# Supporting Information for:

# Self-Assembled Dipoles of *o*-Carborane on Gate Oxide Tuning Charge Carriers in Organic Field Effect Transistors

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## 1. Synthesis

**General:** The reagents and starting materials employed were commercially available and used without any further purification or prepared following reported methods as indicated. Anhydrous and O<sub>2</sub>-free THF was purified by an Advanced Technology Pure-Solv PS-MD-4 system. NMR spectra were recorded on a Brucker 500 MHz spectrometer. Chemical shift values ( $\delta$ ) are expressed in parts per million using residual solvent protons as internal standard (<sup>1</sup>H NMR,  $\delta$ (H) is 7.26 ppm for CDCl<sub>3</sub>, <sup>13</sup>C NMR,  $\delta$ (C) is 77.16 ppm for CDCl<sub>3</sub>). Mass spectra were recorded on a Therno Finnigan MAT 95 XL spectrometer. Melting points, without calibration, were measured using a Nikon Polarized Light Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage.

12-cyclohexyldodecylphosphonic acid (CDPA) was synthesized following the reported procedures.<sup>1</sup>



## 1-Bromo-12-o-carboranyldodecane (2)

At 0 °C, 1 eq. of *n*-BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) was slowly added to a solution of *o*-carborane (1.44 g, 10 mmol) in 30 mL of diethyl ether. After being stirred for 1 hour, 1,12-dibromododecane (3.28 g, 10 mmol) was added to the resulting solution of 1-lithio*o*-carborane in one portion at 0 °C. Then the solution was warmed to room temperature and kept stirring for overnight. The reaction mixture was quenched with water and extracted with diethyl ether (30 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under a reduced pressure. The resulting crude mixture was purified with flash chromatography on silica gel using hexane as eluent to give **2** as colorless oil. Yield: 50% (1.95 g, 5 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 3.56 (s, 1H), 3.40 (s, 2H), 2.18 (m, 2H), 1.85 (s, 2H), 1.42 (s, 4H), 1.25 (s, 14H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 75.6, 61.1, 38.2, 34.2, 32.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.9, 28.3; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): -2.4 (1B), -5.9 (1B), -9.3 (2B), -12.2 (6B). HRMS-EI<sup>+</sup> (m/z): [M<sup>+</sup>] calculated for C<sub>12</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>2</sub>: 391.2827, found: 391.2834.



#### Diethyl 12-o-carboranyldodecylphosphonate (3)

3.4 mL (20 mmol) of triethyl phosphite and 882 mg (2 mmol) of 1-bromo-12-*o*-carboranebased dodecane were heated at 160 °C for 2 days with continuous stirring under an atmosphere of nitrogen. After removal of excessive triethyl phosphite with a flow of air, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (2:1) as the eluent to give **3** as colorless oil. Yield: 71% (718 mg, 1.6 mmol). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 4.07 (m, 4H), 3.57 (s, 1H), 2.17 (m, 2H), 1.86 (s, 1H), 1.69 (m, 3H), 1.31 (m, 24H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 75.6, 61.4 (d, <sup>2</sup>*J*<sub>C-P</sub> = 6.4 Hz), 61.1, 38.2, 30.7 (d, <sup>3</sup>*J*<sub>C-P</sub> = 17.0 Hz), 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 29.0, 25.8 (d, <sup>1</sup>*J*<sub>C-P</sub> = 140.6 Hz), 22.5 (d, <sup>2</sup>*J*<sub>C-P</sub> = 5.0 Hz), 16.6 (d, <sup>3</sup>*J*<sub>C-P</sub> = 6.0 Hz); <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): -2.4 (1B), -5.9 (1B), -9.3 (2B), -12.2 (6B). HRMS-EI<sup>+</sup> (m/z): [M<sup>+</sup>] calculated for C<sub>12</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>2</sub>: 471.4011, found: 471.4004.



#### 12-o-carboranyldodecylphosphonic acid (CBPA)

0.63 mL (4.7 mmol) of trimethylsilylbromide was added to a solution of **3** (710 mg, 1.6 mmol) in 3 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> at 0°C under a nitrogen atmosphere. The reaction mixture was stirred under the nitrogen atmosphere overnight at room temperature. After addition of 5 mL of water, the reaction mixture was stirred for 2 hours resulting white emulsion. The solvents (CH<sub>2</sub>Cl<sub>2</sub> and water) were removed under a flow of air overnight resulting in light yellow oil. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and hexane was then added into the solution. The resulting mixture was cooled to -15 °C, and the resulting white precipitates were collected by filtration. Yield: 12% (77 mg, 0.2 mmol). 84 ~ 86 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.40 (br s, 2H), 3.56 (s, 1H), 2.18 (m, 2H), 1.74 (s, 3H), 1.60 (s, 2H), 1.37 (m, 17H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 75.6, 61.1, 38.2, 30.6 (d, <sup>3</sup>*J*<sub>C-P</sub> = 17.0 Hz), 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.1, 25.4 (d, <sup>1</sup>*J*<sub>C-P</sub> = 145.2 Hz), 22.2; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): -2.4 (1B), -5.9 (1B), -9.3 (2B), -12.2 (6B). HRMS-EI<sup>+</sup> (m/z): [M<sup>+</sup>] calculated for C<sub>12</sub>H<sub>7</sub>FN<sub>2</sub>O<sub>2</sub>: 391.3418, found: 391.3416.

NMR spectra (\*: peak for residue solvent)



Figure S1. <sup>1</sup>H NMR spectrum of 1-bromo-12-o-carboranyldodecane (2) in CDCl<sub>3</sub>



Figure S2. <sup>13</sup>C NMR spectrum of 1-bromo-12-o-carboranyldodecane (2) in CDCl<sub>3</sub>



Figure S3. <sup>11</sup>B {<sup>1</sup>H} NMR spectrum of 1-bromo-12-*o*-carboranyldodecane (2) in CDCl<sub>3</sub>



Figure S4. <sup>1</sup>H NMR spectrum of diethyl 12-o-carboranyldodecylphosphonate (3) in CDCl<sub>3</sub>



Figure S5. <sup>13</sup>C NMR spectrum of diethyl 12-*o*-carboranyldodecylphosphonate (3) in CDCl<sub>3</sub>



Figure S6. <sup>11</sup>B  $\{^{1}H\}$  NMR spectrum of diethyl 12-*o*-carboranyldodecylphosphonate (3) in CDCl<sub>3</sub>.



Figure S7. <sup>1</sup>H NMR spectrum of CBPA in CDCl<sub>3</sub>



Figure S9. <sup>11</sup>B {<sup>1</sup>H} NMR spectrum of CBPA in CDCl<sub>3</sub>

# **2. DFT Calcuations**

Molecular geometries of CBPA and CDPA were optimized the B3LYP level of the density functional theory (DFT) with the 6-31G(d,p) basis set, and their dipole moments were calculated at the B3LYP level of DFT with the 6-31++G(d, p) basis set using the Gaussian 09 program.<sup>2</sup>

Optimized Cartesian coordinates at B3LYP/6-31G(d,p) level of theory

# CBPA

|   | Х        | Y        | Z        |
|---|----------|----------|----------|
| В | -7.15709 | 0.471865 | 1.382178 |
| В | -8.38938 | 1.631868 | 0.876018 |
| В | -8.8827  | 0.079991 | 1.588102 |
| С | -6.67451 | -0.34736 | -0.05966 |
| В | -6.97035 | 1.339274 | -0.15327 |
| В | -8.57277 | 1.48965  | -0.90081 |
| В | -7.44217 | 0.238524 | -1.46832 |
| В | -9.36548 | -1.01528 | 0.268101 |
| В | -9.75985 | 0.714203 | 0.177902 |
| С | -7.80065 | -1.04498 | 0.925192 |
| В | -7.94476 | -1.30499 | -0.75663 |
| В | -9.17092 | -0.15312 | -1.27516 |
| С | -5.28073 | -0.99073 | -0.07945 |
| С | -4.09625 | -0.01713 | -0.12779 |
| С | -2.75459 | -0.76172 | -0.11548 |
| С | -1.53943 | 0.1731   | -0.15031 |
| С | -0.20104 | -0.57532 | -0.12253 |
| С | 1.022333 | 0.349073 | -0.14366 |
| С | 2.356296 | -0.40668 | -0.10457 |
| С | 3.584606 | 0.511289 | -0.11875 |
| С | 4.914802 | -0.25045 | -0.06987 |
| С | 6.145421 | 0.664356 | -0.08212 |
| С | 7.46931  | -0.10787 | -0.0236  |
| С | 8.693588 | 0.820564 | -0.03652 |
| Р | 10.26877 | -0.06847 | -0.0097  |
| 0 | 10.26354 | -0.72059 | 1.4837   |
| 0 | 11.34033 | 1.156009 | 0.064754 |
| 0 | 10.56485 | -1.05193 | -1.08608 |
| Н | -6.37876 | 0.49735  | 2.270794 |
| Н | -8.51972 | 2.651926 | 1.465013 |
| Н | -9.27619 | -0.10889 | 2.68763  |
| Н | -6.04423 | 2.060319 | -0.28469 |
| Н | -8.83326 | 2.424149 | -1.58215 |
| Н | -6.81786 | 0.212215 | -2.47399 |
| Н | -10.0774 | -1.93323 | 0.491811 |
| Н | -10.8802 | 1.088197 | 0.276821 |
| Н | -7.44488 | -1.8917  | 1.498302 |
| Н | -7.63714 | -2.36375 | -1.18046 |

| Η | -9.85469 | -0.39891 | -2.21141 |
|---|----------|----------|----------|
| Н | -5.23095 | -1.66293 | -0.94152 |
| Н | -5.18538 | -1.6216  | 0.812306 |
| Н | -4.1443  | 0.66854  | 0.726342 |
| Н | -4.1659  | 0.602998 | -1.02891 |
| Н | -2.70984 | -1.44803 | -0.97285 |
| Н | -2.69785 | -1.39396 | 0.782239 |
| Н | -1.58813 | 0.863268 | 0.703591 |
| Н | -1.58855 | 0.800879 | -1.05092 |
| Н | -0.1518  | -1.26223 | -0.97937 |
| Н | -0.15988 | -1.20894 | 0.77499  |
| Н | 0.970802 | 1.038921 | 0.710672 |
| Н | 0.986968 | 0.979222 | -1.04364 |
| Н | 2.408252 | -1.09526 | -0.95991 |
| Н | 2.387524 | -1.03915 | 0.794125 |
| Н | 3.530965 | 1.202897 | 0.734067 |
| Н | 3.558384 | 1.140029 | -1.02007 |
| Н | 4.969264 | -0.94215 | -0.92224 |
| Н | 4.939955 | -0.87879 | 0.831688 |
| Н | 6.092021 | 1.359204 | 0.767883 |
| Н | 6.127225 | 1.288229 | -0.98681 |
| Н | 7.534095 | -0.79805 | -0.87343 |
| Н | 7.496583 | -0.72484 | 0.882469 |
| Н | 8.683551 | 1.502707 | 0.821606 |
| Н | 8.705213 | 1.442673 | -0.93862 |
| Н | 10.72382 | -1.57251 | 1.469801 |
| Н | 12.13332 | 0.92356  | -0.44047 |
|   |          |          |          |

CDPA

|   | Х        | Y        | Ζ        |
|---|----------|----------|----------|
| С | 6.510627 | -0.86733 | 0.181188 |
| С | 5.259156 | -0.13224 | -0.31777 |
| С | 3.946227 | -0.81202 | 0.092109 |
| С | 2.699676 | -0.06861 | -0.40381 |
| С | 1.37735  | -0.69057 | 0.061284 |
| С | 0.141404 | 0.06743  | -0.43913 |
| С | -1.18673 | -0.51078 | 0.064088 |
| С | -2.41504 | 0.253653 | -0.44513 |
| С | -3.74562 | -0.29658 | 0.082402 |
| С | -4.96948 | 0.466416 | -0.43918 |
| С | -6.29669 | -0.07253 | 0.108667 |
| С | -7.51202 | 0.693185 | -0.43732 |
| Р | -9.08684 | 0.127122 | 0.249235 |
| 0 | -10.1557 | 1.019391 | -0.59612 |
| 0 | -9.20821 | -1.37699 | -0.36624 |
| 0 | -9.29777 | 0.182753 | 1.721028 |
| С | 7.852087 | -0.21731 | -0.20742 |

| С | 9.035574 | -1.14256 | 0.137994 |
|---|----------|----------|----------|
| С | 10.39444 | -0.52402 | -0.2246  |
| С | 10.57884 | 0.852374 | 0.429419 |
| С | 9.41329  | 1.788973 | 0.083163 |
| С | 8.056411 | 1.164269 | 0.444849 |
| Н | 6.493127 | -1.89527 | -0.20807 |
| Н | 6.464619 | -0.96047 | 1.276554 |
| Н | 5.252162 | 0.897327 | 0.062281 |
| Н | 5.300226 | -0.05052 | -1.41352 |
| Н | 3.931969 | -1.84407 | -0.28625 |
| Н | 3.908602 | -0.89151 | 1.188036 |
| Н | 2.743995 | 0.975416 | -0.06175 |
| Н | 2.715609 | -0.02583 | -1.50225 |
| Н | 1.325022 | -1.73598 | -0.27478 |
| Н | 1.361357 | -0.72524 | 1.160011 |
| Н | 0.215087 | 1.12024  | -0.13085 |
| Н | 0.1413   | 0.075137 | -1.53849 |
| Н | -1.26401 | -1.56526 | -0.23699 |
| Н | -1.18861 | -0.50952 | 1.163406 |
| Н | -2.3248  | 1.312339 | -0.16281 |
| Н | -2.42405 | 0.234269 | -1.54427 |
| Н | -3.83611 | -1.35729 | -0.1913  |
| Н | -3.74092 | -0.26655 | 1.181053 |
| Н | -4.87422 | 1.529814 | -0.1779  |
| Н | -4.98462 | 0.423294 | -1.53742 |
| Н | -6.39835 | -1.13417 | -0.14585 |
| Н | -6.2971  | -0.01201 | 1.203711 |
| Н | -7.44095 | 1.761461 | -0.20299 |
| Н | -7.5761  | 0.609394 | -1.52848 |
| Н | -10.9104 | 1.24178  | -0.0314  |
| Н | -9.65118 | -1.95469 | 0.272386 |
| Н | 7.853171 | -0.07343 | -1.30058 |
| Н | 9.01332  | -1.35756 | 1.217038 |
| Н | 8.912268 | -2.10721 | -0.37066 |
| Н | 11.20666 | -1.19919 | 0.071003 |
| Н | 10.46236 | -0.41634 | -1.31667 |
| Н | 10.63098 | 0.729381 | 1.52074  |
| Н | 11.5321  | 1.297627 | 0.119904 |
| Н | 9.531966 | 2.751648 | 0.595115 |
| Н | 9.434019 | 2.006542 | -0.9944  |
| Н | 7.990073 | 1.050089 | 1.537584 |
| Н | 7.250045 | 1.847787 | 0.156179 |



**Figure S10** Energy minimized models and calculated dipole moments of CBPA and CDPA. (The dipole directs from the positive end to the negative end.)

## 3. Formation and characterization of SAMs

#### (1) Formation of the SAM-modified $AlO_x$

A highly doped silicon wafer (resistivity smaller than 0.008  $\Omega$ ·cm) was cut into small squares of 1.2 cm × 1.2 cm. After cleaning with ultra-sonication in acetone, isopropanol and ethanol successively for 10 minutes, it was washed with H<sub>2</sub>O, dried with a stream of N<sub>2</sub> gas, and finally treated with O<sub>2</sub> plasma for 2 minutes. Al(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O (0.563 g) was dissolved in ethanol (3 mL) and stirred for 12 hours, resulting a solution of Al(NO<sub>3</sub>)<sub>3</sub> in ethanol (0.5 mol L<sup>-1</sup>), which was spin-coated onto the cleaned Si substrate at 5000 rpm for 40 second under ambient conditions. The resulting film was baked at 300 °C for 30 minutes to achieve complete decomposition of nitrate and a high degree of dehydration. To form the SAM-modified AlO<sub>x</sub>, the AlO<sub>x</sub>-coated Si wafer was treated with O<sub>2</sub> plasma for 1.5 minutes and soaked in a solution of corresponding phosphonic acid in isopropanol (0.5 mg ml<sup>-1</sup>) at room temperature for 12 hours, rinsed with isopropanol subsequently and dried with a flow of nitrogen.

#### (2) Measurement of capacitance and leakage current

The frequency-dependent capacitance of SAM-modified AlO<sub>x</sub> was measured with a HP 4284A Precision LCR Meter in a frequency range of 100 Hz to 100 kHz from a metal-insulatormetal structure, where vacuum-deposited gold (0.2 mm × 1 mm) was the top electrode and a highly doped silicon substrate was the bottom electrode. The average capacitance per unit area (*Ci*) of CBPA- and CDPA-modified AlO<sub>x</sub> was measured as  $147 \pm 11$  and  $143 \pm 12$  nF cm<sup>-2</sup>, respectively, at the lowest frequency (100 Hz). The average *Ci* of AlO<sub>x</sub> was measured as 181  $\pm 13$  nF cm<sup>-2</sup> at the lowest frequency (100 Hz). The *Ci* of CBPA-AlO<sub>x</sub>, CDPA-AlO<sub>x</sub> and bare AlO<sub>x</sub> was measured from 36, 48 and 16 independent metal-insulator-metal structures, respectively. The capacitance slightly varied among different devices because the spin-coating process was not able to yield the AlO<sub>x</sub> layer with the same thickness. Leakage current density of CBPA- and CDPA-modified AlO<sub>x</sub> was measured from the same metal-insulator-metal structure with a voltage from -5 V to 5 V using a JANIS ST-500 Micromanipulated Probe Station and a Keithley 4200 Semiconductor Characterization System as shown in Figure S10.



**Figure S11.** (a) Capacitance density versus frequency under 0 V bias voltages, and (b) leakage current density versus bias voltage characteristics of the CBPA- and CDPA-modified  $AlO_x$  dielectric.

(3) Surface roughness

The surface morphology of SAM-modified substrate was characterized by atomic force microscopy (AFM). The topographic images were collected with a Nanoscope IIIa Multimode Microscope (Digital Instruments) using tapping mode and in air under ambient conditions.



**Figure S12.** AFM images of (a) CDPA-modified surface (RMS roughness 0.118 nm) and (b) CBPA-modified surface (RMS roughness 0.094 nm).

#### (4) Surface compositions

Core level X-ray photoelectron spectroscopy (XPS) spectra for CBPA-modified  $AlO_x$  substrate was analyzed. The binding energies have been corrected for charging according to previously reported methods,<sup>3</sup> and the energy scale for XPS spectra was calibrated by setting the Al (2p) peak binding energy at 74.7 eV.<sup>4</sup> The chemical bonding environments and corresponding binding energies are summarized in Table S1 and the fitting experimental spectra are shown in Figure S12. SAM stoichiometries were calculated with resulting XPS peak intensities (*I*) as following equation:

$$\frac{C}{B} = \frac{I_{C1s}/ASF_C}{I_{B1s}/ASF_B} \quad (S1)$$

Here ASF is the atomic sensitivity factor, which is 0.205 for C (1s) and 0.088 for B (1s). The previous studies have demonstrated that the B (1s) spectrum for the plasma enhanced chemical vapor deposition (PECVD) o-carborane film is well fit by three B chemical bonding environments corresponding to (i) a B atom connect with 2B atoms (B<sup>2</sup>-B), (ii) a B atom connect with a C and a B (BC-B), and (iii) a B atom link with 2C atoms (C<sup>2</sup>-B). The binding energies of B<sup>2</sup>-B, BC-B and C<sup>2</sup>-B were 188.4, 189.2 and 189.9 eV on the basis of this empirical fit, and the relative intensity ratio of three bonds was 4:4:2.5, 6 Our experimental results indicated that B (1s) spectrum of CBPA-modified AlOx contained three bonding environments (B<sup>2</sup>-B, BC-B and C<sup>2</sup>-B) with binding energies of 189.5, 190.3 and 191.6 eV as shown in Figure S12a. The calculated intensity ratio of three components for B (1s) core level of CBPAmodified AlO<sub>x</sub> substrate was 4:4:2 according to the fitting spectrum, which agreed with the ratio in o-carborane molecule. The C (1s) spectrum of the CBPA-modified AlOx also involved three components as shown in Figure S12b, (i) a C atom connect B atoms (C-B) with the ocarborane contribution, (ii) a C atom link with a C (C-C), and (iii) a B atom link with P atom (C-P). The binding energies of them were 284.8, 285.3 and 287.1 eV, respectively. According to the Equation S1, the relative atom ratio for C and B in CBPA-modified AlO<sub>x</sub> is approximately 1.3 in agreement with the theoretical calculation (1.4), this confirms CBPA well grows on the AlO<sub>x</sub>.

|           | <b>B</b> (1s)            |                        |     | C (1s)             |                             |                                       |     |
|-----------|--------------------------|------------------------|-----|--------------------|-----------------------------|---------------------------------------|-----|
|           | Binding                  | Binding                |     | Binding            | Bind                        | ling                                  |     |
|           | Environment              | Energy (eV             | /)  | Environmen         | nt Energy                   | y (eV)                                |     |
|           | $B^2$ -B                 | 189.5                  |     | C-B                | 284                         | 4.8                                   |     |
|           | BC-B                     | 190.3                  |     | C-C                | 285                         | 5.3                                   |     |
|           | $C^2$ -B                 | 191.6                  |     | C-P                | 28                          | 7.1                                   |     |
| (a)<br>12 | 000 - <b>B (1s)</b><br>E | 9 <sup>2</sup> -В ВС-В | (Ľ  | )) 40000<br>C (1s) | с-в                         |                                       |     |
| 8 Inte    | 000 -                    |                        |     | 20000 -<br>10000 - | C-P                         | · · · · · · · · · · · · · · · · · · · |     |
|           | 184 186 188<br>Bindin    | 190 192 194            | 196 | 282 28             | 34 286 288<br>Binding Energ | 290 292<br>av (eV)                    | 294 |

Table S1. Chemical bonding environments and corresponding binding energies for CBPA modified  $AlO_x/Si$  substrate.

**Figure S13.** The experimental core level XPS for CBPA-modified  $AlO_x$ : (a) the B (1s) and (b) the C (1s) spectra for CBPA-modified  $AlO_x$ .

#### (5) Measurement of contact angle and determination of surface energy

The contact angle measurement was carried out on a contact angle goniometer (OCA25, Data Physics, Germany). The surface energy were then calculated using the equation:

 $(1 + \cos \theta)\gamma_l = 2(\gamma_s^D \gamma_l^D)^{1/2} + 2(\gamma_s^P \gamma_l^P)^{1/2}$  (S2) Here  $\theta$  is the equilibrium contact angle made by each liquid on the solid surface,  $\gamma$  is the surface energy. The superscripts *D* and *P* refer to the dispersive and the polar components, respectively. The subscripts *l* and *s* refer to the liquid and solid, respectively. The dispersion and polar components of the surface tension for water are 21.8 mN m<sup>-1</sup> and 50.9 mN m<sup>-1</sup>, respectively. The dispersion and polar components of the surface tension for CH<sub>2</sub>I<sub>2</sub> are 50 mN m<sup>-1</sup> and 0 mN m<sup>-1</sup>, respectively.



Figure S14. Images for a drop of water and  $CH_2I_2$  on the CBPA-modified  $AlO_x$  for measurement of contact angles.

**Table S2.** Summary contact angle and surface energy of the SAM-modified  $AlO_x$  dielectrics and calculated surface energy

| SAM  | Contact Angle (°) |           | Surface Energy (10 <sup>-3</sup> N m <sup>-1</sup> ) |            |      |
|------|-------------------|-----------|--|------------|------|
|      | Water             | $CH_2I_2$ | $\gamma^D$   | $\gamma^P$ | γ    |
| CBPA | 81.1              | 43.8      | 37.0   | 3.7        | 40.7 |
| CDPA | 99.8              | 54.3      | 31.3   | 0.3        | 31.6 |

(6) Kelvin probe force microscope (KPFM)

The KPFM images and data were collected with a Bruker Dimension Icon instrument using electrical and magnetic mode and in air under ambient conditions.

# 4. Fabrication and characterization of organic field effect transistors (OFETs)

(1) Materials

Pentacene (99.99%) was purchased from the TCI supplier and used without purification. 4Cl-TAP <sup>7, 8</sup> was prepared following the reported procedures and purified by recrystallization from dichloromethane and ethyl acetate for twice.

## (2) Fabrication of organic semiconductor thin films

Thin films of pentacene were deposited onto the SAM-modified AlO<sub>x</sub> using an Edwards Auto 306 vacuum system at a pressure of  $3.8 \times 10^{-6}$  torr or lower, with a deposition rate of  $2 \sim 3 \text{ nm min}^{-1}$  to a thickness of 40 nm as measured by a quartz crystal sensor, and thin films of pentacene were deposited onto bare AlO<sub>x</sub> using an Edwards Auto 500 coating system under the same conditions. The substrate was kept at 80 °C by heating with a radiant heater if not otherwise noted. Thin films of 4Cl-TAP were prepared by immersing the SAM-modified AlO<sub>x</sub>-Si substrate into a solution of 4Cl-TAP (1.2 mg mL<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub> and acetone (4:1 by volume) and then pulling it up with a syringe pump at a speed of 5 µm s<sup>-1</sup> under ambient conditions.

#### (3) Deposition of gold to form electrodes

The prepared organic thin films were placed in a vacuum oven overnight to completely remove solvent residues. To form top-contact source and drain electrodes, a 30 nm-thick layer of gold was deposited through a shadow mask onto the organic films using an Edward Auto 306 vacuum deposition system at a pressure of  $4.0 \times 10^{-6}$  torr or lower. The patterns on the shadow mask for the conduction channel lengths (*L*) and widths (*W*) were 50 µm (*L*) × 1 mm (*W*), 100 µm (*L*) × 1 mm (*W*) and 150 µm (*L*) × 1 mm (*W*). The exact channel lengths were slightly varied because the different angles between the substrate and the evaporation source during the deposition of gold. For calculation of mobility, the exact channel widths and lengths were measured using the Nikon 50iPOL microscope, which was equipped with a SPOT Insight CCD camera (Diagnostic Instrument).

- (4) Characterization of thin films
- (a) Reflected polarized-light microscopy

Polarized optical images of organic thin films were obtained using a Nikon 50IPOL Microscope.



Figure S15. Reflected polarized-light micrographs for dip-coated thin films of 4Cl-TAP on different CBPA- and CDPA- modified  $AlO_x$ .

(b) X-ray diffraction (XRD)

XRD data of the pentacene and 4Cl-TAP thin films deposited on the CBPA- and CDPAmodified  $AlO_x$  were carried out on a SmartLab X-Ray Refractometer.



**Figure S16.** X-ray diffractions of thin films of (a) pentacene and (b) 4Cl-TAP on CBPA- and CDPA-modified AlO<sub>x</sub>-Si.

#### (c) Atomic force microscopy (AFM)

The AFM images were collected with a Nanoscope IIIa Multimode Microscope (Digital Instruments) using tapping mode and in air under ambient conditions.



**Figure S17.** AFM section analysis for the films of 4Cl-TAP on the CBPA and CDPA-modified AlO<sub>x</sub>.

## (d) Electrical measurements

The current-voltage measurement was carried out on a JANIS ST-500 Micromani-pulated Probe Station with a Keithley 4200 Semiconductor Characterization System at room temperature. Pentacene was measured in air, 4Cl-TAP was tested in a background pressure of  $1.0 \times 10^{-4}$  torr or lower if not specified elsewhere.



**Figure S18.** Output *I-V* curves of the best-performing OFETs of pentacene on (a) CBPAmodified  $AlO_x$  and (b) on CDPA-modified  $AlO_x$  as measured in air; (c) p-channel and (d) nchannel output *I-V* curves of the best-performing OFET of 4Cl-TAP on CBPA-modified  $AlO_x$ as measured in vacuum; (e) transfer and (f) output *I–V* curve of the best-performing OFET of 4Cl-TAP on CDPA-modified  $AlO_x$  as measured in vacuum.



**Figure S19.** The statistics histograms of measured field effect mobilities for OFETs of pentacene (tested in air) and 4Cl-TAP (tested in vacuum) on CBPA- and CDPA-modified AlO<sub>x</sub>.



**Figure S20.** (a) transfer and (b) output *I*-*V* curve of the best-performing OFET of pentacene on unmodified AlO<sub>x</sub> substrates. The substrates were not heated during pentacene evaporation.

**Table S3**. Field-effect mobilities ( $\mu_{FET}$ ) and threshold voltages ( $V_{th}$ ) of OTFTs fabricated on unmodified AlO<sub>x</sub> at different substrate temperatures ( $T_{sub}$ ) as controlled by a radiant heater.

|           |                    | $\mu_{FET} \ (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ |         | $V_{d}$ (V)    |
|-----------|--------------------|---|---------|----------------|
|           |                    | average   | highest |                |
| Dontacono | $T_{sub} = r.t.$   | $0.98\pm0.64$   | 2.2     | $-1.73\pm0.39$ |
| I emacene | $T_{sub} = 80 \ C$ | $0.10\pm0.08$   | 0.24    | $-1.44\pm0.29$ |

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