Supporting Information

Air-stable ambipolar organic transistors based on charge-transfer complexes containing dibenzopyrrolopyrrole

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Redox potentials

Cyclic voltammograms were measured on an ALS model 701E electrochemical analyzer in 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-$Bu_4N \cdot PF_6$) solutions of dichloromethane at a scan rate of 20, 50, and 100 mV/s (Figure S1). The reference electrode was $Ag/AgNO_3$ with a glassy carbon working electrode and a Pt supporting electrode. The measured potentials were converted to the HOMO/LUMO levels assuming the ferrocene/ferrocenium redox potential to be –4.80 eV from the vacuum level, and compared with the previous reports (Table S1).[32]

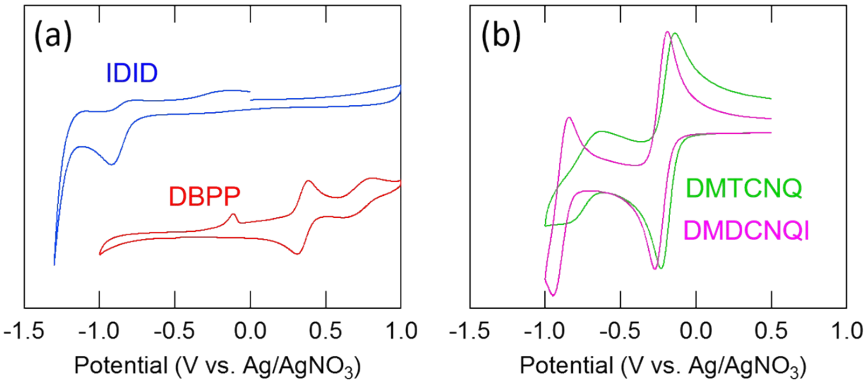

Figure S1. Cyclic voltammetry of (a) DBPP and IDID, and (b) DMDCNQI and DMTCNQ in dichloromethane, where E^{redox} (*vs.* $Ag/AgNO_3$) ~ 0.0 V *vs.* F_c/F_c^+.

Table S1. Redox potentials of DBPP and IDID.

	Source	E^{redox} (V)	$E_{\text{HOMO/LUMO}}$ (eV)[a]
DBPP oxidation, HOMO	Ref. 45a	0.24 V *vs* Ag/AgCl	-4.7
	Ref. 46c	0.67 V *vs* Ag/AgCl[b]	-5.1
	This work	0.30 V *vs* F_c/F_c^+	-5.1
IDID reduction, LUMO	Ref. 46a	-0.54 V *vs* Ag/AgCl	-3.9
	Ref. 46b,c	-0.45 V *vs* Ag/AgCl	-4.0
	This work	-0.80 V *vs* F_c/F_c^+	-4.0
DMDCNQI reduction, LUMO	Ref. 52	+0.22 V vs Ag/AgCl	-4.7
	This work	-0.14 V *vs* F_c/F_c^+	-4.66
DMTCNQ reduction, LUMO	Ref. 53	+0.22 V vs Ag/AgCl	-4.7
	This work	-0.10 V *vs* F_c/F_c^+	-4.70

[a] Energy levels are estimated from $-E_{\text{HOMO/LUMO}} = E^{\text{redox}}$ (*vs* Ag/AgCl) + 4.44 eV = E^{redox} (*vs* F_c/F_c^+) + 4.8 eV.[32]

[b] Oxidation of IDID.

Estimation of the degree of charge-transfer (ρ)

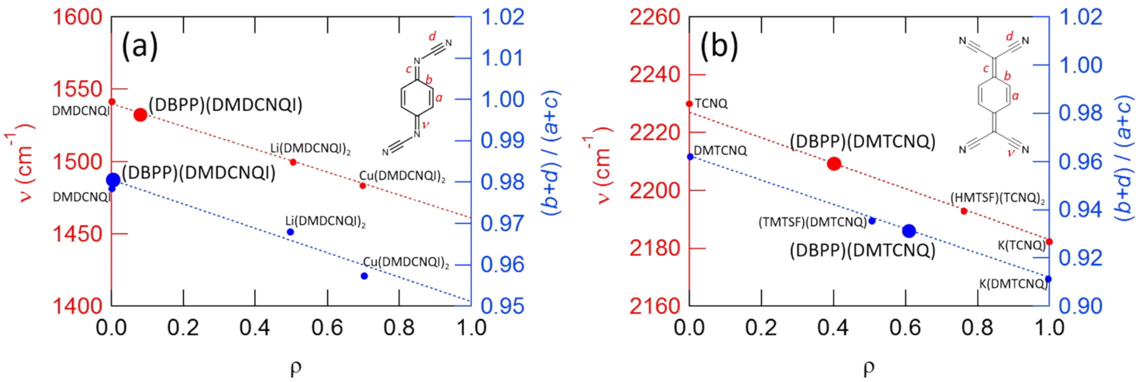

Figure S2. Estimation of ρ from IR spectra and bond lengths in (a) (DBPP)(DMDCNQI),[56,57] and (b) (DBPP)(DMTCNQ),[58,59] where $\delta = (b + d)/(a + c)$.

Absorption spectra

Absorption spectra of the component molecules and the charge-transfer complexes were measured on a Shimadzu UV spectrometer UV-1800 in the form of KBr pellets.

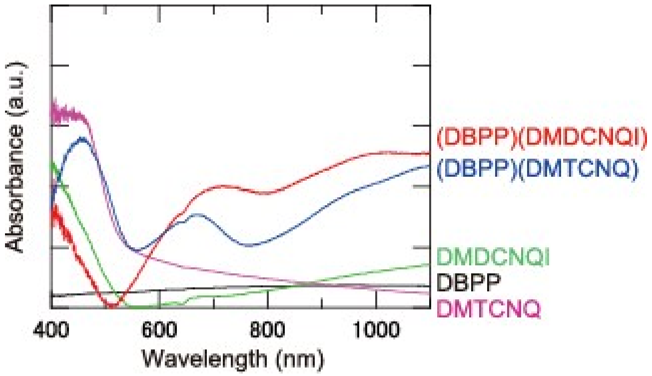

Figure S3. Absorption spectra of the component molecules and the charge-transfer complexes.

XRD patterns

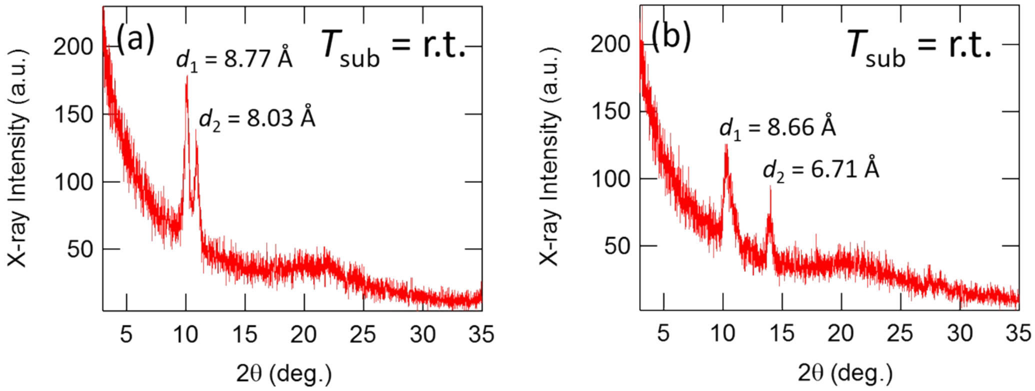

Figure S4. X-ray diffraction of (a) (DBPP)(DMDCNQI) and (b) (DBPP)(DMTCNQ).

The XRD peak of (DBPP)(DMDCNQI) at d_1 = 8.77 Å is close to $c \sin \alpha \sin \beta = 8.50$ Å, indicating that the molecules are standing perpendicular to the substrate (Fig. S4a). The peak at d_2 = 8.03 Å is attributable to neutral DMDCNQI (d = 8.1 Å), but the XRD of DMDCNQI affords very sharp peaks.[36] Since this peak is not removed by changing the fabrication conditions,[35] we cannot exclude the possibility of a different orientation coming from the mix-stacked complex.

(DBPP)(DMTCNQ) affords similar d_2 = 8.66 Å; though the exact relation to the crystal lattice is not obvious, this value is similar to that of the DMDCNQI complex, and possibly associated with the layer structure of the mix-stacked complex. This complex again affords another peak at d = 6.71 Å, which is not likely to be related to the neutral species.[46a,S1] This d value is similar to those of side-on molecules (6.3 - 6.5 Å),[S2] so the presence of side-on arrangement is suggested.

Transistor characteristics

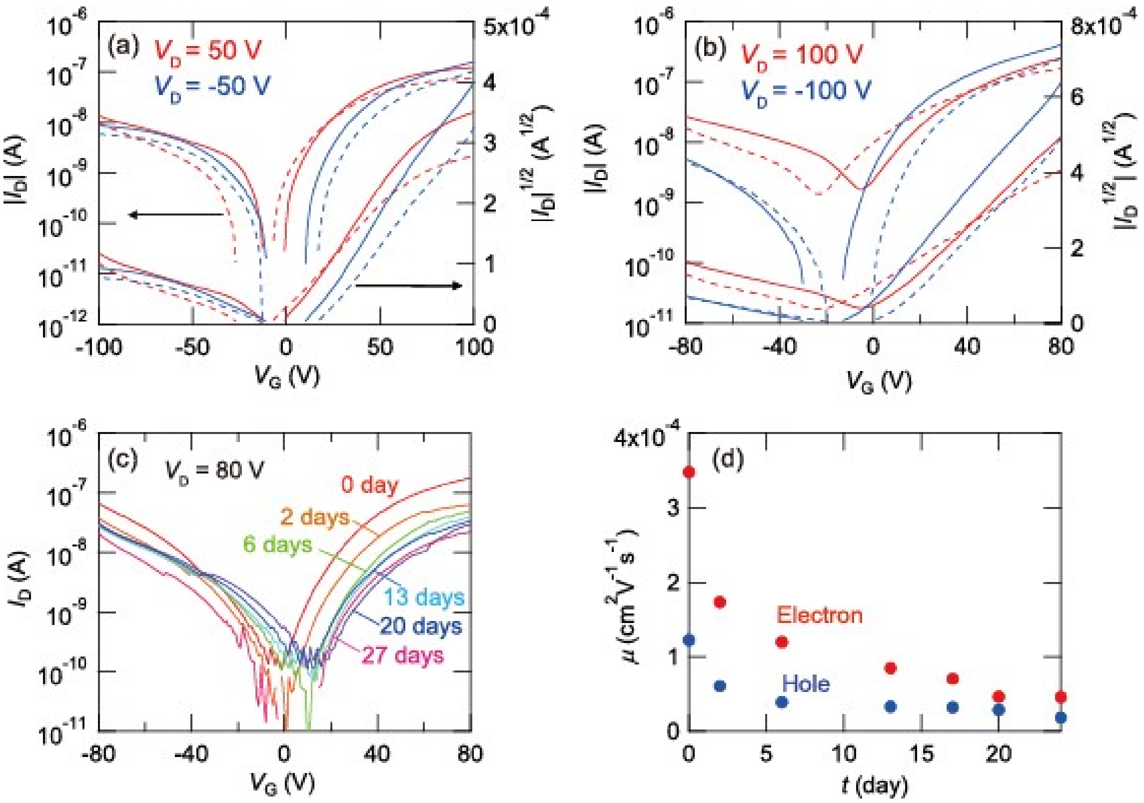

Figure S5. (a) (b) Transfer characteristics of a thin-film transistor based on (DBPP)(DMDCNQI) measured under vacuum (solid curves) and in air (dotted curves). The mobilities are $\mu_h/\mu_e = 1.5\times10^{-5}/4.1\times10^{-4}$ cm^2 V^{-1} s^{-1} under vacuum and $\mu_h/\mu_e = 1.5\times10^{-5}/3.7\times10^{-4}$ cm^2 V^{-1} s^{-1} in air. (c) Long-term transfer characteristics, and (d) mobility drop of a thin-film transistor based on (DBPP)(DMDCNQI) measured in air after the storage in ambient conditions.

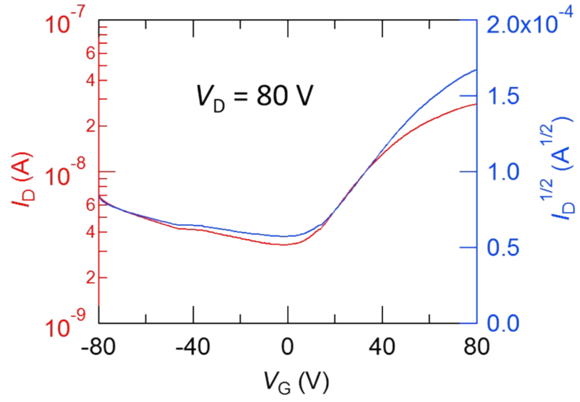

Figure S6. Transfer characteristics of a thin-film transistor based on (DBPP)(DMTCNQ). The resulting electron mobility is 8.5×10^{-5} cm^2 V^{-1} s^{-1}.

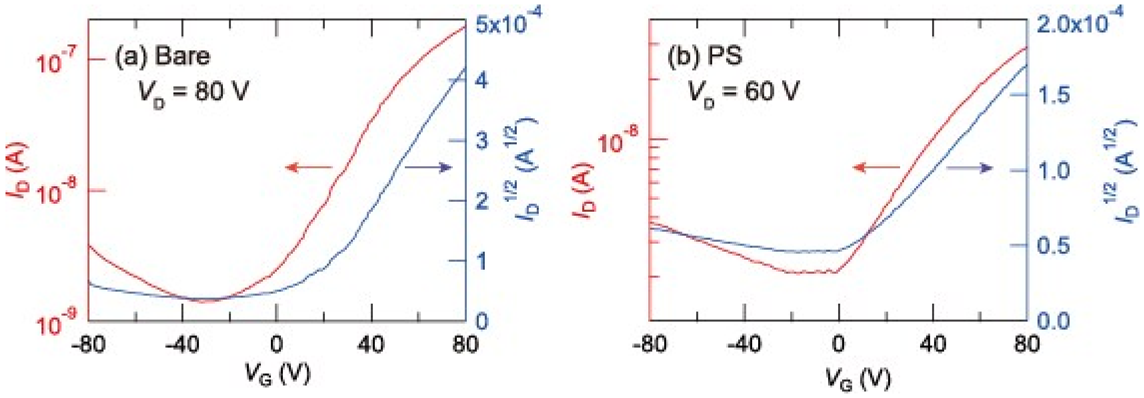

Figure S7. Transfer characteristics of single-crystal transistors based on (DBPP)(DMTCNQ) fabricated on (a) bare SiO_2 (L = 130 μm and W = 32 μm), and (b) PS-treated substrates (L = 110 μm and W = 16 μm). The mobilities are $\mu_e = 0.023$ cm^2 V^{-1} s^{-1} and 3.0×10^{-3} cm^2 V^{-1} s^{-1}, respectively.

References

S1 R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr*. 1965, **18**, 932.

S2 S. Tamura, T. Kadoya, T. Kawamoto and T. Mori, *Appl. Phys. Lett.*, 2013, **102**, 063305.