Organic field-effect transistors based on heterocyclic co-oligomers containing a pyrazine ring

Takahiro Kojima, [†] *Jun-ichi Nishida,* [†] *Shizuo Tokito* [§]*, Hirokazu Tada,* [‡] *and Yoshiro Yamashita.* [†][*]

[†] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502. [‡] Institute for Molecular Science, Myodaiji, Okazaki 444-8585. [§] NHK Science and Technical Research Laboratories, Kinuta, Setagaya-ku, Tokyo 157-8510.

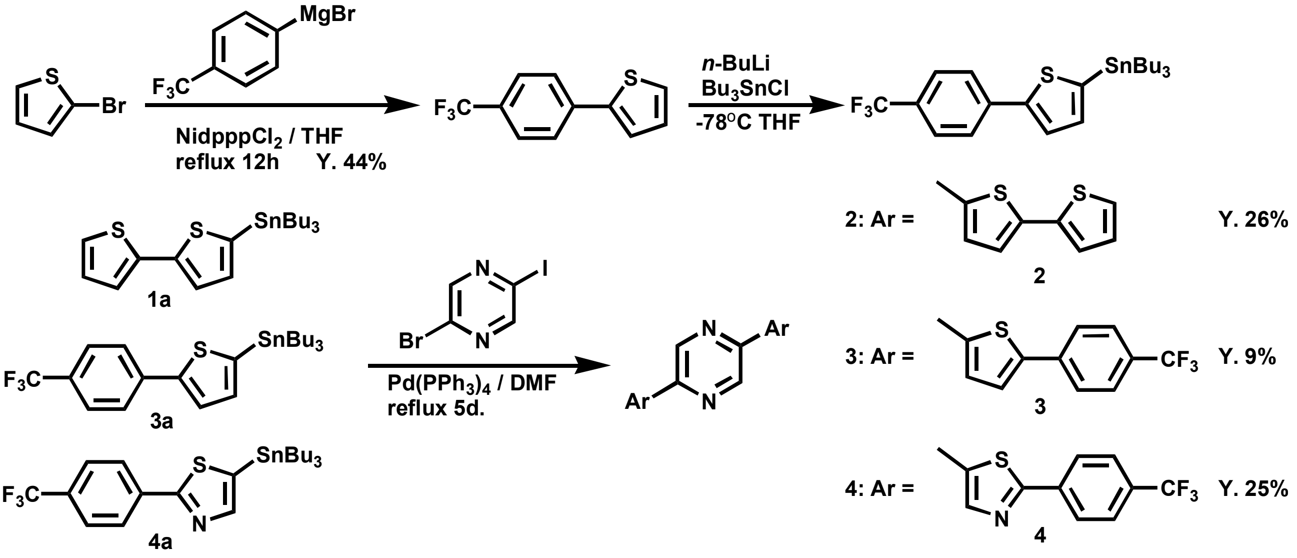
E-mail: Yoshiro@echem.titech.ac.jp

Experimental section

General.

Melting points were obtained on a Yanaco melting point apparatus and uncorrected. EI mass spectra were collected on a JEOL JMS-700 mass spectrometer. UV-vis spectra were recorded on a SHIMADZU MultiSpec-1500. Differential pulse voltammogram was recorded on a BAS-100B system containing terabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 mol dm^{-3} in dry dichloromethane). 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.

Synthesis of pyrazine derivatives.



Compound **2**

A mixture of **2a** (1.82 g, 4.0 mmol), 2-bromo-5-iodopyrazine (571.5 mg, 2.0 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) in DMF (30 ml) was refluxed for 5d. The mixture was cooled to room temperature and the solution was filtered. The black residue was purified by sublimation to give **2** (215 mg, 26%) as orange powder. m.p. 268－269℃. MS(EI) m/z 408 (M^+). Anal. Calcd for $C_{20}H_{12}N_2S_4$.:C, 58.79; H, 2.96; N, 6.86; S, 31.39. Found : C, 58.59; H, 3.12; N, 6.91; S, 31.40.

Compound 3

A mixture of **3a** (3.93 g, 7.6 mmol), 2-bromo-5-iodopyrazine (1.08 g, 3.8 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) in DMF (20 ml) was refluxed for 5d. The mixture was cooled to room temperature and the solution was filtered. The black residue was purified by sublimation to give **3** (175 mg, 9%) as orange powder. m.p. 276－277℃. MS(EI) m/z 533 (M^+). Anal. Calcd for $C_{26}H_{14}F_6N_2S_2$.: C, 58.64; H, 2.65; N, 5.26; S, 12.04.

Found : C, 58.42; H, 2.83; N, 5.49; S, 12.14.

Compound **4**

A mixture of **4a** (2.4 g, 4.6 mmol), 2-bromo-5-iodopyrazine (653 mg, 2.3 mmol), Pd(PPh_3)$_4$ (50 mg, 0.04 mmol) in DMF (30ml) was refluxed for 5d. The mixture was cooled to room temperature and the solution was filtered. The black residue was purified by sublimation to give **4** (313 mg, 25%) as orange powder. m.p. 348－350℃. MS(EI) m/z 535 (M^+). Anal. Calcd for $C_{26}H_{12}F_6N_4S_2$.: C, 53.93; H, 2.26; N, 10.48; S, 12.00 Found : C, 53.88; H, 2.13; N, 10.47; S, 12.04.

Fabrication of OFETs.

(Top-contact) OFETs were constructed on heavily doped n-type silicon wafers covered with 2000 Å-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 Ås^{-1} under pressure of 10^{-5} Pa. The thickness of the semiconductor layer was 500 Å. 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 100, 75, 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) The heavily doped n-type silicon was used as substrate, and a layer of 600 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 6 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 **1-4** by bottom-contact configuration are shown in Fig. S1-S4.

Measurements of air-stability of FET devices were carried out by using bottom contact type devices. The air stability was investigated by measurement of the device which was exposed for 1d in air. The output and transfer characteristics of **1-2** in air are shown in Fig. S5-S6 and the result is summarized in Table S1.

X-ray Diffraction Studies.

X-ray diffraction (XRD) measurements were carried out with a JEOL JDX-3530 X-ray diffractometer system. XRD patterns were obtained using Bragg-Brentano geometry with CuKα radiation as an X-ray source with an acceleration voltage of 40 kV and a beam current of 30 mA.

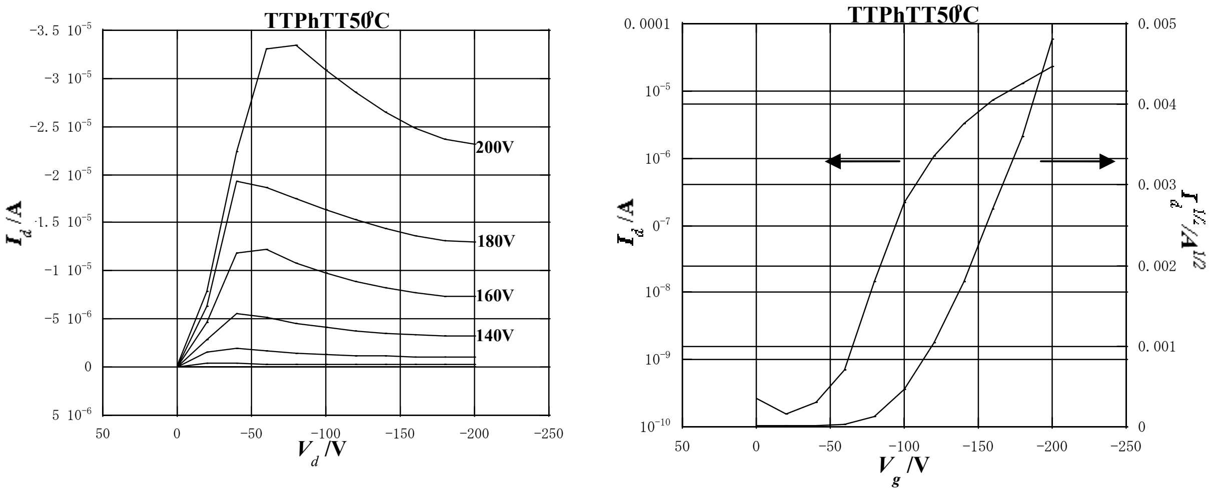


Fig.S1 Output and transfer characteristics of **1**

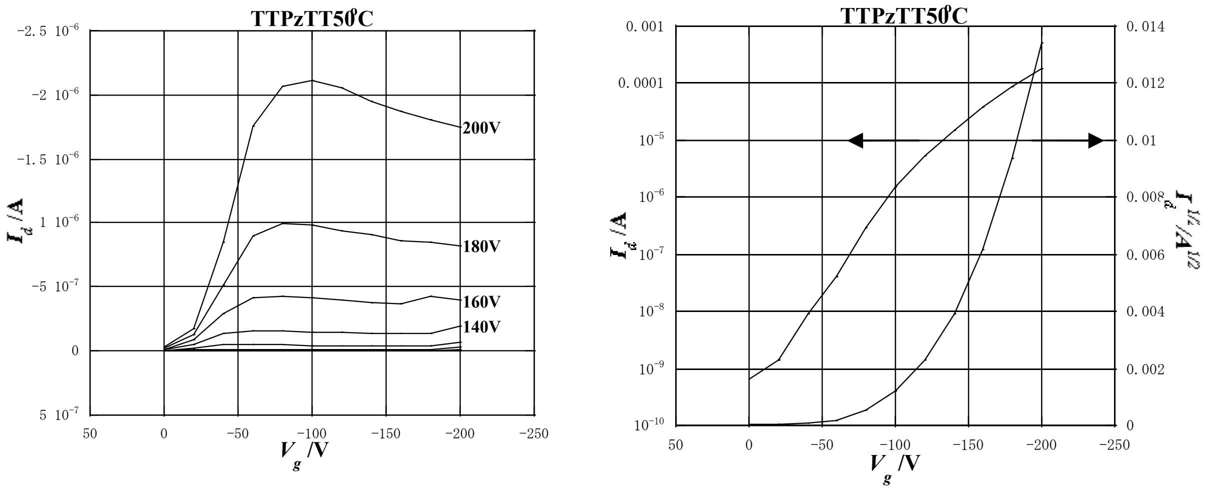


Fig.S2 Output and transfer characteristics of **2**

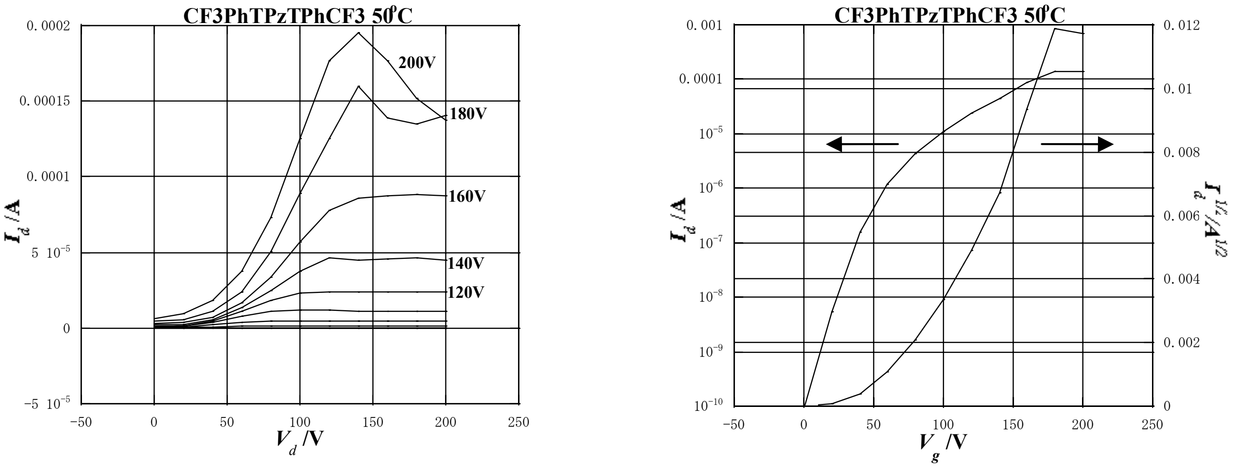


Fig.S3 Output and transfer characteristics of **3**

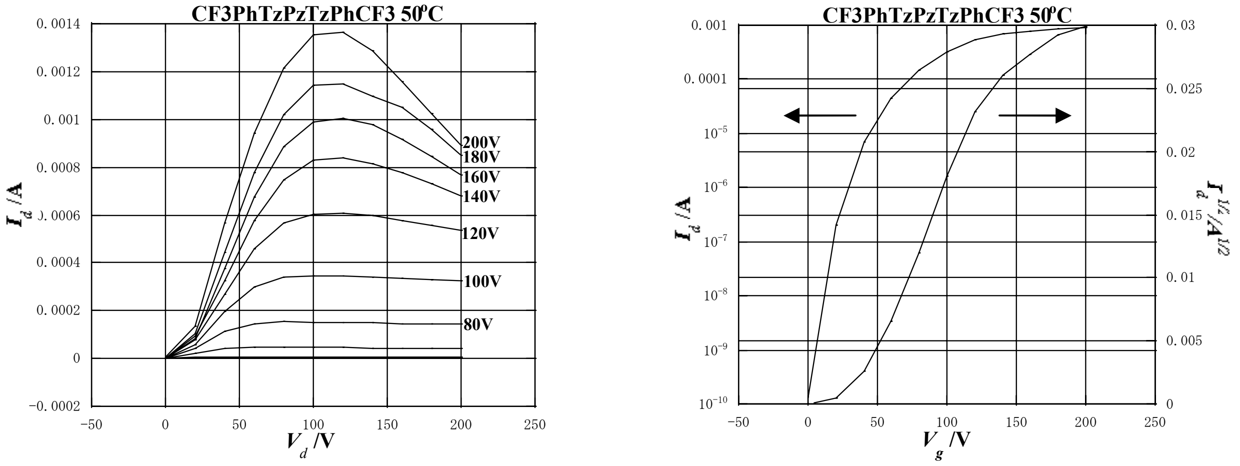


Fig.S4 Output and transfer characteristics of **4**

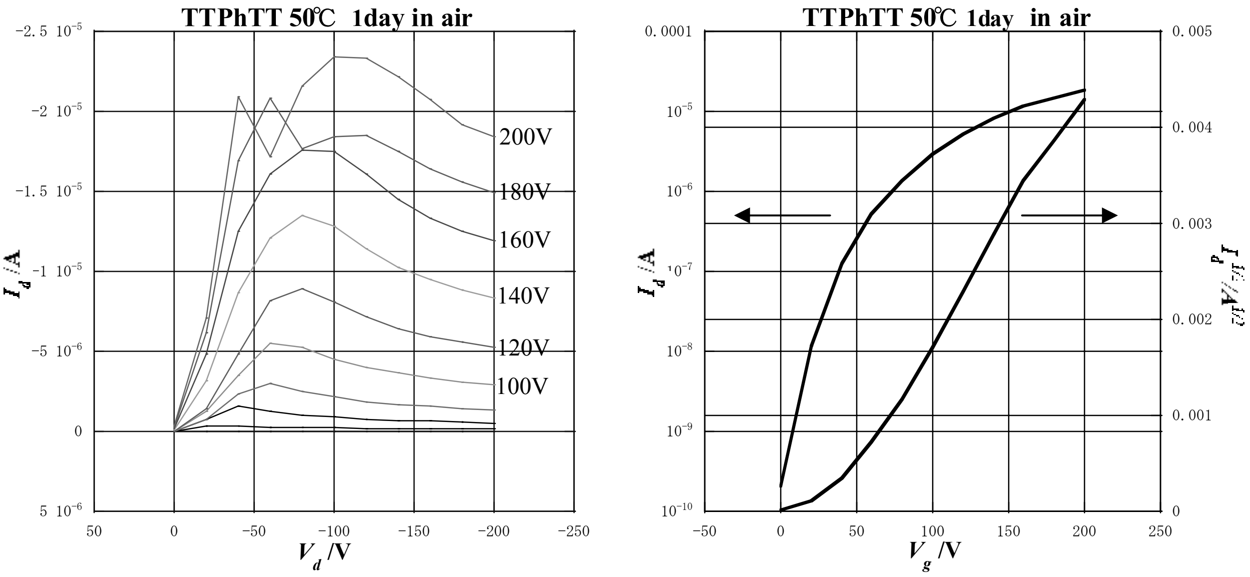


Fig.S5 Output and transfer characteristics in air of 1

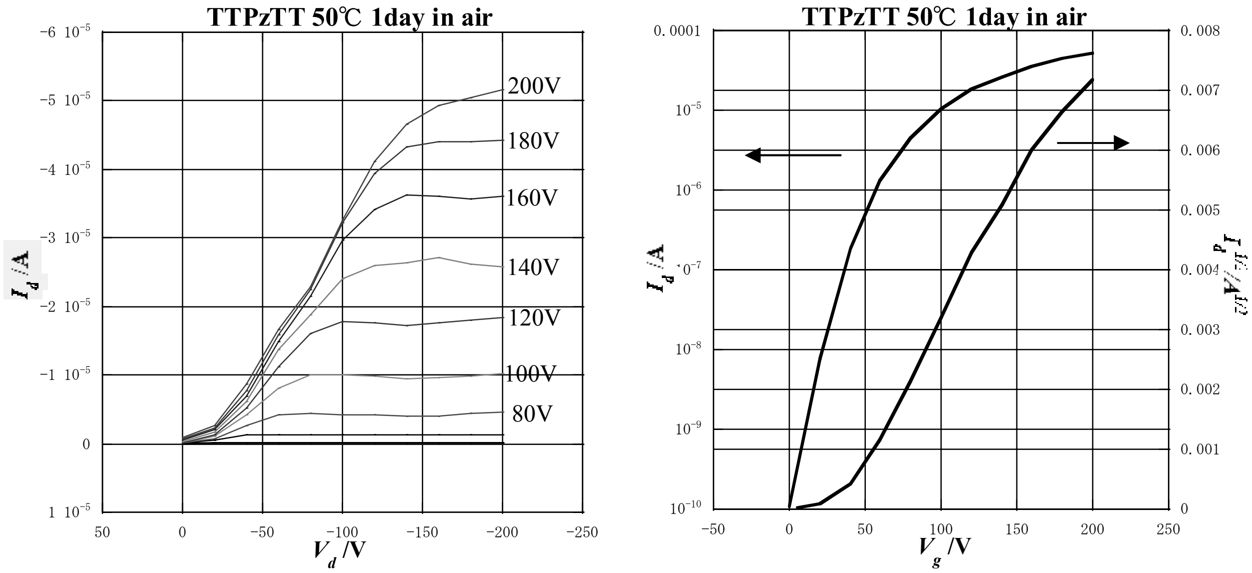


Fig.S6 Output and transfer characteristics in air of 2

Table S1: Air stability of bottom contact FET devices

Compound	condition	T_{sub} (℃)	Mobility (cm^2/Vs)	on/off ratio	Threshold (V)
1	vacuum	50	3.8×10^{-4}	1.0×10^{6}	+102
	air	50	3.3×10^{-5}	1.2×10^{5}	+40
2	vacuum	50	1.1×10^{-3}	2.5×10^{6}	+123
	air	50	8.7×10^{-5}	4.8×10^{5}	+41

electrode: Au, SiO_2/Si substrates, SiO_2:600nm,

channel length 25μm, channel width 6mm

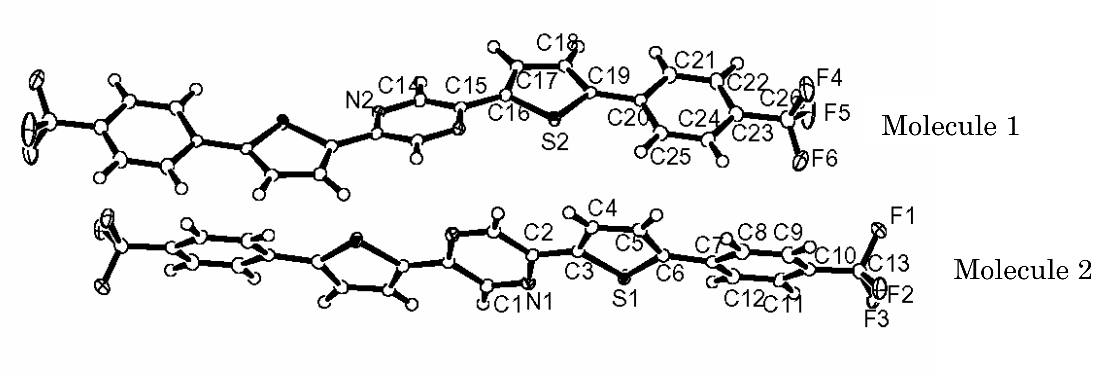


Fig.S7 Molecular structure of **3**..