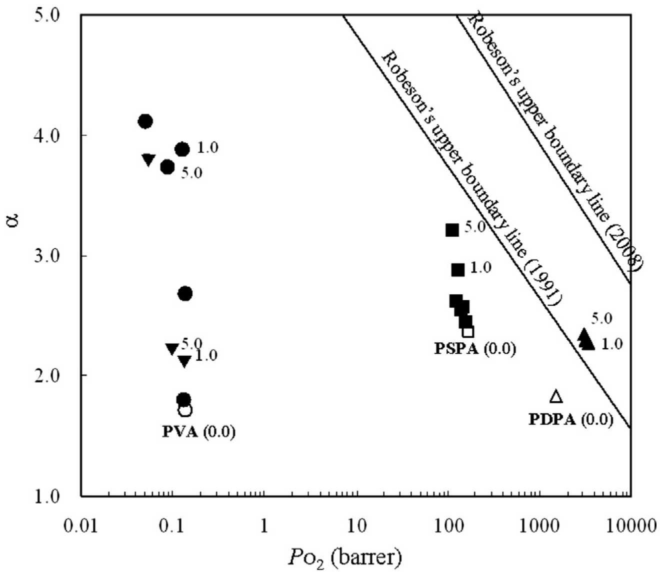


Fig. 1. Oxygen permselectivity of **T-EO** containing polymer membranes.

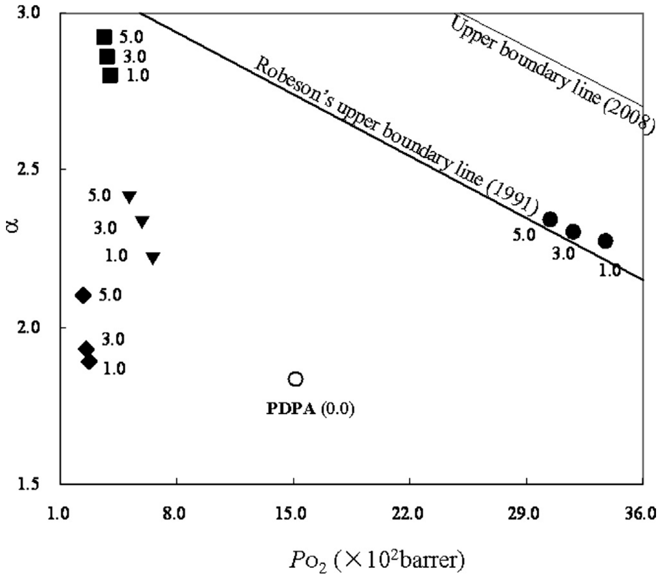


Fig. 2. Oxygen permselectivity of PDPA-based polymer membranes.

3.3.3. *Poly(p-trimethylsilylphenylacetylene) (PSPA)-based membranes modified by the four kinds of 2D surface modifiers*

Fig. 3 shows oxygen permselectivity of PSPA-based polymer membranes. In all the blend membranes, oxygen permselectivities were higher than that of the pure PSPA membrane(○) although the permeability decreased. In particular, since the plot of a **T-TES**/PSPA membrane(▲) is closest to the Robeson's boundary line among the four additives, the performance is relatively good.

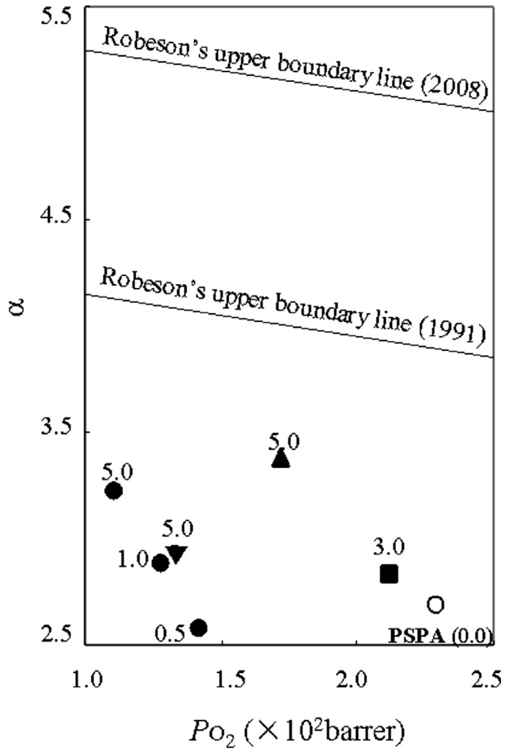


Fig. 3. Oxygen permselectivity of PSPA-based polymer membranes.

3.3.4. Summary of oxygen permselectivity thorough the surface-modified membranes

Fig. 4 shows the results of oxygen permselectivity of all the blend membranes in this study together with other membranes (+) having excellent performances reported by other researchers [39–43]. All the oxygen permselectivities in this study were higher than that of the corresponding pure membrane, i.e., PVA(○), PDPA(Δ), or PSPA(□) membrane, respectively. In particular, **T-EO**/PDPA membranes(▲) and a **T-TES**/PSPA membrane(■) showed relatively good performances whose plots are over or close to the Robeson's upper boundary line in 1991 [4]. Among the five additives (Chart 2), **T-EO** was the best to improve the performance of the original membranes (●, ▲). In summary, only small amounts (1.0–5.0 wt%) of the 2D modifiers were enough for the effective improvement of oxygen permselectivities.

3.4. Reasons of the improvements of oxygen permselectivities

3.4.1. Structures of the blend membranes

To know structures of the membrane surface, contact angles of water droplets and ATR-IR on the membrane surface were measured. The results are listed in Tables 1–3. Table 1 shows the values of contact angles of water droplets on the surface of **T-EO** containing blend polymer membranes whose permselectivities have been shown in Fig. 1. As shown in Table 1, nos. 1–6, judging from the contact angles, **T-EO** was accumulated at the surface in the **T-EO**/PVA membranes prepared by Method I whose performances were improved efficiently. On the other hand, since the **P-EO**/PVA membranes prepared by Method I whose performances were not improved efficiently showed almost no change in the contact angles, **P-EO** was not accumulated at the surface (Table 1, nos. 7–9).

In the case of the **T-EO**/PSPA membranes prepared by Method II whose performances were improved efficiently, judging from the contact angles, **T-EO** was found to be accumulated at the surface (Table 1, nos. 15–17). On the other hand, since the **T-EO**/PSPA membranes prepared by Method I whose performances were not improved efficiently showed almost no change in the contact angles, **T-EO** was not accumulated at the surface (Table 1, nos. 12–14).

Table 2 shows the values of contact angles of water droplets and ATR-IR at the surface of the PDPA-based polymer blend membranes prepared by Method II whose performances were improved efficiently. The θ values show all the additives were present at the surfaces because the surface became more hydrophilic. In addition, since the ratios (A_S) of absorbance (A_{3450}) for OH to that (A_{1250}) for

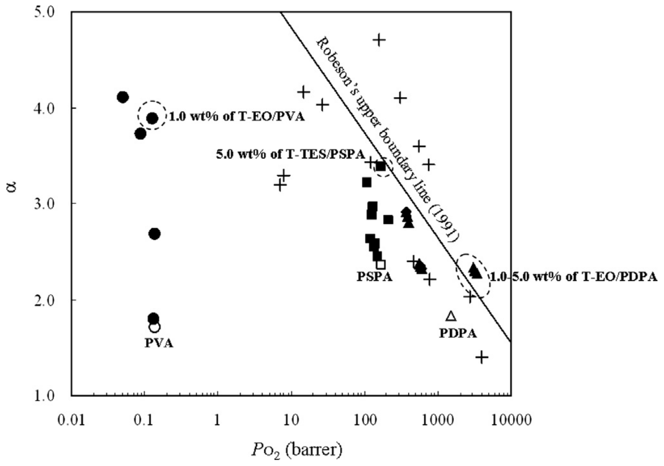


Fig. 4. Oxygen permselectivity of all the surface-modified polymer membranes in this study.

Table 2
Characterization of the surfaces of PDPA-based polymer membranes.[a]

No.	Additives[b]	Content (wt%)	θ(°)[c]	A_S[d] ($\times10^{-1}$)	A_B[e] ($\times10^{-2}$)	R[f]
1	None	0.0	103	–	–	–
2	**T-EO**	1.0	93.5	7.03	7.10	9.90
3		3.0	92.2	7.58	8.64	8.77
4		5.0	89.6	7.73	9.73	7.94
5	**T-TB**	1.0	96.1	3.03	9.22	3.28
6		3.0	93.2	4.42	9.35	4.72
7		5.0	92.5	5.59	16.0	3.49
8	**T-Do**	1.0	90.7	5.00	6.71	7.45
9		3.0	85.1	5.14	7.83	6.56
10		5.0	83.9	5.40	12.8	4.21
11	**T-S3**	1.0	93.1	3.22	8.80	3.65
12		3.0	89.9	4.01	9.91	4.04
13		5.0	86.8	4.10	11.8	3.47

[a] Prepared by Method II using PDPA as a base polymer (Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent).
[b] For the code, see Chart 2.
[c] Advancing contact angles for water droplets on the air surface of the blend membranes.
[d] $A_S = A_{3450}/A_{1250}$ of ATR-FTIR.
[e] $A_B = A_{3450}/A_{1250}$ of FTIR.
[f] $R = A_S/A_B$.

Table 3
Characterization of the surfaces of PSPA-based polymer membranes.[a]

No.	Additives[b]	Contents (wt%)	θ(°)[c]
1	None	0.0	106
2	**T-EO**	0.50	100
3		1.0	95.0
4		5.0	87.0
5	**T-TB**	3.0	97.9
6	**T-TES**	5.0	96.5
7	**T-Do**	5.0	97.1

[a] Prepared by Method II using PSPA as a base polymer(Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent).
[b] For the code, see Chart 2.
[c] Advancing contact angles for water droplets on the air surface of the blend membranes.

Table 4
Aging effects of the contact angles of the surfaces of PDPA-based polymer membranes.[a]

No.	Additives[b]	Content (wt%)	θ (°)[c]	
			Original	3 months
1	None	0.0	103	96.3
2	**T-EO**	1.0	93.5	94.6
3		3.0	92.2	94.0
4		5.0	89.6	93.2
5	**T-TB**	1.0	96.1	96.4
6		3.0	93.2	93.8
7		5.0	92.5	92.6
8	**T-Do**	1.0	90.7	91.7
9		3.0	85.1	85.7
10		5.0	83.9	84.1
11	**T-S3**	1.0	93.1	93.7
12		3.0	89.9	90.4
13		5.0	86.8	89.5

[a] Prepared by Method II using PDPA as a base polymer (Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent).
[b] For the code, see Chart 2.
[c] Advancing contact angles for water droplets on the air surface of the blend membranes just after the membrane fabrication and 3 months after the membrane fabrication under air.

Table 5

Oxygen permselectivity of the **T-EO** containing polymer membranes.

No.[a]	Additives[b]	Content (wt%)	P_{O_2} ($\times 10^{-2}$ barrer)[c]	D_{O_2}[d] ($\times 10^{-2}$)	S_{O_2}[e]	P_{O_2}/P_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
1	None(PVA)	0.0	13.7	9.41	1.45	1.71	1.21	1.42
2	**T-EO** (Method I)[f]	0.06	13.5	10.91	1.24	1.80	1.11	1.62
3		0.50	13.7	8.05	1.70	2.68	1.12	2.39
4		1.0	12.7	8.02	1.58	3.88	1.11	3.49
5		5.0	8.8	5.64	1.57	3.73	1.01	3.68
6		10.0	5.1	3.22	1.59	4.11	0.93	4.44
7	**P-EO** (Method I)[f]	1.0	12.9	7.68	1.68	2.15	1.08	1.99
8		5.0	8.8	5.83	1.51	2.25	1.12	2.00
9		10.0	4.9	3.33	1.47	3.82	1.14	3.35
10		100(**P-EO**)	136	13.4	10.1	1.19	1.00	1.18
No.[a]	Additives[b]	Content (wt%)	P_{O_2} (barrer)[c]	D_{O_2}[d]	S_{O_2}[e]	P_{O_2}/P_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
11	None(PSPA)	0.0	171	3.35	51.1	2.36	0.95	2.48
12	**T-EO** (Method I)[f]	0.50	150	2.95	50.8	2.45	0.98	2.51
13		1.0	136	2.60	52.4	2.55	1.04	2.45
14		5.0	120	2.32	51.8	2.63	1.02	2.58
15	**T-EO** (Method II)[f]	0.50	142	3.25	43.7	2.58	0.97	2.66
16		1.0	128	3.10	41.3	2.88	1.02	2.82
17		5.0	111	2.98	37.2	3.22	1.06	3.16

[a] Nos. 2–9: Prepared by Method I using PVA as a base polymer; no.10: a pure **P-EO** membrane; nos.12–14: Prepared by Method I using PSPA as a base polymer; nos.15–17: Prepared by Method II using PSPA as a base polymer.

[b] For the code, see Chart 2.

[c] 1 barrer = 10^{-10}cm^3(STP)·cm cm^{-2} s^{-1} cmHg^{-1}.

[d] In 10^{-7} cm^2 s^{-1}.

[e] In 10^{-3} cm^3(STP) cm^{-3} cmHg^{-1}.

[f] Method I: Casting a solution of the base polymer and 2D surface modifier in a common solvent; Method II: Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.

$SiCH_3$ of the surface in the infrared spectra were much higher than those of the bulk (A_B), in other words, A_S values were much higher than A_B values (i.e., $R = A_S/A_B > 1.0$), the accumulation of the additives was confirmed. Table 3 shows the values of contact angles of water droplets at the surface of the PSPA-based polymer blend membranes prepared by Method II whose performances were improved efficiently. The θ values show all the additives were present at the surfaces because the surface became more hydrophilic similarly to those of the PDPA-based membranes prepared by Method II.

In summary, it was found that all the additives were accumulated at the surface in all the blend membranes containing the 2D surface modifiers. The possible supramolecular structure of **T-EO** at the surface of the **T-EO**/PVA membrane is shown in Chart 5. The three hydrophilic oligoethylene oxide groups in **T-EO** can work as anchors. In the case of the **T-EO**/PDPA and the **T-EO**/PSPA membranes, the three oligoethylene oxide groups in **T-EO** can not work as anchors. Instead, the hydrophobic part, i.e., the benzene derivatives may have interaction with the hydrophobic substrate polymers.

In order to estimate stability of the modified surface, aging effects of the contact angles were measured. Table 4 shows aging effects of the contact angles on the PDPA-based polymer membranes. Since almost no change in the contact angles was observed, it was found that the surface layer was stable.

3.4.2. *Reason of the improvements of oxygen permselectivities*

As described in Sections 3.2 and 3.3.1, in all the blend membranes containing the 2D surface modifiers, the oxygen permselectivities were higher than the corresponding pure base polymer membranes and the additives were accumulated at the surface. Therefore, the surface layer must play an important role. To discuss the reason of the enhancement, diffusion coefficients (D) were estimated by the time lag methods and then solution coefficients (S) were calculated from $P = D \times S$. The results are listed in Tables 5–7. Table 5 shows the values of P, D, and S of oxygen and nitrogen and their ratios, i.e.,

Table 6

Oxygen permselectivity of the PDPA-based polymer membranes.[a]

No.	Additives[b]	Content (wt%)	P_{O_2}[c] (barrer)	D_{O_2}[d]	S_{O_2}[e]	P_{O_2}/P_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
1	None	0.0	1520	0.488	311	1.83	1.78	1.03
2	**T-EO**	1.0	3380	0.112	3030	2.27	1.36	1.67
3		3.0	3190	0.098	3230	2.30	1.26	1.83
4		5.0	3055	0.087	3440	2.34	1.17	2.00
5	**T-TB**	1.0	404	0.252	160	2.80	1.43	1.96
6		3.0	385	0.249	155	2.86	1.38	2.07
7		5.0	366	0.243	151	2.92	1.31	2.24
8	**T-Do**	1.0	604	0.275	219	2.32	1.48	1.57
9		3.0	577	0.312	186	2.35	1.43	1.64
10		5.0	549	0.361	152	2.38	1.36	1.75
11	**T-S3**	1.0	278	0.0375	742	1.89	1.40	1.35
12		3.0	256	0.0378	678	1.93	1.40	1.37
13		5.0	236	0.0371	636	2.10	1.38	1.50

[a] Prepared by Method II using PDPA as a base polymer (Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.).

[b] For the code, see Chart 2.

[c] 1 barrer = 10^{-10} cm^3(STP)·cm cm^{-2} s^{-1} cmHg^{-1}.

[d] In 10^{-6} cm^{-2} s$^{-1.}$

[e] In 10^{-3} cm^3(STP)·cm^{-3} cmHg^{-1}.

Table 7
Oxygen permselectivity of the PSPA-based polymer membranes.[a]

No.	Additives[b]	Contents (wt%)	P_{O_2}[c] (barrer)	D_{O_2}[d]	S_{O_2}[e]	P_{O_2}/P_{N_2}	D_{O_2}/D_{N_2}	S_{O_2}/S_{N_2}
1	None	0.0	229	3.02	76.0	2.69	1.41	1.91
2	**T-EO**	0.50	142	3.25	43.7	2.58	0.97	2.66
3		1.0	128	3.10	41.3	2.88	1.02	2.82
4		5.0	111	2.98	37.2	3.22	1.06	3.16
5	**T-TB**	3.0	212	3.86	55.0	2.83	0.98	2.90
6	**T-TES**	5.0	172	–	–	3.38	–	–
7	**T-Do**	5.0	132	0.981	135	2.96	1.17	2.54

[a] Prepared by Method II using PSPA as a base polymer (Method II : Casting a mixed solution of a 2D surface modifier in a polar solvent and a base polymer in a nonpolar solvent.).
[b] For the code, see Chart 2.
[c] 1 barrer = 10^{-10}cm^3(STP)·cm cm^{-2} s^{-1} cmHg^{-1}.
[d] In 10^{-7} cm^2 s^{-1}.
[e] In 10^{-3} cm^3(STP)·cm^{-3} cmHg^{-1}.

P_{O_2}/P_{N_2} (=α), D_{O_2}/D_{N_2}, and S_{O_2}/S_{N_2} through the **T-EO** containing blend polymer membranes. As shown in Table 5, nos. 1–6, in the **T-EO**/PVA membranes, the enhancements of α values were found to be mainly caused by those of S_{O_2}/S_{N_2} and the decreases of P_{O_2} values were found to be caused by those of D_{O_2}. The extent of increase of α and S_{O_2}/S_{N_2} values in 1.0 or 5.0 wt% of **T-EO**/PVA membranes were higher than those in 1.0 or 5.0 wt% of **P-EO**/PVA membranes (Table 5, nos. 4,5 and 7,8). Therefore, **T-EO** was more effective than **P-EO** for enhancing the performances because **T-EO** could show a better surface layer. In the case of the **T-EO**/PSPA membranes prepared by Method II (Table 5, nos. 15–17), increase of α values were found to be caused by those of S_{O_2}/S_{N_2} similarly to those in **T-EO**/PVA. On the other hand, in **T-EO**/PSPA prepared by Method I showed almost no effects on enhancing S_{O_2}/S_{N_2} (Table 5, nos. 12–14). Therefore, the surface thin layers produced by the 2D additives were effective for enhancing S_{O_2}/S_{N_2}. Tables 6and 7 show the values of P, *D*, and S of oxygen and nitrogen and their ratios, i.e., P_{O_2}/P_{N_2} (=α), D_{O_2}/D_{N_2}, and S_{O_2}/S_{N_2} through the PDPA- and PSPA-based blend polymer membranes, respectively. All the enhancements of α were found to be caused by those of S_{O_2}/S_{N_2}.

4. Conclusions

In this article, a facile synthesis of five 2D surface modifiers including two new compounds are reported by the SCAT(highly selective photocyclic aromatization) reaction and effective enhancement of α (= P_{O_2}/P_{N_2}) through the three polymer membranes are reported by adding a small amount of the 2D surface modifiers. Among the five 2D surface modifiers, **T-EO** showed the best performance for the enhancement. The α values in **T-EO**/PVA increased with no decrease in P_{O_2} and the α and P_{O_2} values in **T-EO**/PDPA increased simultaneously. These improvements were thought to be caused mainly by improvement of the solution selectivity on the membrane surface where the 2D surface modifiers were accumulated. In all the blend membranes, **T-EO**/PDPA, **T-TB**/PDPA, and **T-TES**/PSPA membranes showed relatively good performance, since the plots in the P_{O_2}-α graph were close to the upper boundary line by Robeson in 1991 [4]. Since all the membranes showed better permselectivities than the corresponding substrate membranes, it is very promising for the future.

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