Nonvolatile Memory Organic Field Effect Transistor Induced by the Steric Hindrance Effects of Organic Molecules

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I. Synthesis of the Push-Pull Organic Molecules

All experiments were performed under a nitrogen atmosphere in a dry box or by standard Schlenk techniques. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich (Seoul, South Korea).

1. 2-(5-Bromothiophen-2-yl)-5,5-dimethyl-1,3-dioxane (H2). 5-Bromothiophene-2-carbaldehyde, H1 (10.0 g, 52.3 mmol), neopentylglycol (6.54 g, 62.8 mmol), and p-toluenesulfonic acid (0.90 g, 5.2 mmol) were dissolved in benzene (100 mL). The reaction mixture was refluxed for 3 h and then cooled and washed with 2% NaHCO₃ (aq) three times. The combined benzene layers were then dried with Na₂SO₄, filtered, and evaporated in vacuo. The product was recrystallized from hexane. Yield: 14.2 g (98%).
1. 2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (H3). H2 (4 g, 14.4 mmol) was lithiated with a hexane solution of 1.6 M n-butyllithium (10.8 mL, 17.3 mmol, 1.2 eq) in THF at -78 °C under nitrogen atmosphere. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.2 mL, 15.7 mmol, 1.1 eq) was added at -78 °C and stirred at room temperature for 6 h under nitrogen atmosphere. It was then purified by silica gel column chromatography using hexane as an eluent. Yield: 4.1 g (88%). 1H-NMR (400 MHz, CDCl3): δ 7.47 (d, 1H, JHH = 3.5 Hz), 7.16 (d, 1H, JHH = 3.5 Hz), 5.62 (s, 1H), 3.71 (d, 2H, JHH = 11.0 Hz), 3.59 (d, 2H, JHH = 11.0 Hz), 1.29 (s, 12H), 1.22 (s, 3H), 0.75 (s, 3H). 13C-NMR (100 MHz, CDCl3): δ 148.39, 136.52, 126.16, 97.98, 83.99, 77.38, 30.14, 24.66, 22.83, 21.77. Elemental analysis: Anal. Calcd for C16H25BO4S: C, 59.27; H, 7.77; S, 9.89. Found: C, 59.21; H, 7.79; S, 9.93.

1. 3. 5-Bromo-4-methylthiophene-2-carbaldehyde (Me2). 2-Bromo-3-methylthiophene, Me1 (10 g, 56.4 mmol) was allowed to dissolve completely in 40 mL DMF. The POCl3 (10.3 mL, 112.8 mmol, 2.0 eq) was added dropwise to the mixture at 0 °C. The reaction mixture was then heated to 70 °C with stirring for 6 h. Upon cooling, the mixture was poured into an ice-bath and neutralized with Na2CO3. The product was extracted with chloroform and purified by silica gel column chromatography using dichloromethane (DCM)/hexane as an eluent. Yield: 8.7 g (92%). 1H-NMR (400 MHz, CDCl3): δ 9.70 (s, 1H), 7.44 (s, 1H), 2.21 (s, 3H). 13C-NMR (100 MHz, CDCl3): δ 181.79, 142.61, 139.09, 137.61, 122.57, 15.23.

1. 4. 2-(5-Bromo-4-methylthiophen-2-yl)-5,5-dimethyl-1,3-dioxane (Me3). Me2 (10.0 g, 48.7 mmol), neopentylglycol (6.08 g, 58.4 mmol), and p-toluenesulfonic acid (0.84 g, 5.2 mmol) were dissolved in benzene (100 mL). The reaction mixture was refluxed for 3 h and then cooled and washed with 2% NaHCO3 (aq) three times. The combined benzene layers were then dried with Na2SO4, filtered,
and evaporated in vacuo. The product was recrystallized from hexane. Yield: 13.9 g (98%). MP 74 °C. 

$^1$H-NMR (400 MHz, CDCl$_3$): δ 6.78 (s, 1H), 5.47 (s, 1H), 3.70 (d, 2H, $J_{HH} = 11.0$ Hz), 3.57 (d, 2H, $J_{HH} = 11.0$ Hz), 2.12 (s, 3H), 1.22 (s, 3H), 0.76 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 140.62, 136.49, 126.78, 109.83, 97.81, 77.30, 30.09, 22.93, 21.71, 15.11.

1. 5. 2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Me4). Me3 (5 g, 17.1 mmol) was lithiated with a hexane solution of 1.6 M n-butyllithium (12.8 mL, 20.5 mmol, 1.2 eq) in THF at -78 ºC under a nitrogen atmosphere. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.8 mL, 18.6 mmol, 1.1 eq) was added at -78 ºC and stirred at room temperature for 6 h under a nitrogen atmosphere. It was purified by silica gel column chromatography using hexane as an eluent. Yield: 4.9 g (85%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 6.97 (s, 1H), 5.56 (s, 1H), 3.70 (d, 2H, $J_{HH} = 11.0$ Hz), 3.58 (d, 2H, $J_{HH} = 11.0$ Hz), 2.38 (s, 3H), 1.26 (s, 12H), 1.21 (s, 3H), 0.75 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 141.32, 136.52, 126.16, 97.98, 83.99, 77.38, 30.14, 24.66, 22.83, 21.77. Elemental analysis: Anal. Calcd for C$_{17}$H$_{27}$BO$_4$S: C, 60.36; H, 8.05; S, 9.48. Found: C, 60.41; H, 7.99; S, 952.

\[ \text{N}-(4-	ext{iodophenyl})-\text{N-phenylnaphthalen-1-amine (1).} \]

$^1$N-(4-iodophenyl)-N-phenylnaphthalen-1-amine (1) was synthesized by Ullmann reaction of 1,4-diiodobenzene (70 g, 212 mmol, 7.0 eq) with N-phenyl-1-naphthylamine (6.5 g, 30 mmol, 1.0 eq) in dichlorobenzene at 180 ºC for 20 h in the presence of copper powder (1.89 g), K$_2$CO$_3$ (28.96 g), and 18-crown-6-ether (1.5 g). After the reaction,
the mixture was cooled, the dichlorobenzene removed under vacuum, and the remaining solid sublimed to remove excess 1,4-diiodobenzene. The product was then purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 6.44 g (51%). MP 196 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.87 (d, 2H, $J_{HH} = 8.7$ Hz), 7.76 (d, 1H, $J_{HH} = 8.2$ Hz), 7.47-7.43 (m, 4H), 7.35 (dd, 1H, $J_{HH} = 7.8$, 7.4 Hz), 7.29 (d, 1H, $J_{HH} = 7.4$ Hz), 7.20 (d, 1H, $J_{HH} = 8.2$ Hz), 7.18 (d, 1H, $J_{HH} = 7.4$ Hz), 7.04 (d, 2H, $J_{HH} = 8.2$ Hz), 6.96 (dd, 1H, $J_{HH} = 7.8$, 7.4 Hz), 6.73 (d, 2H, $J_{HH} = 8.7$ Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 148.26, 147.68, 142.88, 137.85, 135.25, 130.99, 129.23, 128.44, 127.19, 126.78, 126.56, 126.31, 126.23, 123.98, 123.01, 122.51.

2. 2. $N$-(4-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)phenyl)-$N$-phenyl-naphthalen-1-amine (2). 2 was synthesized by Suzuki coupling of 1 (1.0 g, 2.37 mmol) with H3 (0.92 g, 2.84 mmol, 1.2 eq) in toluene/2.0 M K$_2$CO$_3$ (aq) at 110 °C for 16 h under a nitrogen atmosphere in the presence of tetrakis(triphenylphosphine)palladium(0) (0.14 g, 0.12 mmol, 5.0 mol%). It was then purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.94 g (81%). MP 194 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, 1H, $J_{HH} = 8.4$ Hz), 7.89 (d, 1H, $J_{HH} = 8.2$ Hz), 7.79 (d, 1H, $J_{HH} = 8.2$ Hz), 7.50-7.35 (m, 6H), 7.23 (d, 1H, $J_{HH} = 8.2$ Hz), 7.21 (d, 1H, $J_{HH} = 7.4$ Hz), 7.11-7.05 (m, 4H), 7.01-7.96 (m, 3H), 5.62 (s, 1H), 3.78 (d, 2H, $J_{HH} = 11.0$ Hz), 3.65 (d, 2H, $J_{HH} = 11.0$ Hz), 1.31 (s, 3H), 0.80 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 147.89, 144.64, 143.09, 139.37, 135.21, 131.13, 129.11, 128.35, 127.44, 127.22, 126.59, 126.55, 126.44, 126.29, 126.13, 125.86, 124.09, 122.29, 122.10, 121.30, 121.27, 98.30, 77.44, 30.11, 22.93, 21.76.

2. 3. 5-(4-(Naphthalen-1-yl(phenyl)amino)phenyl)thiophene-2-carbaldehyde (3). 2 (0.8 g, 1.63 mmol) was dissolved in THF (80 mL) and water (20 mL). Trifluoroacetic acid (10 mL) was then added to the reaction mixture. The resulting reaction mixture was stirred for 3 h at room temperature, carefully quenched with saturated NaHCO$_3$ (aq), and extracted with ether. The combined ether phases were then washed with 2% NaHCO$_3$ (aq), dried over Na$_2$SO$_4$, and evaporated in vacuo. It was purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.63 g (95%). MP 182 °C. $^1$H-
NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 7.92 (d, 1H, J₆₇ = 7.8 Hz), 7.88 (d, 1H, J₆₇ = 7.8 Hz), 7.80 (d, 1H, J₆₇ = 7.8 Hz), 7.64 (d, 1H, J₆₇ = 4.0 Hz), 7.48-7.44 (m, 4H), 7.37 (d, 1H, J₆₇ = 4.0 Hz), 7.36 (d, 1H, J₆₇ = 4.0 Hz), 7.24-7.21 (m, 3H), 7.15 (d, 2H, J₆₇ = 7.8 Hz), 7.03 (t, 1H, J₆₇ = 4.0 Hz), 6.95 (d, 2H, J₆₇ = 7.8 Hz).

13C-NMR (100 MHz, CDCl₃): δ 182.42, 154.61, 149.57, 147.14, 142.50, 140.97, 137.69, 135.20, 130.97, 129.28, 128.46, 127.31, 127.15, 127.02, 126.63, 126.29, 126.25, 125.14, 123.81, 123.21, 123.11, 122.53, 120.11.

FTIR (KBr, cm⁻¹): ν 1666.

2. 4.  2-((5-(4-(Naphthalen-1-yl(phenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile (4).

An ethanol solution containing 3 (0.5 g, 1.23 mmol) and malononitrile (0.1 g, 1.51 mmol) was refluxed for 18 h. The cooled reaction mixture was then extracted with DCM and purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.37 g (64%). MP 218 °C. ¹H-NMR (400 MHz, CDCl₃): δ 7.90 (d, 1H, J₆₇ = 8.8 Hz), 7.88 (d, 1H, J₆₇ = 8.8 Hz), 7.82 (d, 1H, J₆₇ = 7.2 Hz), 7.67 (s, 1H), 7.60 (d, 1H, J₆₇ = 4.0 Hz), 7.50-7.41 (m, 4H), 7.38 (d, 1H, J₆₇ = 8.0 Hz), 7.35 (d, 1H, J₆₇ = 7.2 Hz), 7.28-7.24 (m, 3H), 7.16 (d, 2H, J₆₇ = 8.0 Hz), 7.05 (t, 1H, J₆₇ = 7.2 Hz), 6.90 (d, 2H, J₆₇ = 8.8 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 168.42, 152.42, 150.39, 149.80, 147.27, 142.78, 142.69, 135.55, 135.01, 131.90, 131.51, 129.87, 129.65, 128.80, 127.73, 127.49, 127.01, 126.62, 124.72, 124.10, 123.74, 123.69, 119.91, 114.84, 113.86. FTIR (KBr): the C=C ring stretch 1491.23, 1505.22 and 1590.99 cm⁻¹, the C≡N stretch 2219.49 cm⁻¹, aromatic C-H stretch 3033.31 and 3050.88 cm⁻¹. EI-MS (m/z): 453. Elemental analysis: Anal. Calcd for C₃₀H₁₉N₃S: C, 79.44; H, 4.22; N, 9.26; S, 7.07. Found: C, 79.51; H, 4.25; N, 9.24; S, 6.99.
3. 1. Synthesis of N-(4-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methylthiophen-2-yl)phenyl)-N-phenynaphthalen-1-amine (5). 5 was synthesized by Suzuki coupling of 1 (1.0 g, 2.37 mmol) with Me4 (0.96 g, 2.84 mmol, 1.2 eq) in toluene/2.0 M K$_2$CO$_3$ (aq) at 110 °C for 16 h under nitrogen atmosphere in the presence of tetrakis(triphenylphospine)palladium(0) (0.14 g, 0.12 mmol, 5.0 mol%). It was purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.96 g (80%). MP 198 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.86 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.75 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.47 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.44 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.35 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.33 (d, 1H, $J_{\text{HH}}$ = 8.2 Hz), 7.24-7.17 (m, 4H), 7.07 (d, 2H, $J_{\text{HH}}$ = 8.2 Hz), 6.99-6.91 (m, 4H), 5.55 (s, 1H), 3.73 (d, 2H, $J_{\text{HH}}$ = 11.0 Hz), 3.61 (d, 2H, $J_{\text{HH}}$ = 11.0 Hz), 2.22 (s, 3H), 1.26 (s, 3H), 0.82 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 147.94, 147.51, 143.16, 137.91, 135.24, 131.87, 131.24, 129.52, 129.11, 128.94, 128.36, 127.52, 127.36, 126.62, 126.46, 126.32, 126.14, 124.15, 122.25, 122.04, 120.89, 98.30, 77.48, 30.15, 22.93, 21.79, 15.00.

3. 2. 4-Methyl-5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiophene-2-carbaldehyde (6). 5 (0.8 g, 1.58 mmol) was dissolved in THF (80 mL) and water (20 mL). Then, trifluoroacetic acid (10 mL) was added to the reaction mixture. The resulting reaction mixture was stirred for 3 h at room temperature, carefully quenched with saturated NaHCO$_3$ (aq), and extracted with ether. The combined ether phases were then washed with 2% NaHCO$_3$ (aq), dried over Na$_2$SO$_4$, evaporated in vacuo, and purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.63 g (95%). MP
179 °C. 1H-NMR (400 MHz, CDCl3): δ 9.78 (s, 1H), 7.94 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.89 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.80 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.52-7.46 (m, 4H), 7.38-7.36 (m, 2H) 7.30 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.23 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.21 (d, 1H, \(J_{HH} = 8.4\) Hz), 7.15 (d, 2H, \(J_{HH} = 7.5\) Hz), 7.00-6.98 (m, 3H), 2.32 (s, 3H). 13C-NMR (100 MHz, CDCl3): δ 182.44, 149.07, 148.81, 147.27, 142.63, 140.24, 139.57, 135.20, 133.73, 131.07, 129.42, 129.22, 128.68, 128.40, 127.38, 126.94, 126.57, 126.27, 126.20, 125.56, 123.87, 122.98, 122.86, 119.96, 15.16. FTIR (KBr, cm\(^{-1}\)): ν 1671.

3. 2-((4-Methyl-5-(4-(naphthalen-1-yl(phenyl)amino)phenyl)thiophen-2-yl)methylene)malononitrile(7). An ethanol solution containing 6 (0.5 g, 1.19 mmol) and malononitrile (0.1 g, 1.51 mmol) was refluxed for 18 h. The cooled reaction mixture was extracted with DCM and purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.41 g (74%). MP 220 °C. 1H-NMR (400 MHz, CDCl3): δ 7.89 (d, 2H, \(J_{HH} = 8.8\) Hz), 7.81 (d, 1H, \(J_{HH} = 8.2\) Hz), 7.64 (s, 1H), 7.50-7.45 (m, 3H), 7.39 (d, 1H, \(J_{HH} = 7.2\) Hz), 7.36 (d, 1H, \(J_{HH} = 7.2\) Hz), 7.30 (d, 2H, \(J_{HH} = 8.2\) Hz), 7.23 (d, 2H, \(J_{HH} = 7.2\) Hz), 7.16 (d, 2H, \(J_{HH} = 7.2\) Hz), 7.03 (t, 1H), 6.95 (d, 2H, \(J_{HH} = 8.8\) Hz), 2.33 (s, 3H). 13C-NMR (100 MHz, CDCl3): δ 168.42, 152.42, 150.39, 149.80, 147.27, 142.78, 142.69, 135.55, 135.01, 131.90, 131.32, 129.87, 129.65, 128.80, 127.73, 127.49, 127.01, 126.62, 124.72, 124.10, 123.74, 123.69, 119.91, 114.84, 113.86. FTIR (KBr): the C=C ring stretch 1491.23, 1505.22 and 1590.99 cm\(^{-1}\), the C≡N stretch 2219.49 cm\(^{-1}\), aliphatic C-H stretch 2961.24 and 2923.60 cm\(^{-1}\), aromatic C-H stretch 3033.31 and 3050.88 cm\(^{-1}\). EI-MS (m/z): 467. Elemental analysis: Anal. Calcd for C\(_{31}\)H\(_{21}\)N\(_3\)S: C, 79.63; H, 4.53; N, 8.99; S, 6.86. Found: C, 79.59; H, 4.49; N, 9.02; S, 6.91.

II. Infrared Spectroscopy of PPOMs

Figure S1 shows the FTIR of PPOMs. The C≡N stretch and C=C ring stretch in the both QH and QMe were detected at 2219.49, 1590.99, 1505.22, and 1491.23 cm\(^{-1}\), respectively and also the aromatic C-H stretching peaks were observed at 3033.31 and 3050.88 cm\(^{-1}\) in the both QH and QMe. On the other
hand, the aliphatic C-H stretching peaks at 2961.24 and 2923.60 cm\(^{-1}\) were present only in QMe, not in QH.

![FTIR spectra of PPOMs (QH and QMe).](image)

**Fig. S1** FTIR spectra of PPOMs (QH and QMe).

***III. X-ray diffraction of PPOMs***

Fig. S2 displays out-of-plane X-ray diffraction patterns of the QH and QMe on the PMMA/SiO\(_2\)/Si substrates, which were obtained from a D8 Discover thin-film diffractometer with Cu Ka radiation (\(\lambda = 1.54056\) Å). Both films of the QH and QMe/PMMA/SiO\(_2\)/Si substrates indicated only a sharp peak occurring at 2\(\theta\) = 32.86 and 32.84, respectively, which corresponded to a d-spacing of the QH (1.166 Å) and QMe (1.179 Å), respectively. Therefore, PPOMs formed on PMMA//SiO\(_2\)/Si substrates had a uniaxial structure orientated normal to the substrate, with the conduction channels running parallel to the substrate.
**Fig. S2** The XRD patterns of (a) QH and (b) QMe films formed on PMMA/SiO$_2$/Si substrates.

**SUPPLEMENTAL REFERENCES**