Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting information

Charge injection from organic charge-transfer salts to organic semiconductors

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1. Preparation of CT-Salt Particles

For (TTF)[Ni(dmit)$_2$]$_2$, a 6 mL acetonitrile solution of 30 mg (TTF)$_3$(BF$_4$)$_2$ and 5mg PVP was slowly added to a 10 mL acetone solution of 53 mg (n-Bu$_4$N)[Ni(dmit)$_2$] at room temperature.[S1,S2] After 2 h stirring, the suspension was collected by filtration, and dried *in vacuo*. Cu(DMDCNQI)$_2$ was prepared similarly by adding a 5 mL acetonitrile solution of 32 mg CuI and 100 mg PVP to a 20 mL acetonitrile solution of 46 mg DMDCNQI and 300 mg PVP.[S3] For (TTF)(TCNQ), a 5 mL acetonitrile solution of 23 mg TTF and 5 mg PVP was slowly added to a 7 mL acetone solution of 23 mg TCNQ. For (BEDT-TTF)$_2$I$_3$, a 10 mL acetonitrile solution of 20 mg iodine and 100 mg PVP was added to a 15 mL 1,1,2-trichloroethane solution of 15 mg BEDT-TTF and 150 mg PVP at 70 ℃. After 1 h stirring at 70 ℃, this solution was cooled to room temperature and evaporated *in vacuo* to a half volume. Finally 15 mL methanol was added, and the precipitate was collected by filtration.

(TTF)[Ni(dmit)$_2$]$_2$ and (TTF)(TCNQ) were easily dispersed with the use of a small amount of PVP, but much more PVP was necessary to obtain satisfactory dispersions of Cu(DMDCNQI)$_2$ and (BEDT-TTF)$_2$I$_3$. As dispersants, we also investigated ionic liquids and conducting polymers, but some were not stable in water and others were not sufficiently conducting. PVP-stabilized particles were easiest to handle, most stable, and well dispersed in most organic solvents as well as water.

2. Patterning and Device Fabrication

Electrode patterning was achieved by surface selective deposition. Organic transistors were fabricated onto highly doped n-type silicon wafers with a thermally grown silicon dioxide layer of 300 nm thickness (13 nF/cm^2). After the substrates were treated with hexamethyldisilazane (HMDS) vapor, ultraviolet light was irradiated on the electrode area through a shadow mask for 20 min in order to remove the HMDS layer and to give a hydrophilic region (channel length L = 200 μm and channel width W =1000 μm). 5 mg of CT salts prepared above were dispersed in 0.5 mL ethanol/water (1:1) by 1 h sonication, and dropped onto the substrates several times with a glass capillary to give a thin film of the CT salt with a typical thickness of 6-10 μm (Fig. S1). After dried *in vacuo*, organic semiconductors were thermally evaporated on the room-temperature substrates (100 nm for pentacene, 80 nm for C$_{60}$, and 60 nm for 6T), and the transistor properties were recorded both under vacuum and ambient conditions for pentacene and 6T, and under vacuum

(10^{-3} Pa) for C_{60}. The results under vacuum show essentially the same characteristics, so the results in air are depicted in Figs. 2(a) and (b).

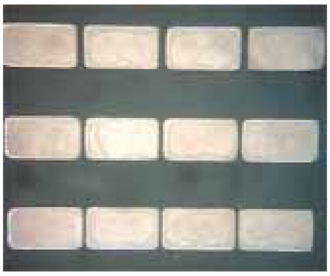

Fig. S1 Optical microscopic image of a substrate with patterned (TTF)[Ni(dmit)$_2$]$_2$.

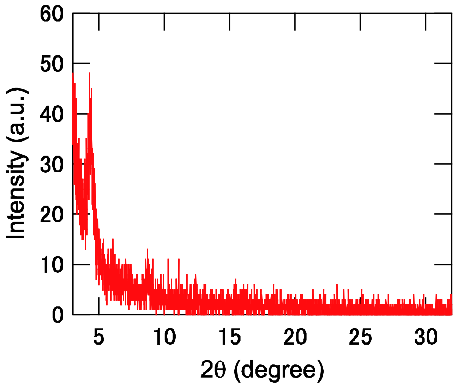

Fig. S2 XRD of PVP-stabilized Cu(DMDCNQI)$_2$ film.

3. Transistor Characteristics

Output characteristics of pentacene and C_{60} transistors with PVP-stabilized (TTF)[Ni(dmit)$_2$]$_2$ electrodes are depicted in Fig. S3. Output and transfer characteristics of a pentacene transistor with (TTF)[Ni(dmit)$_2$]$_2$ electrodes stabilized by ionic liquid, 1-butyl-3-methylimidazolium BF_4 are shown in Fig. S4. Table S1 summarize mobility and other parameters of various transistors obtained from average of several devices. These mobility values are extracted from the transfer characteristics. The total resistance values in Fig. 3 are, however, estimated from the linear region of the output characteristics.

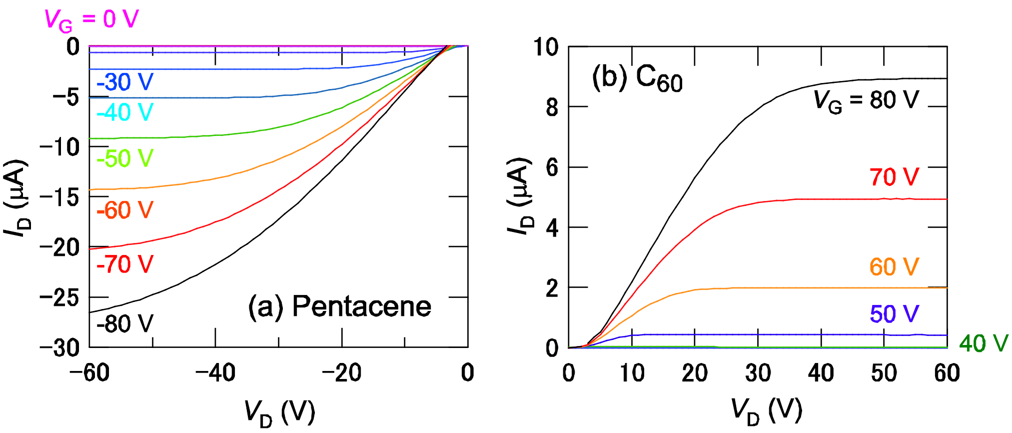

Fig. S3 Output characteristics of (a) pentacene and (b) C_{60} transistors with PVP-stabilized (TTF)[Ni(dmit)$_2$]$_2$ electrodes.

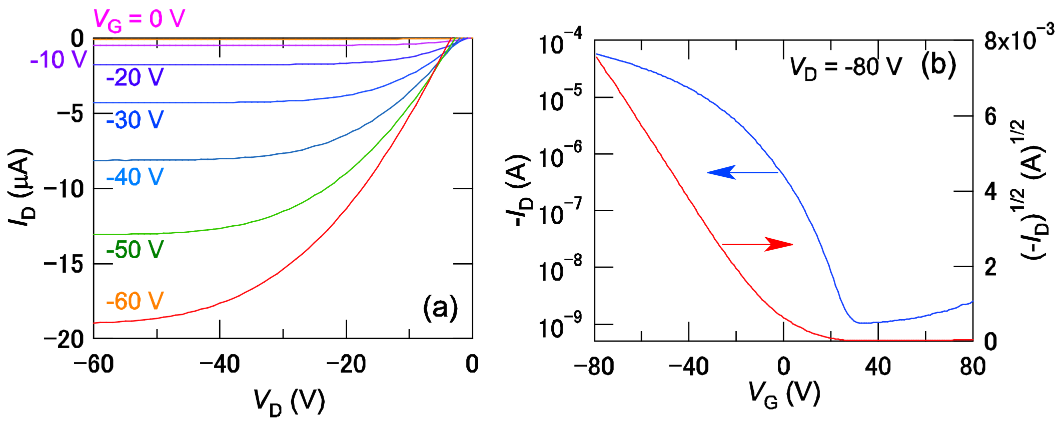

Fig. S4 (a) Output and (b) transfer characteristics of a pentacene transistor with $(TTF)[Ni(dmit)_2]_2$ electrodes stabilized by ionic liquid.

Table S1 Mobility (μ), threshold voltage (V_{th}), and on/off ratio of thin-film transistors with CT salt electrodes.[a]

Semiconductor	Electrode	μ (cm^2/Vs)	V_{th} (V)	on/off ratio
Pentacene	$TTF[Ni(dmit)_2]_2$	0.22	-12	2×10^5
	$TTF[Ni(dmit)_2]_2$/IL[b]	0.18	3	4×10^4
	$Cu(DMDCNQI)_2$	0.23	-6	2×10^5
	(TTF)(TCNQ)	0.17	-14	9×10^4
	$(BEDT\text{-}TTF)_2I_3$	0.056	-5	6×10^4
6T	$TTF[Ni(dmit)_2]_2$	0.047	-14	1×10^4
	$Cu(DMDCNQI)_2$	0.029	-11	1×10^4
	(TTF)(TCNQ)	0.024	-5	1×10^4
	$(BEDT\text{-}TTF)_2I_3$	0.014	-5	2×10^5
C_{60}	$TTF[Ni(dmit)_2]_2$	0.26 n	42	7×10^4
	$Cu(DMDCNQI)_2$	0.18 n	34	1×10^5
	(TTF)(TCNQ)	0.19 n	36	8×10^4
	$(BEDT\text{-}TTF)_2I_3$	0.12 n	30	4×10^4
		0.006 n/0.002 p		

[a] Averaged values for at least several devices. [b] Dispersion in ionic liquid.

Energy levels of organic materials in Fig. 4 are estimated from the redox potentials (*vs*. SCE) by adding 4.44 eV:[S4] 4.78 eV for TTF,[S5] 4.64 eV for TCNQ,[S6] 4.64 eV for DMDCNQI,[S7] 4.65 eV for $[Ni(dmit)_2]$,[S8] 5.0 eV for BEDT-TTF,[S9] 4.85 and 3.2 eV for Pentacence,[S10] 4.9 eV for 6T,[S11] and 6.2 and 3.8 eV for C_{60}.[S12]

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