Supporting Information

High Performance n-Type Field-Effect Transistors Based on Indenofluorenedione and Diindenopyrazinedione Derivatives

Tomohiro Nakagawa, Daisuke Kumaki,† Jun-ichi Nishida, Shizuo Tokito,† Yoshiro Yamashita*

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

† NHK Science and Technical Research Laboratories, Kinuta, Setagaya-ku, Tokyo 157-8510, Japan

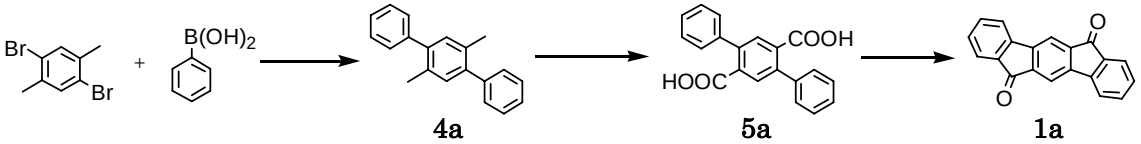
E-mail: yoshiro@echem.titech.ac.jp

General:

Melting points were obtained on a SHIMADZU DSC-60 and uncorrected. EI mass spectra were collected on a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded on a SHIMADZU Multi Spec-1500. Emission spectra were collected on a JASCO FP-6600 spectrometer. Differential pulse voltammograms were recorded on a BAS-100B system containing terabutylammonium hexafluorophoshate ($TBAPF_6$) (0.1 $moldm^{-3}$ in dry DMF). The Pt disk, Pt wire and SCE were used as the working, counter, and reference electrodes, respectively. Elemental analyses were performed at the Tokyo Institute of Technology, Chemical Resources Laboratory.

Synthetic details:

<Compound **1a**>



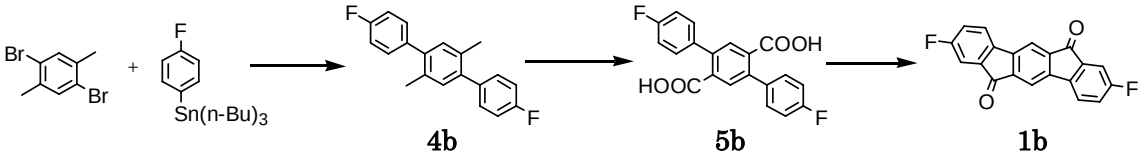
4a **5a** **1a**

The synthetic details of **4a**, **5a** and **1a** are described in reference 5.

Mp : 351-354°C. IR (KBr) : 1714, 1604, 1470, 1429, 1182, 1124, 1086, 919, 755, 723 cm^{-1}. MS/EI

(70 eV) : m/z 282 (M^+). Anal. Calcd. For $C_{20}H_{10}O_2$: C, 85.09; H, 3.57. Found: C, 85.15; H, 3.39.

<Compound **1b**>



4b **5b** **1b**

2,5-Di(4-fluorophenyl)-p-xylene (4b): A mixture of 2,5-dibromo-*p*-xylene (3.66 g, 13.9 mmol) and tributyl-(4-fluorophenyl)stannane (11.3 g, 29.3 mmol) and $Pd(PPh_3)_4$ (548 mg) in toluene (60 ml) was refluxed overnight. The black precipitate was removed by filtration under suction, and the solvent was evaporated. The resulting solid was recrystallized from boiling ethanol: 1.43 g, 35 % yield.

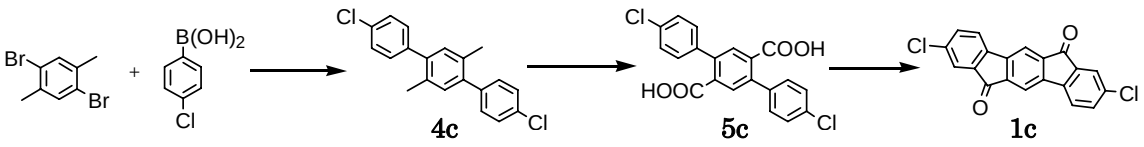
^{1}H-NMR (300 MHz, $CDCl_3$) = 7.32 (m, 4H), 7.11 (m, 6H), 2.29 (s, 6H)

2,5-Di(4-fluorophenyl)terephthalic acid (5b): **5b** was synthesized by following the procedure described for **5a**: 1.60 g >100 % yield.

2,8-Difluoroindeno[1,2-b]fluorene-6,12-dione (1b): **1b** was synthesized by following the procedure described for **1a:** 412 mg, 48 % yield.

Mp : sublimated (ca. 340°C). IR (KBr) : 1714, 1603, 1502, 1454, 1428, 1276, 1258, 1226, 1124, 1086, 922, 882, 838, 817, 780, 662, 496 cm^{-1}. MS/EI (70 eV) : m/z 318 (M^+). Anal. Calcd. For $C_{20}H_8F_2O_2$: C, 75.47; H, 2.53. Found: C, 75.36; H, 2.40.

<Compound **1c**>



4c **5c** **1c**

2,5-Di(4-chlorophenyl)-p-xylene (4c): 4c was synthesized by following the procedure described for **4a:** 971 mg, 79 % yield.

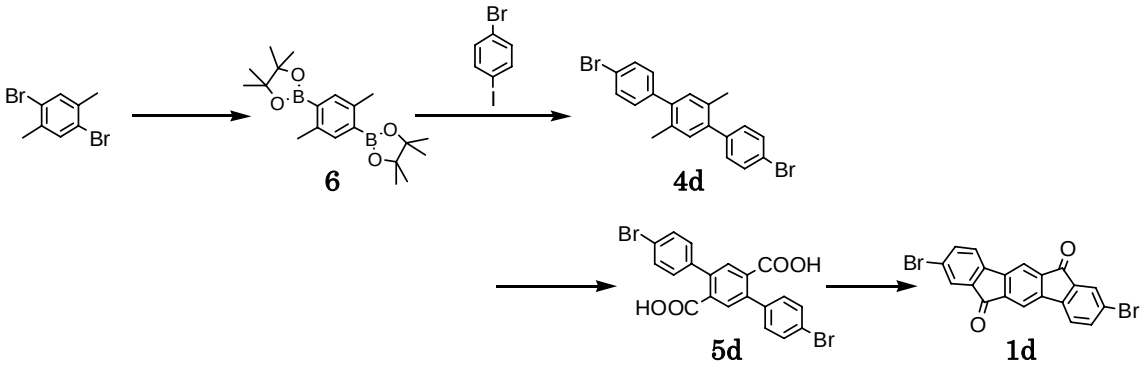
^{1}H-NMR (300 MHz, $CDCl_3$) = 7.40(d, 4H, *J* = 8.1 Hz), 7.30-7.26 (m, 4H), 7.11 (s, 2H), 2.25 (s, 6H)

2,5-Di(4-fluorophenyl)terephthalic acid (5c): **5c** was synthesized by following the procedure described for **5a**: 998 mg, >100 % yield.

2,8-Difluoroindeno[1,2-b]fluorene-6,12-dione (1c): **1c** was synthesized by following the procedure described for **1d**: 425 mg, 59 % yield.

Mp : sublimated (ca. 340°C). IR (KBr) : 1714, 1601, 1435, 1247, 1175, 1128, 1062, 946, 908, 835, 777, 753, 614, 478 cm^{-1}. MS/EI (70 eV) : m/z 350 (M^+). Anal. Calcd. For $C_{20}H_8Cl_2O_2$: C, 68.40; H, 2.30. Found: C, 68.42; H, 2.35.

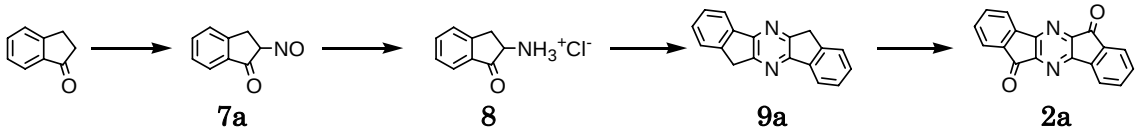
<Compound **1d**>



The synthetic details of **6**, **4d**, **5d** and **1d** are described in reference 6.

Mp : >400°C. IR (KBr) : 1714, 1598, 1435, 1247, 1175, 1127, 1053, 938, 909, 833, 777, 739, 472 cm^{-1}. MS/EI (70 eV) : m/z 440 (M^+). Anal. Calcd. For $C_{20}H_8Br_2O_2$: C, 54.58; H, 1.83. Found: C, 54.43; H, 1.84.

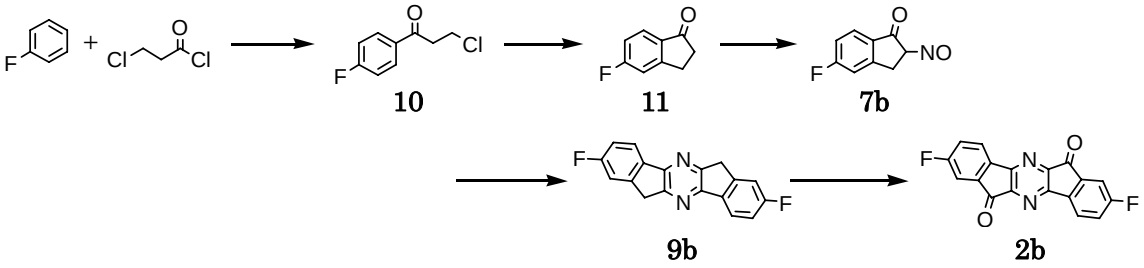
<Compound **2a**>



The synthetic details of **7a**, **8**, **9a** and **2a** are described in reference 7.

Mp : sublimated (ca. 330°C). IR (KBr) : 1728, 1602, 1494, 1466, 1434, 1380, 1234, 1215, 1178, 1142, 925, 758, 731, 704 cm^{-1}. MS/EI (70 eV) : m/z 284 (M^+). Anal. Calcd. For $C_{18}H_8N_2O_2$: C, 76.05; H, 2.84; N, 9.85. Found: C, 76.08; H, 2.82; N, 9.85.

<Compound **2b**>



The synthetic details of **10** and **11** are described in reference 8.

5-Fluoro-1-indanone (7b): Compound **11** (618 mg, 4.12 mmol) was dissolved in benzene (6 ml), and then a mixture of conc. HCl (1 ml) and isoamyl nitrite (670 mg) was added to the solution. After stierring at 40°C for 3h, the suspention was stirred at r.t. overnight. The solid obtained by filtration under suction was dried in a vacuum oven, and was purified by sublimation: 374 mg, 51 % yield.

^{1}H-NMR (300 MHz, $CDCl_3$) = 7.92 (dd, 1H, *J* = 7.2 and 5.4 Hz), 7.13-7.22 (m, 2H), 3.86 (s, 2H)

2,8-Difluorodiindeno[1,2-b;1',2'-e]pyrazine (9b): A mixture of compound **7b** (1.00 g, 5.58 mmol), $Na_2S_2O_4$ (3.18 g), ethanol (5 ml) and ammonium hydroxide (14 %, 10 ml) was refluxed overnight. After, nitrobenzene (15 ml) was added, the solution was refluxed for 30 min. The slurry was filtrated under suction, and the obtained solid was dried in a vacuum oven. The solid was purified by sublimation: 355 mg, 44 % yield.

^{1}H-NMR (300 MHz, $CDCl_3$) = 8.07 (dd, 2H, *J* = 8.8 and 5.4 Hz), 7.34 (dd, 2H, *J* = 8.6 and 2.4 Hz), 7.21 (dd, 2H, *J* = 8.8 and 2.4 Hz), 4.05 (s, 4H)

2,8-Difluorodiindeno[1,2-b;1',2'-e]pyrazine-6,12-dione (2b): 2b was synthesized by following the procedure described for **2a**: 201 mg, 63 % yield.

Mp : sublimated (ca. 320°C). IR (KBr) : 1732, 1598, 1504, 1464, 1429, 1385, 1284, 1253, 1206, 1151, 1138, 1071, 974, 890, 860, 824, 789, 620, 498 cm^{-1}. MS/EI (70 eV) : m/z 320 (M^+). Anal. Calcd. For $C_{18}H_6F_2N_2O_2$: C, 67.51; H, 1.89; N, 8.75. Found: C, 67.27; H, 1.94; N, 8.67.

Absorption spectra:

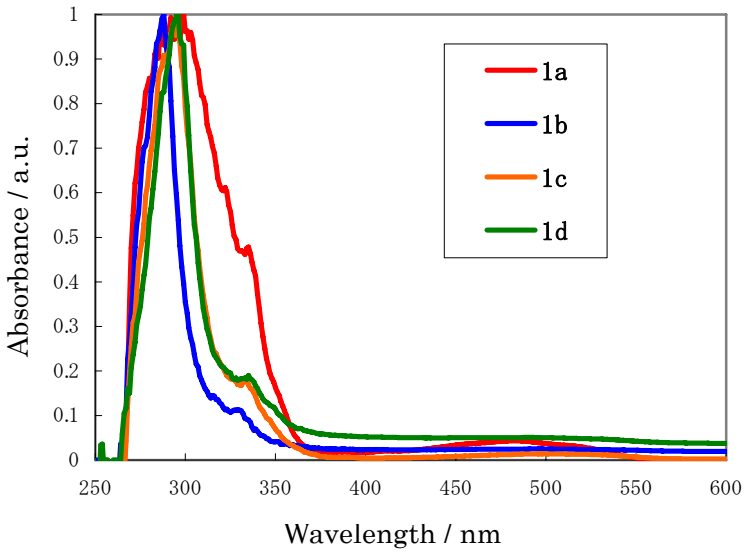


Figure S1. Absorption spectra of **1a–d**.

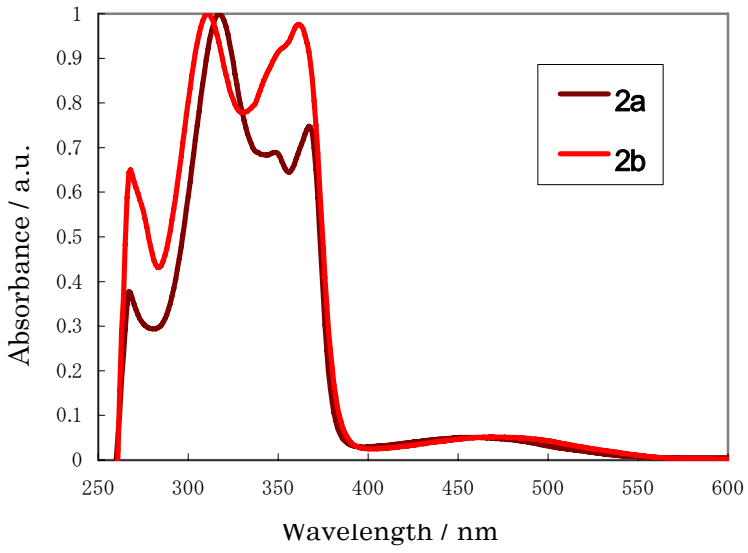


Figure S2. Absorption spectra of **2a,b**.

Differential pulse voltammograms:

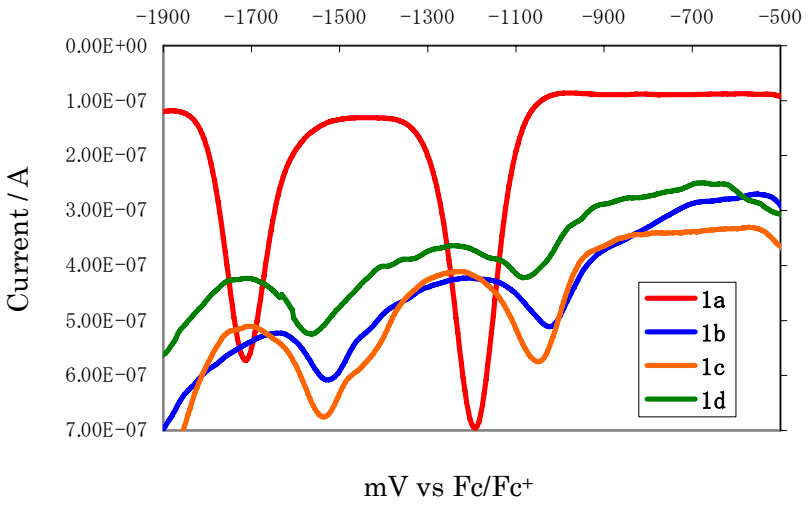


Figure S3. Differential pulse voltammograms of **1a–d.**

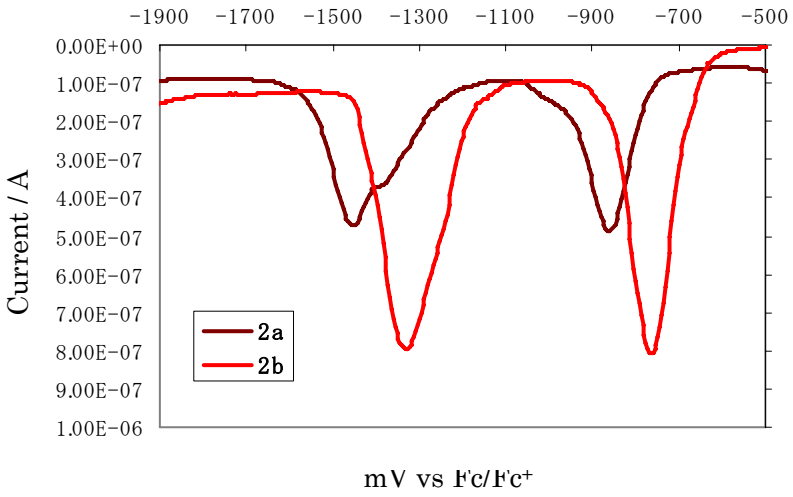


Figure S4. Differential pulse voltammograms of **2a,b.**

Fabrication of OFET:

(top-contact geometry)

OFETs were constructed on heavily doped n-type silicon wafers covered with 200 nm-thick thermally grown silicon dioxide. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. Organic compounds were deposited on the silicon dioxide by vacuum evaporation at a rate of 0.3–0.5 $Å s^{-1}$ under pressure of 10^{-5} Pa. The thickness of the semiconductor layer was 50 nm. During the evaporation, the temperature of the substrate was maintained by heating a copper block on which the substrate was mounted. Gold was used as source and drain electrodes and deposited on the organic semiconductor layer through a shadow mask with a channel width (W) of 1000 μm and a channel length (L) of 50 μm. Finally, the FET measurements were carried out at room temperature in the vacuum chamber (10^{-5} Pa) without exposure to air with Hewlett-Packard 4140A and 4140B models.

(bottom-contact geometry)

The heavily doped n-type silicon was used as substrate, and a layer of 300 nm of SiO_2 (grown by thermal oxidation) was used as the gate dielectric layer. Cr (10 nm)/Au (20 nm) were successively evaporated and photolithographically delineated to obtain the source and drain electrodes. The channel length and width were 25 μm and 294 mm, respectively. Organic thin films (50 nm) were deposited on the channel regions by vacuum evaporation (10^{-5} Pa). The output and transfer characteristics of **1** and **2** by bottom-contact configuration are shown in Fig. S5-S10. The deposition temperature of **1a–d** is about 180, 200, 220, 230 °C, respectively. And that of 2a and 2b is 200 and 180 °C.

I_d versus V_d and I_d versus V_g characteristics:

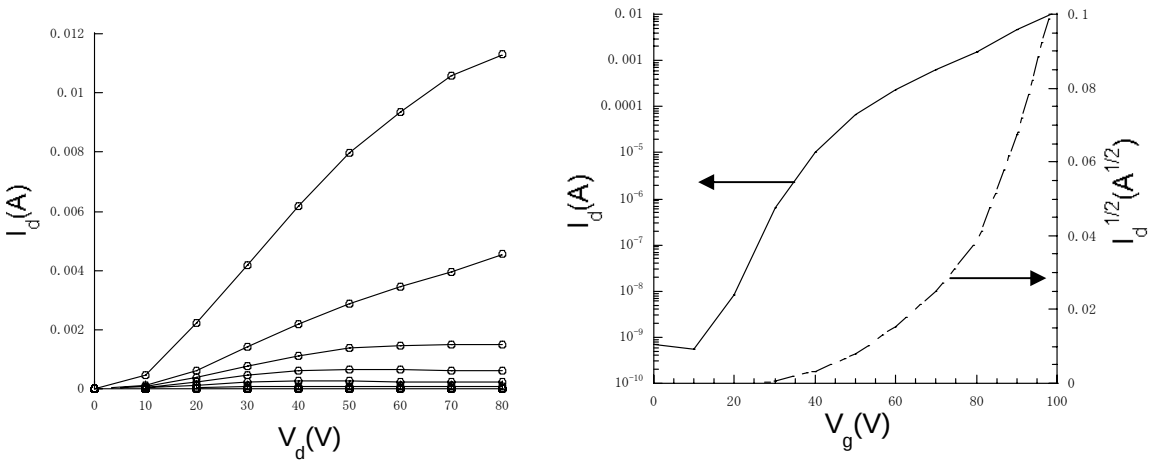


Figure S5. Output and transfer characteristic of **1b** with bottom-contact geometry.

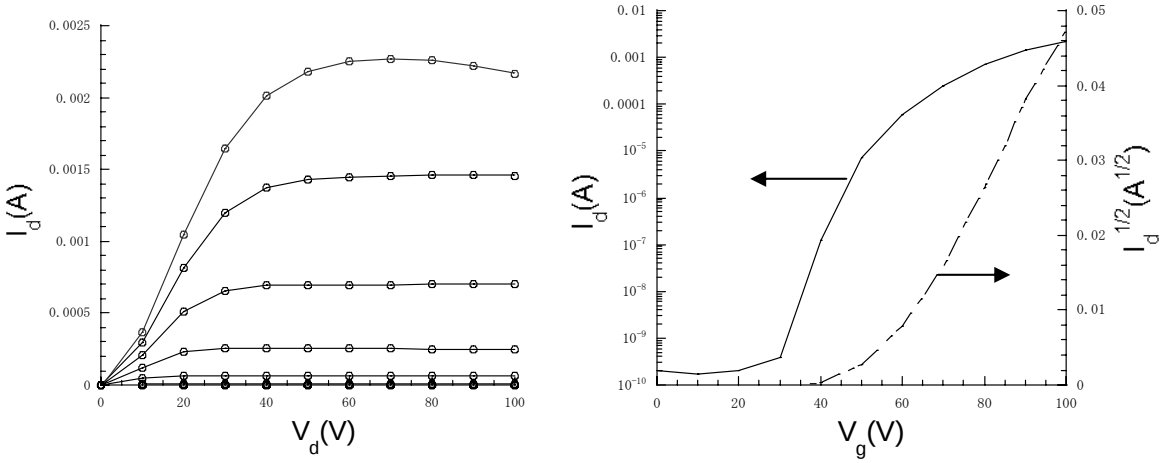


Figure S6. Output and transfer characteristic of **1c** with bottom-contact geometry.

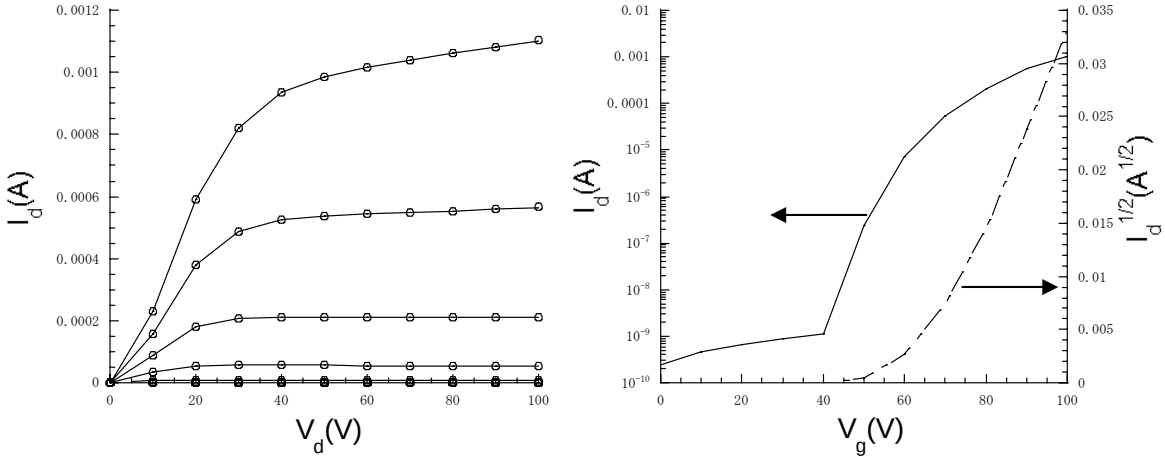


Figure S7. Output and transfer characteristic of **1d** with bottom-contact geometry .

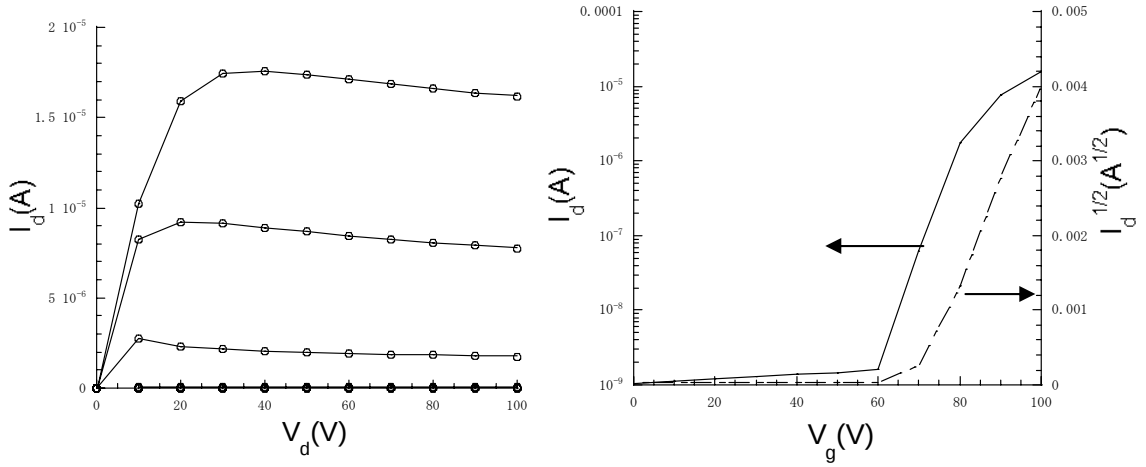


Figure S8. Output and transfer characteristic of **2a** with bottom-contact geometry.

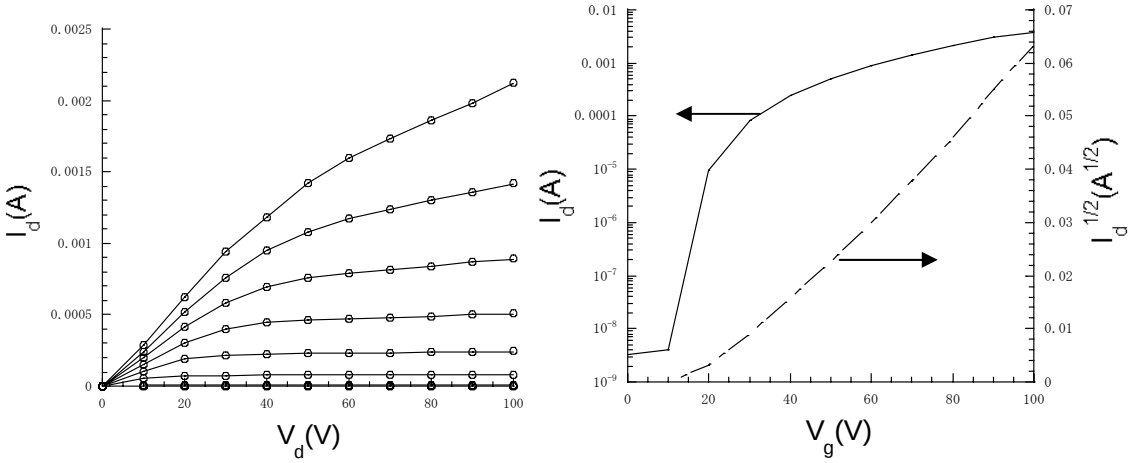


Figure S9. Output and transfer characteristic of **2b (black)** with bottom-contact geometry.

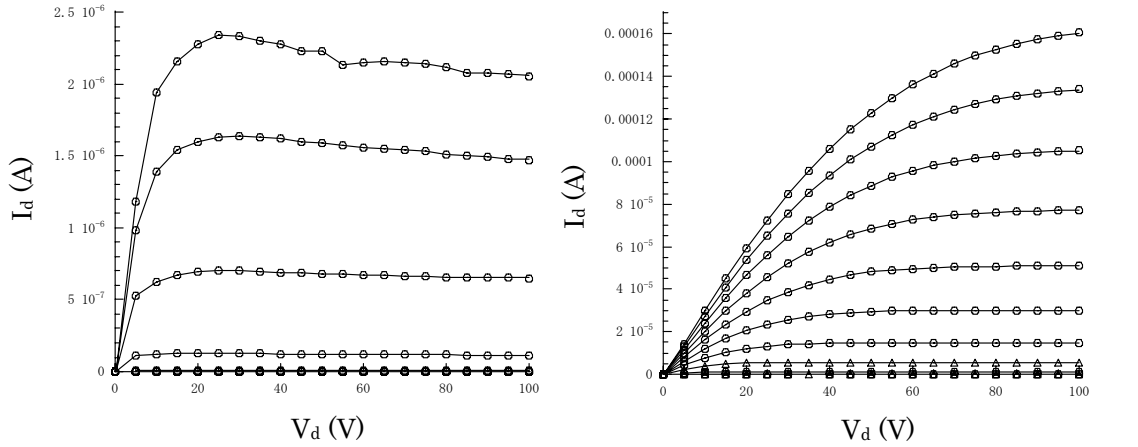
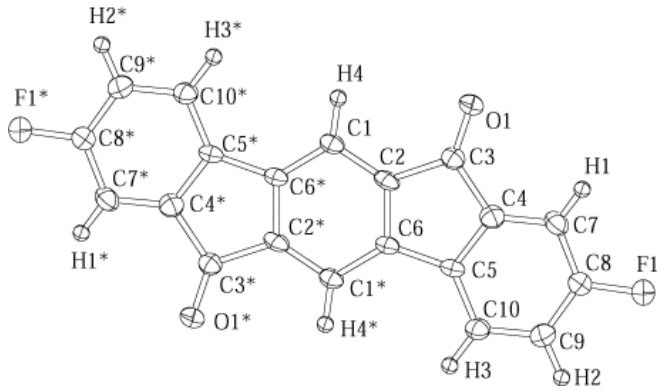


Figure S10. Output characteristics of **1b** and **2b (black)** with top-contact geometry.

X-ray crystallographic data:

The measurements were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer (Mo-Kα radiation, λ = 0.71075 Å). The data were collected at 93 K and the structures were solved by the direct method (SIR97) and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions.

<ORTEP drawing, lattice parameter, bond length and bond angle of **1b**>



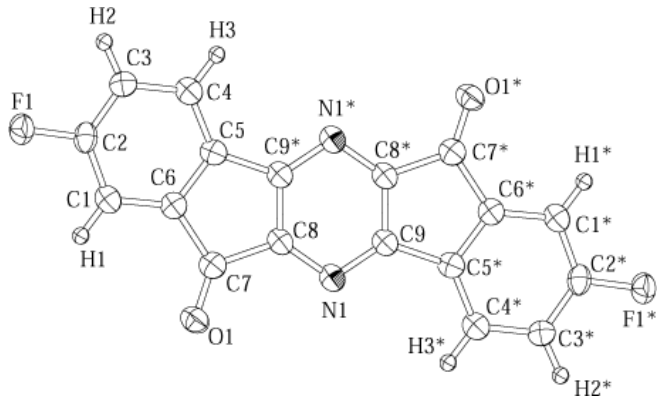
a	= 3.718(7) Å	α	= 100.42(8)°	**V**	= 323(3) Å^3
b	= 6.23(1) Å	β	= 96.69(7)°	**Z**	= 1
c	= 14.34(3) Å	γ	= 92.52(7)°	Space group	$P\bar{1}$(#2)

atom	atom	distance	atom	atom	distance
F(1)	C(8)	1.373(8)	C(4)	C(5)	1.395(10)
O(1)	C(3)	1.204(8)	C(4)	C(7)	1.379(9)
C(1)	C(2)	1.405(9)	C(5)	C(6)	1.469(9)
C(1)	C(6)	1.406(9)	C(5)	C(10)	1.410(10)
C(2)	C(3)	1.492(9)	C(7)	C(8)	1.37(1)
C(2)	C(6)	1.387(10)	C(8)	C(9)	1.37(1)
C(3)	C(4)	1.505(10)	C(9)	C(10)	1.397(9)
C(7)	H(1)	0.94	C(10)	H(3)	0.98
C(9)	H(2)	0.98			

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(6)	114.5(6)	C(4)	C(5)	C(10)	119.8(6)
C(1)	C(2)	C(3)	126.8(6)	C(6)	C(5)	C(10)	131.4(6)
C(1)	C(2)	C(6)	124.1(6)	C(1)	C(6)	C(2)	121.4(6)
C(3)	C(2)	C(6)	109.1(6)	C(1)	C(6)	C(5)	129.6(6)

O(1)	C(3)	C(2)	127.8(6)	C(2)	C(6)	C(5)	109.0(6)
O(1)	C(3)	C(4)	127.6(6)	C(4)	C(7)	C(8)	115.7(7)
C(2)	C(3)	C(4)	104.5(6)	F(1)	C(8)	C(7)	118.4(6)
C(3)	C(4)	C(5)	108.5(6)	F(1)	C(8)	C(9)	117.5(7)
C(3)	C(4)	C(7)	128.6(7)	C(7)	C(8)	C(9)	124.1(7)
C(5)	C(4)	C(7)	122.8(6)	C(8)	C(9)	C(10)	120.3(7)
C(4)	C(5)	C(6)	108.8(6)	C(5)	C(10)	C(9)	117.2(6)
C(4)	C(7)	H(1)	121.7	C(8)	C(9)	H(2)	121.0
C(5)	C(10)	H(3)	121.0	C(8)	C(7)	H(1)	122.5
C(10)	C(9)	H(2)	118.6	C(9)	C(10)	H(3)	122.6

<ORTEP drawing, lattice parameter, bond length and bond angle of **2b (red solid)**>

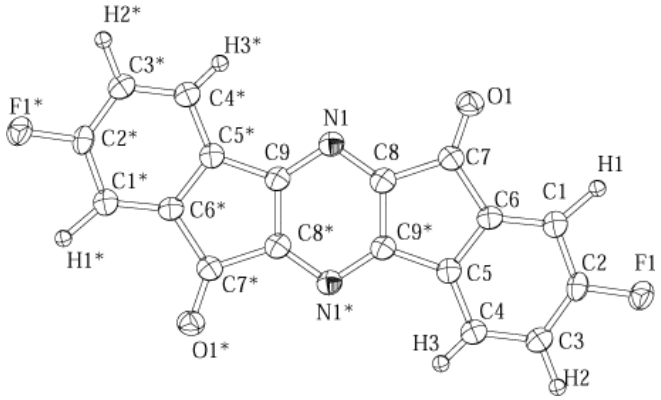


a	= 6.22(2) Å	α	= 90°	**V**	= 639 Å^3
b	= 7.75(2) Å	β	= 97.5(1)°	**Z**	= 2
c	= 13.38(3) Å	γ	= 90°	Space group	$P2_1/n$

atom	atom	distance	atom	atom	distance
F(1)	C(2)	1.358(4)	C(3)	C(4)	1.389(5)
O(1)	C(7)	1.206(3)	C(4)	C(5)	1.381(4)
N(1)	C(8)	1.333(4)	C(5)	C(6)	1.396(4)
N(1)	C(9)	1.335(3)	C(5)	C(9)	1.469(5)
C(1)	C(2)	1.378(4)	C(6)	C(7)	1.494(5)
C(1)	C(6)	1.386(4)	C(7)	C(8)	1.508(4)
C(2)	C(3)	1.370(4)	C(8)	C(9)	1.399(4)
C(1)	H(1)	0.95	C(4)	H(3)	0.96
C(3)	H(2)	0.97			

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	N(1)	C(9)	111.6(3)	C(1)	C(6)	C(7)	128.6(3)
C(2)	C(1)	C(6)	115.4(3)	C(5)	C(6)	C(7)	109.8(3)
F(1)	C(2)	C(1)	117.6(3)	O(1)	C(7)	C(6)	128.5(3)
F(1)	C(2)	C(3)	117.7(3)	O(1)	C(7)	C(8)	127.4(3)
C(1)	C(2)	C(3)	124.7(3)	C(6)	C(7)	C(8)	104.0(3)
C(2)	C(3)	C(4)	119.2(3)	N(1)	C(8)	C(7)	126.1(3)
C(3)	C(4)	C(5)	118.2(3)	N(1)	C(8)	C(9)	125.3(3)
C(4)	C(5)	C(6)	121.0(3)	C(7)	C(8)	C(9)	108.7(3)
C(4)	C(5)	C(9)	130.8(3)	N(1)	C(9)	C(5)	127.6(3)
C(6)	C(5)	C(9)	108.2(2)	N(1)	C(9)	C(8)	123.2(3)
C(1)	C(6)	C(5)	121.6(3)	C(5)	C(9)	C(8)	109.2(3)
C(2)	C(1)	H(1)	122.9	C(4)	C(3)	H(2)	120.3
C(6)	C(1)	H(1)	121.7	C(3)	C(4)	H(3)	121.3
C(2)	C(3)	H(2)	120.5	C(5)	C(4)	H(3)	120.5

<ORTEP drawing, lattice parameter, bond length and bond angle of **2b (black solid)**>



a	= 3.788(6) Å	α	= 90°	**V**	= 630 Å^3
b	= 10.79(2) Å	β	= 97.47(7)°	**Z**	= 2
c	= 15.55(3) Å	γ	= 90°	Space group	$P2_1/c$

atom	atom	distance	atom	atom	distance
F(1)	C(2)	1.353(3)	C(3)	C(4)	1.387(3)
O(1)	C(7)	1.215(3)	C(4)	C(5)	1.387(3)
N(1)	C(8)	1.334(3)	C(5)	C(6)	1.409(3)
N(1)	C(9)	1.347(3)	C(5)	C(9)	1.464(3)
C(1)	C(2)	1.390(3)	C(6)	C(7)	1.496(3)
C(1)	C(6)	1.376(3)	C(7)	C(8)	1.506(3)
C(2)	C(3)	1.380(3)	C(8)	C(9)	1.410(3)
C(1)	H(1)	1.17	C(4)	H(3)	0.96
C(3)	H(2)	1.06			

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	N(1)	C(9)	111.8(2)	C(1)	C(6)	C(7)	128.7(2)
C(2)	C(1)	C(6)	115.5(2)	C(5)	C(6)	C(7)	109.1(2)
F(1)	C(2)	C(1)	117.8(2)	O(1)	C(7)	C(6)	128.0(2)
F(1)	C(2)	C(3)	117.7(2)	O(1)	C(7)	C(8)	127.1(2)
C(1)	C(2)	C(3)	124.5(2)	C(6)	C(7)	C(8)	104.8(2)
C(2)	C(3)	C(4)	118.8(2)	N(1)	C(8)	C(7)	126.5(2)

C(3)	C(4)	C(5)	119.0(2)	N(1)	C(8)	C(9)	125.3(2)
C(4)	C(5)	C(6)	120.1(2)	C(7)	C(8)	C(9)	108.2(2)
C(4)	C(5)	C(9)	131.5(2)	N(1)	C(9)	C(5)	127.7(2)
C(6)	C(5)	C(9)	108.4(2)	N(1)	C(9)	C(8)	122.9(2)
C(1)	C(6)	C(5)	122.1(2)	C(5)	C(9)	C(8)	109.4(2)
C(2)	C(1)	H(1)	110.4	C(4)	C(3)	H(2)	118.2
C(6)	C(1)	H(1)	133.9	C(3)	C(4)	H(3)	129.3
C(2)	C(3)	H(2)	122.9	C(5)	C(4)	H(3)	111.6