# **Electronic Supplementary Information**

# Photochemical synthesis and device application of acene-phenacene hybrid molecules, dibenzo[n]phenacenes (n = 5-7)

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### Experimental

#### 1. Synthesis of materials

#### 1-1. (*E*)-1,2-Bis(1-anthryl)ethene 2



A solution of 1-bromoanthracene **1** (257 mmol), (*E*)-1,2-bis(tributylstannyl)ethene (274 mg, 0.45 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (52 mg, 0.045 mmol) in toluene (30 ml) was refluxed under an N<sub>2</sub> atmosphere for 13 h. The resulting solution was filtered through a short silica-gel column containing 5% K<sub>2</sub>CO<sub>3</sub>. After removal of the solvent, the residue was washed with toluene/hexane (1/1 mixt.) to afford (*E*)-1,2-bis(1-anthryl)ethene **2** (148 mg, 86%).

Yellow crystals, mp 286–288°C (Lit 277–279°C)<sup>1</sup>

<sup>1</sup>**H** NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  8.84 (s, 2H), 8.50 (s, 2H), 8.15 (s, 2H), 8.08–8.00 (m, 6H), 7.93 (d, 2H, J = 6.7 Hz), 7.58 (dd, 2H, J = 8.4, 6.3 Hz), 7.52–7.45 (m, 4H).

<sup>13</sup>**C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta_{\rm C}$  135.59, 131.96, 131.80, 131.58, 130.03, 129.31, 128.66, 128.58, 127.93, 126.97, 125.68, 125.61, 125.23, 123.48, 122.76.

Anal. Calcd for C<sub>30</sub>H<sub>20</sub>, C, 94.70; H, 5.30. Found, C, 94.70; H, 5.36.

#### 1-2. Dibenzo[*b*,*n*]picene (DP5P)



A solution of bis(anthryl)ethene 2 (200 mg, 0.53 mmol) and a small portion of  $I_2$  in toluene (200 ml) was irradiated with black-light lamps (352 nm,  $6 \times 16$  W) for 8.5 h. the precipitate formed was collected and recrystallized from *o*-dichlorobenzene (**A**, 37 mg). The filtrate was

further irradiated for 14 h and the filtrate was collected and recrystallized from *o*-dichlorobenzene (**B**, 11 mg). The filtrate was concentrated and the obtained yellow solid (79 mg) was dissolved in toluene (200 ml) and a small portion of I<sub>2</sub> was added. The resulting solution was irradiated with the black-light lamps with heating at 85–100°C for 20 h. The precipitate formed was collected and recrystallized from *o*-dichlorobenzene (**C**, 32 mg). The total amount of the obtained **DB5P** (**A** + **B** + **C**) was 81 mg (40%).

Pale yellow fine plates, mp >300°C.

<sup>1</sup>**H** NMR (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 80°C)  $\delta_{\rm H}$  9.39 (s, 2H), 9.20 (s, 2H), 9.69 (d, 2H, J= 9.2 Hz), 8.54 (s, 2H), 8.26 (d, 2H, J = 7.5 Hz), 8.14 (two doublets overlap, 4H), 7.76–7.60 (m, 4H).

<sup>13</sup>C NMR was not observed due to the low solubility.

Anal. Calcd. for C<sub>30</sub>H<sub>18</sub>: C, 95.21; H, 4.79. Found: C, 94.51; H, 4.72.

#### 1-3. 4-Ethenylbenzo[a]anthracene 4



A mixture of 4-bromobenzanthracene<sup>2</sup> (600 mg, 1.96 mmol), tributylvinyltin (746 mg, 2.35 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (113 mg, 0.10 mmol) in toluene (30 ml) was refluxed for 15 h. The insoluble materials formed was filtered off and the filtrate was passed through a short silica-gel column containing K<sub>2</sub>CO<sub>3</sub> (10wt%) to afford 4-vinylbenzo[*a*]anthracene **4** (404 mg, 81%). Recrystallization from toluene produced off-white plates of product **4**.

Off-white plates, mp. 191–192°C.

<sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) 9.18 (s, 1H), 8.81 (d, 1H, *J* = 8.0 Hz), 8.37 (s, 1H), 8.13 (m, 1H), 8.05 (m, 1H), 7.97 (d, 1H, *J* = 9.3 Hz), 7.83 (d, 1H, *J* = 7.8 Hz), 7.76 (d, 1H, *J* = 7.0 Hz), 7.66 (t, 1H, *J* = 7.8 Hz), 7.59–7.51 (m, 3H), 5.82 (dd, 1H, *J* = 17.2, 1.1 Hz), 5.54 (dd, 1H, *J* = 10.8, 1.1 Hz).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) 136.48, 134.93, 132.14, 132.10, 130.80, 130.37, 129.36, 129.12, 128.63, 127.85, 127.62, 126.83, 126.70, 126.01, 125.88, 125.38, 122.86, 122.72, 122.04, 117.73.

**HRMS** (FAB) *m*/*z* calcd. for C<sub>20</sub>H<sub>14</sub>, 254.1096 [M<sup>+</sup>]. Found, 254.1100.

#### 1-4. (E)-1-(1-Anthryl)-2-(4-benzo[a]anthryl)ethene 5



A mixture of vinylbenzoanthracene 4 (300 mg, 1.18 mmol), 1-bromoanthacene 1 (306 mg, 1.19 mmol),  $(o-\text{Tol})_3\text{P}$ , and Pd(OAc)<sub>2</sub> in DMF (5 ml) and TEA (3 ml) was evacuated and backfilled with Ar three times. The resulting mixture was heated at 80°C for 17 h. After being cooled to r.t., The precipitate formed was collected and washed with a 1 : 1 mixture of toluene and EtOH to afford (*E*)-1-(1-anthryl)-2-(4-benzo[*a*]anthryl)ethene **5** (334 mg, 65%) as greenish-yellow fine needles. mp >300°C

<sup>1</sup>**H** NMR (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 90°C)  $\delta_{\rm H}$  9.24 (s, 1H), 8.90 (d, 1H, J = 8.0 Hz), 8.28 (s, 1H), 8.49 (s, 1H), 8.40 (s, 1H), 8.20–8.12 (m, 2H), 8.10–7.99 (m, 7H), 7.91–7.7.83 (m, 2H), 7.79 (t, 1H, J = 7.6 Hz), 7.61–7.52 (m, 3H), 7.51–7.44 (m, 2H).

<sup>13</sup>C NMR (151 MHz, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, 90°C) δ<sub>C</sub> 136.31, 135.61, 132.26, 132.22, 132.15, 131.98, 131.76, 131.14, 130.43, 130.17, 129.99, 129.89, 129.65, 129.19, 128.66, 128.62, 128.55, 127.94, 127.78, 127.73, 127.01, 126.82 (2C), 126.06, 125.93, 125.79, 125.71 (2C), 125.31, 123.60, 122.96, 122.86, 122.83, 122.05.

Anal. Calcd. for C<sub>34</sub>H<sub>22</sub>; C, 94.85; H, 5.15. Found; C, 94.85%; H, 5.13%.

#### 1-5. Benzo[b]naphtho[2, 3-m]picene (DB6P)



A solution of (*E*)-1-(1-anthryl)-2-(4-benzo[*a*]anthryl)ethane **5** (200 mg, 0.46 mmol) and a small portion of I<sub>2</sub> in *o*-dichlororbenzene (300 mol) was heated at 85–100°C and irradiated with black-light lamps (352 nm,  $6 \times 16$  W) for 7.2 h. The precipitate formed was collected (63 mg, **A**). The filtrate was irradiated with the black-light lamps for 12.5 h and the precipitated product was collected (26 mg, **B**). The total yield of the product (**A** + **B**) was 89 mg (45%). Pale yellow plates, mp >300°C.

**1H NMR** (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 80°C)  $\delta_H$  9.14 (s, 2H), 9.19 (d, 2H, J = 8.8 Hz), 9.09 (d, 2H, J = 9.0 Hz), 8.83 (d, 2H, J = 8.7 Hz), 8.58 (s, 2H), 8.27 (brd, 2H, J = 7.4 Hz), 8.22 (d, 2H, J = 8.7 Hz), 8.15 (brd, 2H, J = 7.1 Hz), 7.64 (m, 4H).

<sup>13</sup>C NMR spectra were not observed due to the low solubility of **DB6P**.

Anal. calcd. for C<sub>34</sub>H<sub>20</sub>; C, 95.30; H, 4.70. Found; C, 94.54; H, 4.46.

#### 1-7. (E)-1,2-Bis(4-benzoanthryl)ethene 6



A mixture of 4-bromobenzo[*a*]anthracene **3** (612 mg, 2.0 mmol), trans-1,2bis(tributylstannyl)ethene (547 mg, 0.9 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.20 mmol) was refluxed under an Ar atmosphere for 24 h. The precipitate formed was collected and washed with toluene to afford (*E*)-1,2-bis(4-benzo[*a*]anthryl)ethene **6** 358 mg (37%). Recrystallization from *o*-dichlorobenzene gave pale brown plates.

Pale brown plates, mp  $>300^{\circ}$ C.

<sup>1</sup>**H** NMR (600 MHz, 1,1,2,2-tetrachloroethane- $d_2$ , 80°C)  $\delta_H$  9.25 (s, 2H), 8.91 (d, 2H, J = 8.3 Hz), 8.34 (s, 2H), 8.21–8.14 (m, 4H), 8.12–8.07 (m, 2H), 8.054 (d, 2H, J = 7.1 Hz), 8.00 (s, 2H), 7.92 (d, 2H, J = 9.3 Hz), 7.81 (t, 2H,J = 7.6 Hz), 7.65–7.57 (m, 4H).

<sup>13</sup>C NMR spectrum was not observed due to low solubility.

Anal. Calcd. for C<sub>38</sub>H<sub>24</sub>, C, 94.97; H, 5.03. Found, C, 94.63; H, 4.85.

### 1-8. Benz[b]anthra[2,1-m]picene (DP7P)



A solution of (*E*)-1,2-bis(4-benzo[*a*]anthryl)ethene **6** (150 mg, 0.31 mmol) and a small portion of I<sub>2</sub> in *o*-dichlorobenzene (300 ml) was heated at *ca*. 125°C and the solution was irradiated with black-light lamps (365 nm,  $6 \times 16W$ ) at the temperature for 2.2 h. The precipitate formed was collected and washed with boiling *o*-dichlorobenzene to afford **DB7P** (129 mg, 86%). Pale yellow plates, mp >300°C.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were not observed due to the low solubility od **DB7P**.

Anal. Calcd. for C<sub>38</sub>H<sub>22</sub>, C, 95.37; H, 4.63. Found, C, 95.26; H, 4.39.

## 2. NMR, MS and elemental analyses

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on VARIAN NMR System 600 (600 MHz) and JEOL ECZ600 (600 MHz) spectrometers. Elemental analyses were measured on a PERKIN-ELMER 2400II CHN-S analyser at the Micro Elemental Analysis Laboratory of Okayama University. High-resolution mass spectra (FAB) were recorded on a JEOL JMS-700 MStation spectrometer at Institute for Materials Chemistry and Engineering, Kyushu University.



Figure S1.  $^{1}$ H (600 MHz) and  $^{13}$ C (151 MHz) NMR spectra of compound 2 (CDCl<sub>3</sub>).



Figure S2. <sup>1</sup>H NMR spectrum of **DB5P** (600 MHz, 1,1,2,2-tetrachloroenthane-*d*<sub>2</sub>, at 80°C). Asterisked signals are due to the solvent and water.



Figure S3.  $^{1}$ H (600 MHz) and  $^{13}$ C (151 MHz) NMR spectra of compound 4 (CDCl<sub>3</sub>).



Figure S4. <sup>1</sup>H (600 MHz) and <sup>13</sup>C (151 MHz) NMR spectra of compound **5** (1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, at 80°C).



Figure S5. <sup>1</sup>H NMR spectrum of **DB6P** (600 MHz, 1,1,2,2-tetrachloroethane, at 95°C). Asterisked signals are due to the solvent, <sup>13</sup>C satellite, water, and impurity (inset).

#### 3. X-ray diffraction (XRD) measurements and atomic force microscopy (AFM)

X-ray powder diffraction (XRPD) patterns of polycrystalline **DBnP** samples were measured at room temperature using synchrotron radiation at BL12B, SPring-8. The wavelength,  $\lambda$ , of x-ray beam was set to 0.5636 Å. X-ray diffraction patterns of **DBnP** thin films on SiO<sub>2</sub>/Si substrate were measured at room temperature using an X-ray diffractometer (RIGAKU SMARTLAB-PRO) with CuK $\alpha$  radiation ( $\lambda = 1.5418$  Å). The AFM image was measured with an AFM measurement system (SII Nano Technology SPA400). For the XRD and AFM measurements, a 60-nm thin-film of **DBnP** was formed on the SiO<sub>2</sub>/Si substrate by thermal deposition under  $10^{-7}$  Torr.

#### 4. UV-Vis absorption and photoelectron yield measurements

Optical absorption was recorded with a UV-Vis absorption spectrometer (JASCO V-670 iRM EX). Photoelectron yield spectroscopy (PYS) was measured at room temperature under vacuum condition using a PYS spectrometer (Bunko-keiki BIP-KV200BS). 60-nm thick films of **DBnP**s formed on quartz and SiO<sub>2</sub>/Si substrates were prepared for the measurements of the UV-Vis absorption and PYS spectra, respectively.

#### 5. Synthesis of DBnP single crystals

Single crystals of **DBnPs** were prepared by the physical vapor transport method using synthesized powder samples of **DBnPs**. The polycrystalline samples (15-20 mg) of **DBnPs** were placed in a glass tube installed in the two-temperature-zone furnace, and for the preparation of single crystals the glass tube was heated to 240 and 400 °C for **DB5P**, 280 and 430 °C for **DB6P**, and 300 and 480 °C for **DB7P**. During growth of single crystals, Ar gas was shed at 50 mL/min in the glass tube. The single crystals were collected in the lower temperature zone. The single crystals were transparent and plate-like (Figure S10). Their flat side was parallel to the *ab*-plane, and their thickness direction corresponds to the *c*-axis. 200-400 nm-thick crystals were used as active layers of single crystal FET devices.

#### 6. Device fabrication of single-crystal FETs

Single crystals of **DBnPs** was placed on the SiO<sub>2</sub>/Si substrate, in which SiO<sub>2</sub> (300 nm thick) was used as the gate dielectric. The surface of the SiO<sub>2</sub>/Si substrate was coated with parylene to produce a hydrophobic surface. The thickness of the Au source/drain electrodes was 100 nm. 3 nm-thick 2,3,5,6-tetrafluoro-7,7,8,8-teracyano-quinodimethane (F<sub>4</sub>TCNQ) was inserted into the space between the Au electrodes and the single crystal to reduce contact resistance. The Au source/drain electrodes and the F<sub>4</sub>TCNQ were emplaced by thermal deposition at  $10^{-7}$  Torr. The FET characteristics were recorded using a semiconductor parametric analyser (Agilent

B1500A) in an Ar-filled glove box. As seen in the device structures, the source electrode was grounded ( $V_{\rm S} = 0$ ). Negative voltage was applied to  $V_{\rm G}$  and  $V_{\rm D}$  in measurements of transfer and output curves. The measured transfer curves were analysed to determine the FET parameters (mobility ( $\mu_{\rm sat}$ ), threshold voltage ( $V_{\rm th}$ ), on/off ratio and subthreshold swing (S)) using the general metal-oxide-semiconductor (MOS) transistor formula for a saturation regime:

$$I_D = \frac{\mu_{\text{sat}} W C_0}{2L} (V_{\text{G}} - V_{\text{th}})^2,$$

where  $I_D$ ,  $V_G$ ,  $V_{th}$ , W, L and  $C_o$  refer to drain current, gate voltage, threshold voltage, channel width, channel length and capacitance per area of gate dielectric, respectively. The channel width W and the length L for each device are listed in Tables S1-S4. The  $C_o$  values for SiO<sub>2</sub> (300 nm) and ZrO<sub>2</sub> (150 nm) covered with parylene were measured using a precision LCR meter (Agilent E4980A). The  $C_o$  of SiO<sub>2</sub> gate dielectrics for **DB5P**, **DB6P**, and **DB7P** single crystal FETs were 9.95 nF cm<sup>-2</sup>, 9.31 nF cm<sup>-2</sup> and 9.45 nF cm<sup>-2</sup>, respectively, and that of ZrO<sub>2</sub> for **DB6P** single crystal FETs was 42.7 nF cm<sup>-2</sup>, which was determined by extrapolation of the capacitance measured at 20 Hz - 1 MHz to 0 Hz. The condition for a saturation regime,  $V_D > V_G - V_{th}$ , was completely satisfied in the analysis of the transfer curve. The saturation was completely found in the output characteristics of all FET devices fabricated in this study.

#### 7. Device fabrication of thin-film FETs

60 nm thick thin-films of **DBnP**s were formed for an active layer on solid gate dielectrics of 400 nm thick SiO<sub>2</sub> and 150 nm thick ZrO<sub>2</sub> by a thermal deposition of **DBnP**s under a vacuum of  $10^{-7}$  Torr. The surface of the SiO<sub>2</sub> was coated with hexamethyldisilazane (HMDS) to produce a hydrophobic surface, while that of ZrO<sub>2</sub> was covered with 50 nm thick parylene. The shape of the thin film was determined by use of a metal mask. 3 nm thick F<sub>4</sub>TCNQ was deposited on the **DBnP**s' thin films, and 50 nm thick source and drain electrodes were formed by the thermal deposition of Au on the F<sub>4</sub>TCNQ. The device structure is top-contact bottom-gate type. The *W* and *L* for each device are listed in Tables S5-S8. The *C*<sub>0</sub> value of SiO<sub>2</sub> for **DB5P**, **DB6P** and **DB7P** thin film FETs was 8.3 nF cm<sup>-2</sup>, and that of ZrO<sub>2</sub> for **DB6P** thin film FETs was 42.7 nF cm<sup>-2</sup>. The measured transfer curves were analysed to determine the FET parameters using the general MOS transistor formula for a saturation regime in the same matter as the analysis of single crystal FETs.

## Results

## 1. X-ray diffraction patterns



**Figure S6.** (a) Comparison of X-ray powder diffraction patterns of sublimed **DBnP** powders. X-ray diffraction patterns with the patterns calculated using Le Bail fitting of (b) **DB5P**, (c) **DB6P**, and (d) **DB7P**.



Figure S7. Comparison of X-ray diffraction patterns of DBnP thin films on SiO<sub>2</sub>/Si substrates.

## 2. UV-Vis absorption and photoelectron yield spectra



Figure S8. (a) UV-Vis absorption and (b) photoelectron yield spectra of DBnP thin films.

## 3. Surface morphology of DBnP thin films



Figure S9. AFM images (10  $\mu$ m × 10  $\mu$ m scale) of (a) DB5P, (b) DB6P, and (c) DB7P thin films on SiO<sub>2</sub>/Si substrates, respectively. (d), (e), and (f) are enlarged images (1  $\mu$ m × 1  $\mu$ m scale) of (a), (b), and (c), respectively.

## 4. Optical microscope images of DBnP single crystals



Figure S10. Optical microscope images of (a) DB5P, (b) DB6P, and (c) DB7P single crystals.

## 5. Typical FET performances of DBnP single crystal FETs



## 5-1. DBnP single crystal FETs with SiO<sub>2</sub> gate dielectric

**Figure S11.** Transfer and output curves of **DB5P** single crystal FET with SiO<sub>2</sub> gate dielectric. This FET refers to device #4 in Table S1.



**Figure S12.** Transfer and output curves of **DB7P** single crystal FET with SiO<sub>2</sub> gate dielectric. This FET refers to device #2 in Table S3.

## 5-2. DBnP single crystal FETs with ZrO<sub>2</sub> gate dielectric



Figure S13. Transfer and output curves of DB6P single crystal FET with  $ZrO_2$  gate dielectric. This FET refers to device #4 in Table S4.

## 6. Typical FET performances of DBnP thin film FETs





**Figure S14.** Transfer and output curves of **DB5P** thin film FET with SiO<sub>2</sub> gate dielectric. This FET refers to device #2 in Table S5.



**Figure S15.** Transfer and output curves of **DB6P** thin film FET with SiO<sub>2</sub> gate dielectric. This FET refers to device #2 in Table S6.



**Figure S16.** Transfer and output curves of **DB7P** thin film FET with SiO<sub>2</sub> gate dielectric. This FET refers to device #2 in Table S7.

#### 6-2. DB6P thin film FETs with ZrO<sub>2</sub> gate dielectric



**Figure S17.** Transfer and output curves of **DB6P** thin film FET with ZrO<sub>2</sub> gate dielectric. This FET refers to device #4 in Table S8.

## Tables

DB5P SC	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	μ <sub>eff</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>th</sub> (V)	on/off	S (V decade <sup>-1</sup> )	<i>W/L</i> (μm/μm)
#1	1.39	0.64	8.90×10 <sup>-1</sup>	19.4	3.25×10 <sup>8</sup>	1.71	300/250
#2	1.29	0.29	3.74×10 <sup>-1</sup>	45.8	9.16×10 <sup>6</sup>	3.48	410/200
#3	1.07	0.26	2.78×10 <sup>-1</sup>	49.1	1.54×10 <sup>8</sup>	1.34	250/150
#4*	3.21	0.25	8.03×10 <sup>-1</sup>	50.0	1.45×10 <sup>8</sup>	3.49	550/250
#5	1.55	0.22	3.41×10 <sup>-1</sup>	53.0	2.13×10 <sup>7</sup>	2.23	200/250
#6	1.41	0.21	2.96×10 <sup>-1</sup>	54.9	1.21×10 <sup>7</sup>	4.89	300/50
average	1.7(8)	0.3(2)	5(3)×10 <sup>-1</sup>	50(10)	1(1)×10 <sup>8</sup>	3(1)	

Table S1. FET parameters of DB5P single-crystal FETs with  $SiO_2$  gate dielectric.

Table S2. FET parameters of DB6P single-crystal FETs with SiO<sub>2</sub> gate dielectric.

DB6P SC	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	μ <sub>eff</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>th</sub> (V)	on/off	S (V decade⁻¹)	<i>W/L</i> (μm/μm)
#1	1.03	0.94	9.68×10 <sup>-1</sup>	2.84	1.84×10 <sup>7</sup>	1.48	315/50
#2	1.80	0.82	1.48	9.26	1.22×10 <sup>8</sup>	1.26	220/50
#3	2.19	0.76	1.66	12.6	3.36×10 <sup>7</sup>	1.88	580/450
#4	2.39	0.75	1.79	13.4	2.00×10 <sup>7</sup>	1.48	200/450
#5*	2.73	0.66	1.80	18.7	2.05×10 <sup>7</sup>	1.46	700/700
average	2.0(7)	0.8(1)	1.5(4)	11(6)	4(4)×10 <sup>7</sup>	1.5(2)	

Table S3. FET parameters of DB7P single-crystal FETs with SiO<sub>2</sub> gate dielectric.

DB7P SC	µ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	µ <sub>eff</sub> (cm² V⁻¹ s⁻¹)	V <sub>th</sub> (V)	on/off	S (V decade⁻¹)	<i>W/L</i> (μm/μm)
#1	2.07	0.58	1.20	23.6	6.04×10 <sup>7</sup>	2.70	300/50
#2*	2.58	0.55	1.42	25.0	4.87×10 <sup>7</sup>	1.67	270/50
#3	1.35	0.54	7.29×10 <sup>-1</sup>	26.1	9.03×10 <sup>6</sup>	1.06	820/450
#4	1.76	0.53	9.33×10 <sup>-1</sup>	26.6	5.42×10 <sup>6</sup>	1.40	470/50
#5	1.70	0.34	5.78×10 <sup>-1</sup>	41.7	2.09×10 <sup>8</sup>	1.79	470/50
#6	1.48	0.28	4.14×10 <sup>-1</sup>	47.4	2.22×10 <sup>7</sup>	1.58	590/50
average	1.8(5)	0.5(1)	9(8)×10 <sup>-1</sup>	30(10)	6(8)×10 <sup>7</sup>	1.7(6)	

DB7P SC	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	µ <sub>eff</sub> (cm² V⁻¹ s⁻¹)	V <sub>th</sub> (V)	on/off	S (V decade <sup>-1</sup> )	<i>W/L</i> (μm/μm)
#1	2.06	0.75	1.55	2.16	7.49×10 <sup>6</sup>	0.30	175/50
#2	2.03	0.74	1.50	2.22	1.23×10 <sup>7</sup>	0.29	320/50
#3	2.06	0.73	1.50	2.33	1.48×10 <sup>7</sup>	0.28	345/50
#4*	2.54	0.63	1.60	3.32	1.01×10 <sup>6</sup>	0.39	525/450
average	2.2(3)	0.71(6)	1.54(5)	2.5(6)	9(6)×10 <sup>6</sup>	0.32(5)	

Table S4. FET parameters of DB6P single-crystal FETs with ZrO<sub>2</sub> gate dielectric.

DB5P thin-film	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	μ <sub>eff</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>th</sub> (V)	on/off	S (V decade⁻¹)	<i>W/L</i> (μm/μm)
#1	1.77×10 <sup>-2</sup>	0.19	3.36×10 <sup>-3</sup>	55.7	2.34×10 <sup>4</sup>	7.27	500/200
#2*	3.68×10 <sup>-2</sup>	0.18	6.62×10 <sup>-3</sup>	57.1	1.55×10 <sup>4</sup>	6.54	500/450
#3	2.92×10 <sup>-2</sup>	0.17	4.96×10 <sup>-3</sup>	58.2	8.52×10 <sup>3</sup>	7.67	500/450
#4	1.97×10 <sup>-2</sup>	0.17	3.35×10 <sup>-3</sup>	58.6	1.60×10 <sup>4</sup>	5.35	500/450
#5	1.32×10 <sup>-2</sup>	0.17	2.24×10 <sup>-3</sup>	58.7	1.48×10 <sup>4</sup>	7.09	500/250
#6	1.51×10 <sup>-2</sup>	0.12	1.81×10 <sup>-3</sup>	65.1	3.33×10 <sup>4</sup>	8.14	500/150
#7	1.71×10 <sup>-2</sup>	0.11	1.88×10 <sup>-3</sup>	66.7	9.41×10 <sup>3</sup>	7.71	500/300
#8	1.47×10 <sup>-2</sup>	0.11	1.62×10 <sup>-3</sup>	66.6	5.42×10 <sup>3</sup>	9.44	500/100
average	2.0(8)×10 <sup>-2</sup>	0.15(3)	3(2)×10 <sup>-3</sup>	61(5)	1.6(9)×10 <sup>4</sup>	7(1)	

Table S5. FET parameters of DB5P thin-film FETs with SiO<sub>2</sub> gate dielectric.

Table S6. FET parameters of DB6P thin-film FETs with SiO<sub>2</sub> gate dielectric.

DB6P thin-film	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	<b>r</b> <sub>sat</sub>	μ <sub>eff</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>th</sub> (V)	on/off	S (V decade <sup>-1</sup> )	<i>W/L</i> (μm/μm)
#1	5.70×10 <sup>-2</sup>	0.40	2.28×10 <sup>-2</sup>	36.6	3.16×10 <sup>5</sup>	2.62	1000/450
#2*	9.83×10 <sup>-2</sup>	0.38	3.74×10 <sup>-2</sup>	38.7	4.37×10 <sup>5</sup>	2.88	500/250
#3	7.82×10 <sup>-2</sup>	0.37	2.89×10 <sup>-2</sup>	39.7	4.61×10 <sup>5</sup>	4.54	500/50
#4	8.90×10 <sup>-2</sup>	0.35	3.12×10 <sup>-2</sup>	41.3	7.76×10 <sup>5</sup>	4.33	500/135
#5	6.74×10 <sup>-2</sup>	0.30	2.02×10 <sup>-2</sup>	45.7	3.86×10 <sup>5</sup>	3.46	1000/450
average	8(2)×10 <sup>-2</sup>	0.36(4)	2.8(7) ×10 <sup>-2</sup>	40(3)	5(2)×10 <sup>5</sup>	3.6(9)	

Table S7. FET parameters of DB7P thin-film FETs with SiO<sub>2</sub> gate dielectric.

DB7P thin-film	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	r <sub>sat</sub>	µ <sub>eff</sub> (cm² V⁻¹ s⁻¹)	V <sub>th</sub> (V)	on/off	S (V decade <sup>-1</sup> )	<i>W/L</i> (μm/μm)
#1	8.11×10 <sup>-4</sup>	0.21	1.70×10 <sup>-4</sup>	54.1	8.71×10 <sup>3</sup>	2.96	1000/450
#2*	1.14×10 <sup>-3</sup>	0.16	1.82×10 <sup>-4</sup>	60.2	3.78×10 <sup>3</sup>	5.34	1000/450
#3	4.22×10 <sup>-4</sup>	0.14	5.91×10 <sup>-5</sup>	62.6	1.72×10 <sup>3</sup>	3.30	1000/450
average	8(4)×10 <sup>-4</sup>	0.17(4)	1.4(7)×10 <sup>-4</sup>	59(4)	5(4)×10 <sup>3</sup>	4(1)	

DB6P thin-film	μ <sub>sat</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	r <sub>sat</sub>	μ <sub>eff</sub> (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>th</sub> (V)	on/off	S (V decade⁻¹)	<i>W/L</i> (μm/μm)
#1	7.74×10 <sup>-2</sup>	0.32	2.48×10 <sup>-2</sup>	6.98	7.28×10 <sup>6</sup>	0.43	500/50
#2	7.24×10 <sup>-2</sup>	0.31	2.24×10 <sup>-2</sup>	7.02	7.85×10 <sup>5</sup>	0.58	1000/450
#3	6.64×10 <sup>-2</sup>	0.31	2.06×10 <sup>-2</sup>	7.03	1.93×10 <sup>4</sup>	1.52	1000/450
#4*	8.10×10 <sup>-2</sup>	0.30	2.43×10 <sup>-2</sup>	7.15	9.98×10 <sup>3</sup>	0.54	500/250
#5	7.89×10 <sup>-2</sup>	0.20	1.58×10 <sup>-2</sup>	8.91	1.21×10 <sup>5</sup>	0.49	500/135
average	7.5(6)×10 <sup>-2</sup>	0.29(5)	2.2(4)×10 <sup>-2</sup>	7.4(8)	2(3)×10 <sup>6</sup>	0.7(5)	

Table S8. FET parameters of DB6P thin-film FETs with  $ZrO_2$  gate dielectric.

## **Additional References**

- 1. Y. Takeuchi, S. Akiyama and M. Nakagawa, Bull. Chem. Soc. Jpn., 1972, 45, 3183.
- 2. B. P. Cho and R. G. Harvey, J. Org. Chem., 1987, 52, 5668.