

SUPPORTING INFORMATION PARAGRAPH

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

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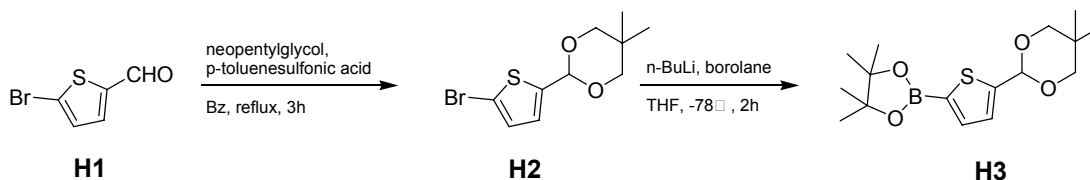
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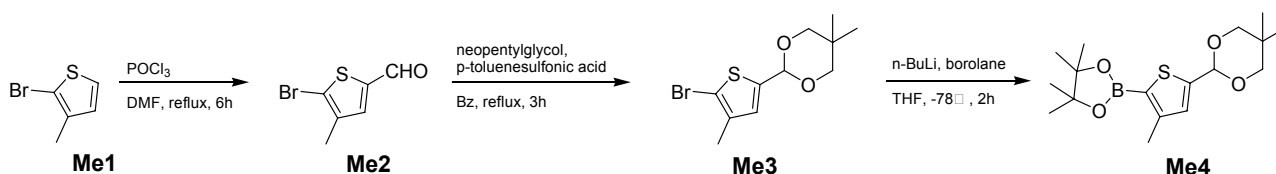
I. Synthesis of the Push-Pull Organic Molecules

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. 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. 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, *J*_{HH} = 3.5 Hz), 7.16 (d, 1H, *J*_{HH} = 3.5 Hz), 5.62 (s, 1H), 3.71 (d, 2H, *J*_{HH} = 11.0 Hz), 3.59 (d, 2H, *J*_{HH} = 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.

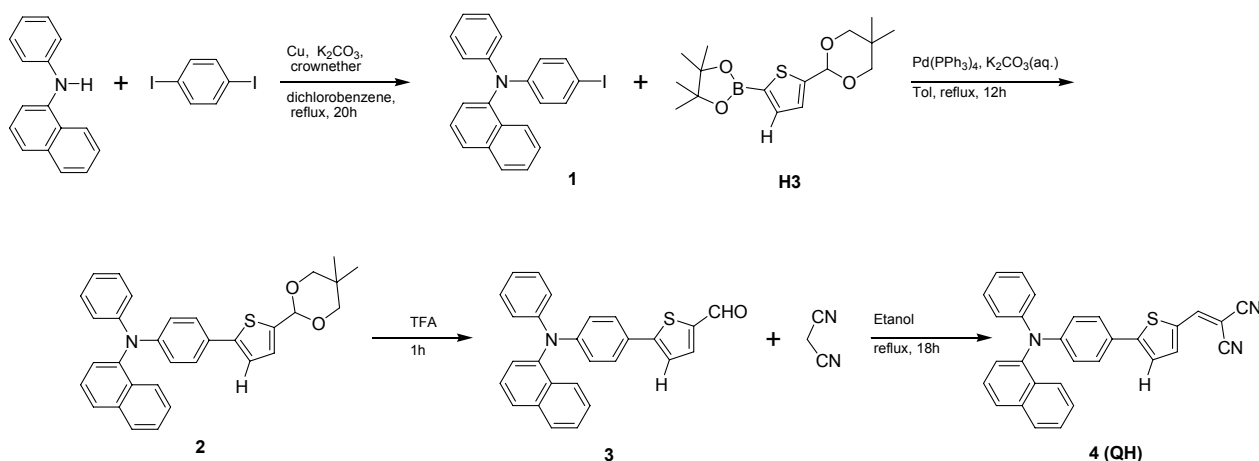


1. 3. 5-Bromo-4-methylthiophene-2-carbaldehyde (Me2). 2-Bromo-3-methylthiophene, **Me1** (10 g, 56.4 mmol) was allowed to dissolve completely in 40 mL DMF. The POCl₃ (10.3 mL, 112.8 mmol, 2.0 eq) was added dropwise to the mixture at 0 °C. The reaction mixture was then heated to 70 °C with stirring for 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. ¹H-NMR (400 MHz, CDCl₃): 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). ¹³C-NMR (100 MHz, CDCl₃): 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 °C 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 °C 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%). ¹H-NMR (400 MHz, CDCl₃): 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). ¹³C-NMR (100 MHz, CDCl₃): 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 C₁₇H₂₇BO₄S: C, 60.36; H, 8.05; S, 9.48. Found: C, 60.41; H, 7.99; S, 9.52.



2. 1. *N*-(4-Iodophenyl)-*N*-phenyl-1-naphthylamine (1). *N*-(4-iodophenyl)-*N*-phenyl-1-naphthylamine (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 °C for 20 h in the presence of copper powder (1.89 g), K₂CO₃ (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. ¹H-NMR (400 MHz, CDCl₃): δ 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). ¹³C-NMR (100 MHz, CDCl₃): δ 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.

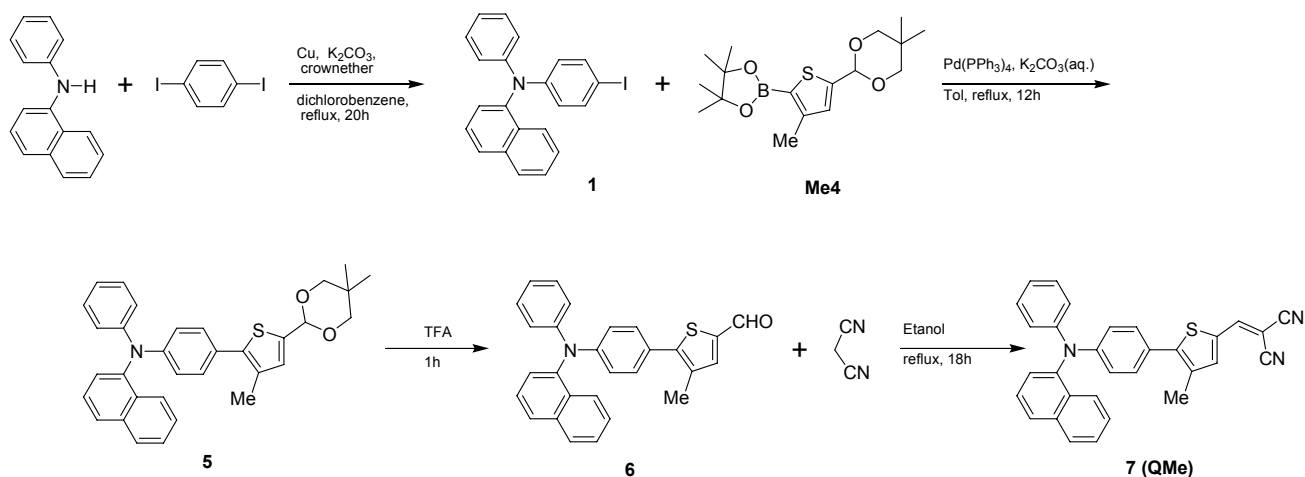
2. 2. N-(4-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)phenyl)-N-phenylnaphthalen-1-amine (2). **2** was synthesized by Suzuki coupling of **1** (1.0 g, 2.37 mmol) with **H3** (0.92 g, 2.84 mmol, 1.2 eq) in toluene/2.0 M K₂CO₃ (aq) at 110 °C for 16 h under a nitrogen atmosphere in the presence of 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. ¹H-NMR (400 MHz, CDCl₃): δ 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). ¹³C-NMR (100 MHz, CDCl₃): δ 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 NaHCO₃ (aq), and extracted with ether. The combined ether phases were then washed with 2% NaHCO₃ (aq), dried over Na₂SO₄, 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. ¹H-

NMR (400 MHz, CDCl_3): δ 9.81 (s, 1H), 7.92 (d, 1H, $J_{\text{HH}} = 7.8$ Hz), 7.88 (d, 1H, $J_{\text{HH}} = 7.8$ Hz), 7.80 (d, 1H, $J_{\text{HH}} = 7.8$ Hz), 7.64 (d, 1H, $J_{\text{HH}} = 4.0$ Hz), 7.48-7.44 (m, 4H), 7.37 (d, 1H, $J_{\text{HH}} = 4.0$ Hz), 7.36 (d, 1H, $J_{\text{HH}} = 4.0$ Hz), 7.24-7.21 (m, 3H), 7.15 (d, 2H, $J_{\text{HH}} = 7.8$ Hz), 7.03 (t, 1H, $J_{\text{HH}} = 4.0$ Hz), 6.95 (d, 2H, $J_{\text{HH}} = 7.8$ Hz). ^{13}C -NMR (100 MHz, CDCl_3): 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, CDCl_3): δ 7.90 (d, 1H, $J_{\text{HH}} = 8.8$ Hz), 7.88 (d, 1H, $J_{\text{HH}} = 8.8$ Hz), 7.82 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.67 (s, 1H), 7.60 (d, 1H, $J_{\text{HH}} = 4.0$ Hz), 7.50-7.41 (m, 4H), 7.38 (d, 1H, $J_{\text{HH}} = 8.0$ Hz), 7.35 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.28-7.24 (m, 3H), 7.16 (d, 2H, $J_{\text{HH}} = 8.0$ Hz), 7.05 (t, 1H, $J_{\text{HH}} = 7.2$ Hz), 6.90 (d, 2H, $J_{\text{HH}} = 8.8$ Hz). ^{13}C -NMR (100 MHz, CDCl_3): 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 $\equiv$ 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 $\text{C}_{30}\text{H}_{19}\text{N}_3\text{S}$: 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*-phenyl-1-naphthalen-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 K₂CO₃ (aq) at 110 °C for 16 h under nitrogen atmosphere in the presence of tetrakis(triphenylphosphine)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. ¹H-NMR (400 MHz, CDCl₃): δ 7.92 (d, 1H, *J*_{HH} = 8.2 Hz), 7.86 (d, 1H, *J*_{HH} = 8.2 Hz), 7.75 (d, 1H, *J*_{HH} = 8.2 Hz), 7.47 (d, 1H, *J*_{HH} = 8.2 Hz), 7.44 (d, 1H, *J*_{HH} = 8.2 Hz), 7.35 (d, 1H, *J*_{HH} = 8.2 Hz), 7.33 (d, 1H, *J*_{HH} = 8.2 Hz), 7.24-7.17 (m, 4H), 7.07 (d, 2H, *J*_{HH} = 8.2 Hz), 6.99-6.91 (m, 4H), 5.55 (s, 1H), 3.73 (d, 2H, *J*_{HH} = 11.0 Hz), 3.61 (d, 2H, *J*_{HH} = 11.0 Hz), 2.22 (s, 3H), 1.26 (s, 3H), 0.82 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 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 NaHCO₃ (aq), and extracted with ether. The combined ether phases were then washed with 2% NaHCO₃ (aq), dried over Na₂SO₄, evaporated *in vacuo*, and purified by silica gel column chromatography using DCM/hexane as an eluent. Yield: 0.63 g (95%). MP

179 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 9.78 (s, 1H), 7.94 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.89 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.80 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.52-7.46 (m, 4H), 7.38-7.36 (m, 2H) 7.30 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.23 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.21 (d, 1H, $J_{\text{HH}} = 8.4$ Hz), 7.15 (d, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.00-6.98 (m, 3H), 2.32 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 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. 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. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.89 (d, 2H, $J_{\text{HH}} = 8.8$ Hz), 7.81 (d, 1H, $J_{\text{HH}} = 8.2$ Hz), 7.64 (s, 1H), 7.50-7.45 (m, 3H), 7.39 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.36 (d, 1H, $J_{\text{HH}} = 7.2$ Hz), 7.30 (d, 2H, $J_{\text{HH}} = 8.2$ Hz), 7.23 (d, 2H, $J_{\text{HH}} = 7.2$ Hz), 7.16 (d, 2H, $J_{\text{HH}} = 7.2$ Hz), 7.03 (t, 1H), 6.95 (d, 2H, $J_{\text{HH}} = 8.8$ Hz), 2.33 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 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 $\equiv$ 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 $\text{C}_{31}\text{H}_{21}\text{N}_3\text{S}$: 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 $\equiv$ 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.

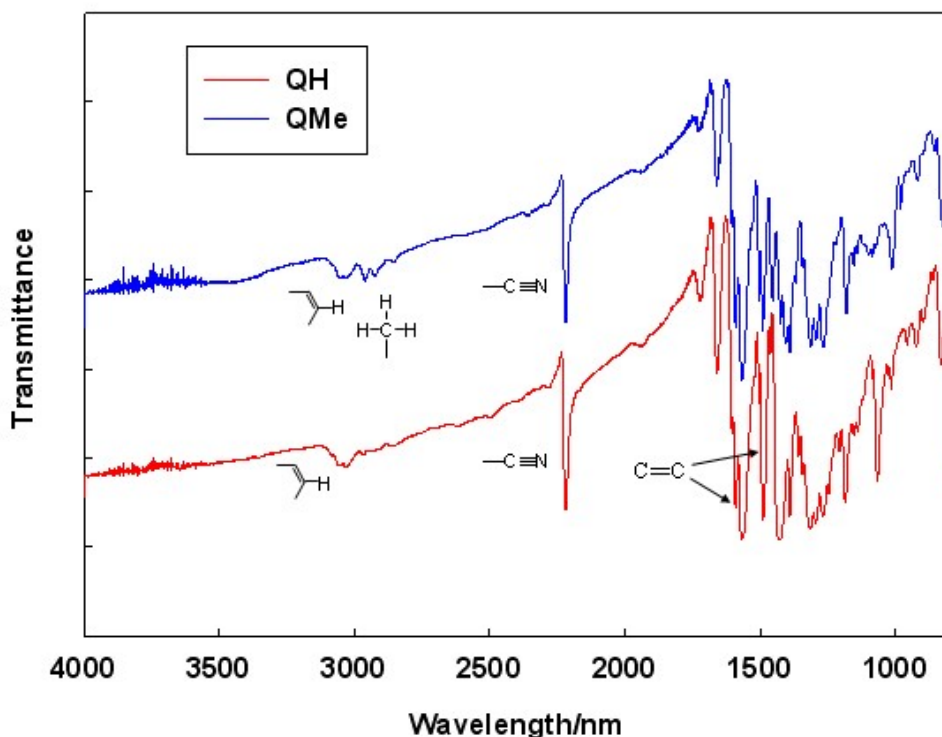


Fig. S1 FTIR spectra of PPOMs (QH and QMe).

III. X-ray diffraction of PPOMs

Fig. S2 displays out-of-plane X-ray diffraction patterns of the QH and QMe on the PMMA/SiO₂/Si substrates, which were obtained from a D8 Discover thin-film diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Both films of the QH and QMe/PMMA/SiO₂/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 ($1.166 \text{ \AA}$) and QMe ($1.179 \text{ \AA}$), respectively. Therefore, PPOMs formed on PMMA//SiO₂/Si substrates had a uniaxial structure orientated normal to the substrate, with the conduction channels running parallel to the substrate.

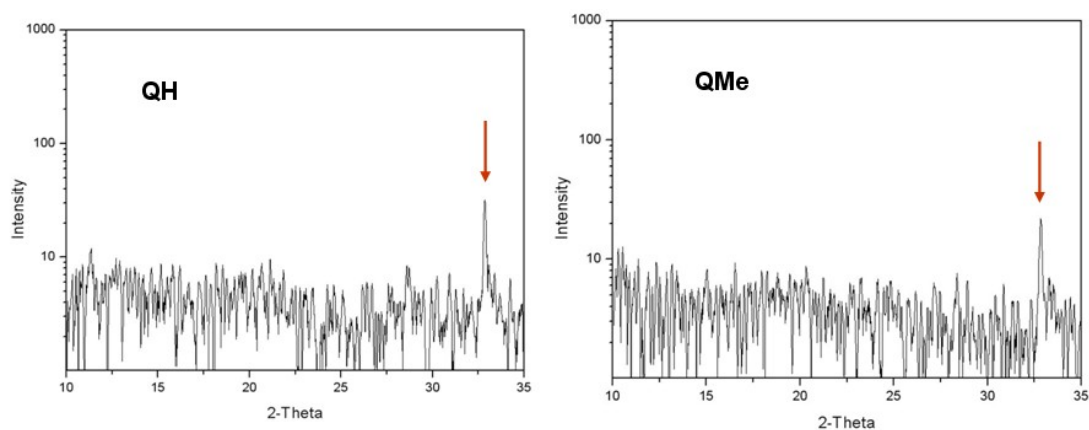


Fig. S2 The XRD patterns of (a) QH and (b) QMe films formed on PMMA/SiO₂/Si substrates.

SUPPLEMENTAL REFERENCES

1. B. E. Koene, D. E. Loy and M. E. Thompson, *Chem. Mater.*, 1998, **10**, 2235.