

Supporting Information

Charge-transfer complexes of sulfur-rich acceptors derived from birhodanines

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Single-crystal structures

The X-ray diffraction data were collected by a Rigaku four-circle diffractometer (AFC-7R) with graphite-monochromatized MoK α radiation ($\lambda = 0.71069 \text{ \AA}$). The structures were solved by the direct method (SIR 2004) and refined by the full-matrix least-squares method by applying anisotropic temperature factors for all non-hydrogen atoms using the SHELXL programs.^{S1-S3} The hydrogen atoms were placed at geometrically calculated positions.

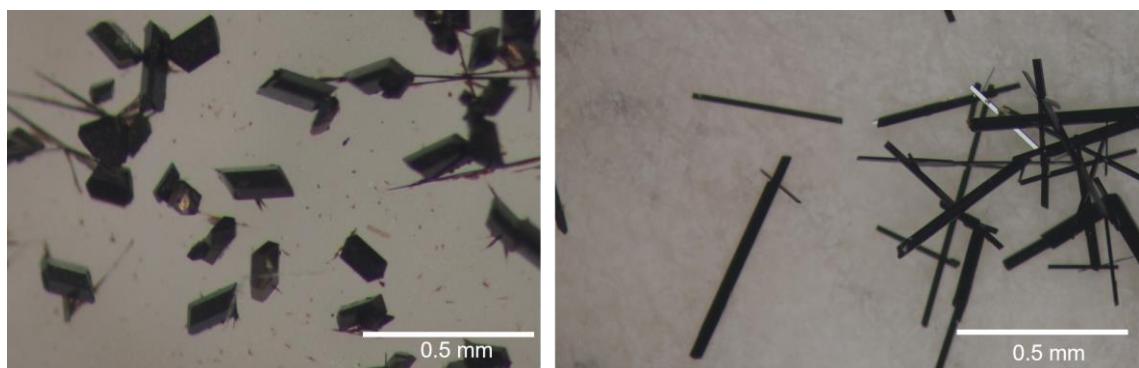
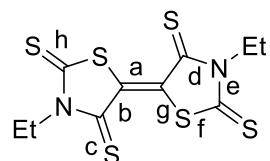


Figure S1. Crystals of (a) (perylene)(SS-Et) and (b) (perylene)(OS-Et).

By comparing bond lengths with those of neutral **SS-Et** and **SS-Et⁻** in $[\text{Fe}(\text{Cp}^*)_2]\text{[SS-Et]}$,^{5a} we can estimate the charge-transfer degree ρ (Table S1). The results demonstrate ρ is practically zero (Fig. S2). In the **SS-Pr** complexes, we cannot estimate similarly, but the bond lengths strongly suggest ρ is close to zero as well (Table S2). Similar comparison is impossible in other complexes, but selected bond lengths are listed in Tables S3-S5. The change is in agreement with the LUMO (Fig. 1(a)); antibonding parts increase and bonding parts shrink.

Table S1. Selected experimental bond lengths (\AA) for **SS-Et**, (pyrene)(**SS-Et**), (perylene)(**SS-Et**), (coronene)(**SS-Et**), and **SS-Et⁻** in $[\text{Fe}(\text{Cp}^*)_2]\text{[SS-Et]}$.



	SS-Et	(pyrene)(SS-Et)	(perylene)(SS-Et)	(coronene)(SS-Et)	SS-Et⁻
a : C–C	1.371(3)	1.371(4)	1.369(6)	1.368(4)	1.408(6)
b : C–C	1.465(5)	1.466(3)	1.457(4)	1.460(6)	1.418(4)
c : C–S	1.648(3)	1.631(2)	1.641(3)	1.632 (4)	1.679(5)
d : C–N	1.386(3)	1.384(3)	1.379(4)	1.389(4)	1.405(7)
e : N–C	1.370(4)	1.369(3)	1.372(4)	1.363(5)	1.359(5)
f : C–S	1.761(6)	1.742(3)	1.743(3)	1.743(4)	1.746(3)
g : C–S	1.751(4)	1.739(2)	1.742(3)	1.743(4)	1.752(5)
h : C–S	1.641(2)	1.636(2)	1.638(3)	1.643(3)	1.665(7)

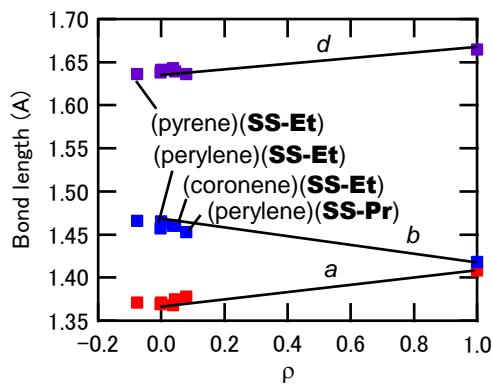
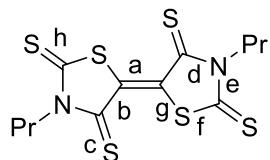


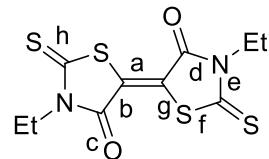
Figure S2. Estimation of charge-transfer degree ρ from the bond lengths.

Table S2. Selected experimental bond lengths (Å) for **SS-Pr**, (pyrene)(**SS-Pr**), (perylene)(**SS-Pr**), and (coronene)(**SS-Pr**).



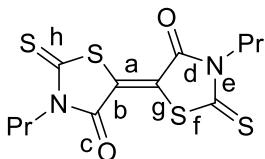
	SS-Pr	(pyrene)(SS-Pr)	(perylene)(SS-Pr)
a : C–C	1.374	1.375	1.378
b : C–C	1.460	1.460	1.453
c : C–S	1.644	1.641	1.636
d : C–N	1.386	1.379	1.394
e : N–C	1.374	1.365	1.373
f : C–S	1.756	1.748	1.742
g : C–S	1.750	1.744	1.745
h : C–S	1.636	1.639	1.636

Table S3 Selected experimental bond lengths (Å) for **OS-Et**, (pyrene)(**OS-Et**), (perylene)(**OS-Et**), and (coronene)(**OS-Et**).



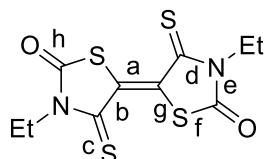
	OS-Et	(pyrene)(OS-Et)	(perylene)(OS-Et)
a : C–C	1.348	1.344	1.354
b : C–C	1.479	1.485	1.483
c : C–O	1.212	1.202	1.208
d : C–N	1.381	1.381	1.389
e : N–C	1.371	1.374	1.377
f : C–S	1.755	1.741	1.756
g : C–S	1.733	1.737	1.720
h : C–S	1.626	1.630	1.612

Table S4 Selected experimental bond lengths (Å) for **OS-Pr**, (pyrene)(**OS-Pr**), (perylene)(**OS-Pr**), and (coronene)(**OS-Pr**).



	OS-Pr	(perylene)(OS-Pr)
a : C–C	1.346	1.374
b : C–C	1.479	1.477
c : C–O	1.210	1.208
d : C–N	1.383	1.388
e : N–C	1.374	1.375
f : C–S	1.757	1.745
g : C–S	1.736	1.732
h : C–S	1.628	1.633

Table S5 Selected experimental bond lengths (Å) for **SO-Et**, (pyrene)(**SO-Et**), (perylene)(**SO-Et**), and (coronene)(**SO-Et**).



	SO-Et	(pyrene)(SO-Et)	(perylene)(SO-Et)	(coronene)(SO-Et)
a : C–C	1.369	1.366	1.353	1.367
b : C–C	1.473	1.477	1.459	1.472
c : C–S	1.641	1.633	1.643	1.635
d : C–N	1.371	1.366	1.365	1.371
e : N–C	1.386	1.386	1.391	1.378
f : C–S	1.777	1.766	1.763	1.775
g : C–S	1.749	1.741	1.758	1.746
h : C–O	1.208	1.204	1.208	1.206

Single-crystal transistors

Microscopic images of single-crystal transistors are shown in Fig. S3. Transistor characteristics of (perylene)(SO-Et) are shown in Fig. S4.

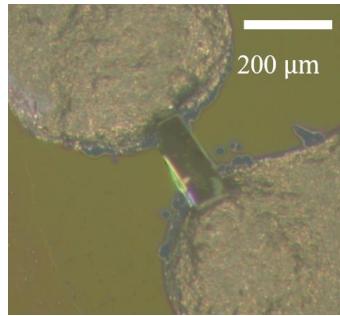


Figure S3. Single-crystal transistor of (coronene)(SS-Et).

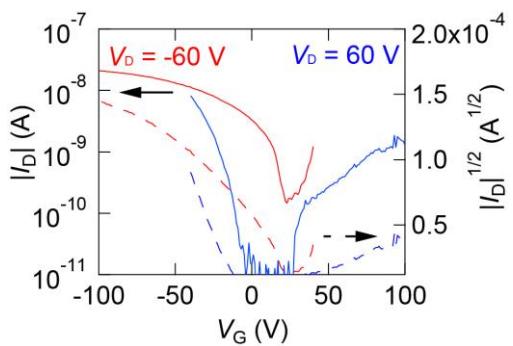


Figure S4. Transfer characteristics of a (perylene)(SO-Et) single-crystal transistor measured under vacuum, where $L/W = 73/23 \mu\text{m}$.

Calculations of transfer integrals

Table S6. Transfers calculated from dimers.

	LUMO+1 (eV)	LUMO (eV)	t_{AA} (meV)	HOMO (eV)	HOMO-1 (eV)	t_{DD} (meV)
(pyrene)(SS-Et)	-4.2602	-4.2790	44.4	-5.6882	-5.7031	109.8
(perylene)(SS-Et)	-4.2820	-4.2834	195.4	-5.3023	-5.3288	82.3
(coronene)(SS-Et)	-4.3176	-4.3191	216.0	-5.6731	-5.6823	117.0
(pyrene)(SS-Pr)	-4.2707	-4.2737	13.1	-5.6925	-5.7076	61.5
(perylene)(SS-Pr)	-4.2780	-4.2811	5.1	-5.3219	-5.3588	56.0
(pyrene)(OS-Et)	-3.7685	-3.7828	3.3	-5.6901	-5.7056	66.4
(perylene)(OS-Et)	-3.7139	-3.7281	3.7	-5.2978	-5.3248	19.1
(perylene)(OS-Pr)	-3.7774	-3.7889	0.9	-5.2685	-5.2941	49.5
(pyrene)(SO-Et)	-3.9421	-3.9528	43.6	-5.6878	-5.7211	45.6
(perylene)(SO-Et)	-3.9675	-3.9920	27.0	-5.3330	-5.3652	54.6
(coronene)(SO-Et)	-3.9286	-3.9428	4.3	-5.7462	-5.7571	11.9

Table S7. Effective transfers calculated by the triad method.

	LUMO+1 (eV)	LUMO (eV)	HOMO (eV)	HOMO-1 (eV)	t_e^{eff} (meV)	t_h^{eff} (meV)
(pyrene)(SS-Et)	-4.2602	-4.2790	-5.6882	-5.7031	9.4	7.5
(perylene)(SS-Et)	-4.2820	-4.2834	-5.3023	-5.3288	0.7	13.3
(coronene)(SS-Et)	-4.3176	-4.3191	-5.6731	-5.6823	0.8	4.6
(pyrene)(SS-Pr)	-4.2707	-4.2737	-5.6925	-5.7076	1.5	7.6
(perylene)(SS-Pr)	-4.2780	-4.2811	-5.3219	-5.3588	1.6	18.5
(pyrene)(OS-Et)	-3.7685	-3.7828	-5.6901	-5.7056	7.2	7.8
(perylene)(OS-Et)	-3.7139	-3.7281	-5.2978	-5.3248	7.1	13.5
(perylene)(OS-Pr)	-3.7774	-3.7889	-5.2685	-5.2941	5.8	12.8
(pyrene)(SO-Et)	-3.9421	-3.9528	-5.6878	-5.7211	5.4	16.7
(perylene)(SO-Et)	-3.9675	-3.9920	-5.3330	-5.3652	12.3	16.1
(coronene)(SO-Et)	-3.9286	-3.9428	-5.7462	-5.7571	7.1	5.4

Table S8. Energy difference, transfers, and contributions to superexchange transfers (meV) in the partition calculations.

(a) (pyrene)(SS-Et)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1216	46	2	L	-1216	46	2
H-1	2084	128	8	H	911	45	-2
H-2	2722	117	-5	H-1	972	31	1
				H-3	1204	45	2
				H-4	1340	55	-2
Total			4				1

(b) (perylene)(SS-Et)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
L+1	-3245	94	-3	L+1	-2708	17	0
H	833	1	0	L	-833	24	-1
H-2	2566	118	5	H	1273	56	2
				H-2	1580	43	-1
Total			2				1

(c) (coronene)(SS-Et)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1193	26	0	L	-1193	1	-1
H-1	1331	45	-2	H-3	1344	13	-1
H-2	2517	102	4	H-4	1590	22	2
H-3	2558	116	5				
Total			8				1

(d) (pyrene)(SS-Pr)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
L	-2357	100	4	L+1	-3130	131	-5
H	1257	202	33	L	-1257	202	33
H-2	2736	117	-5	H	840	82	5
H-3	3165	199	-12	H-4	1510	197	-26
H-4	3860	171	-8				
Total			12				8

(e) (perylene)(SS-Pr)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
L	-1879	54	2	L	-852	69	6
H	852	69	6	H-2	1503	58	2
H-3	2654	119	-5	H-3	1658	55	2
Total			1				8

(f) (pyrene)(OS-Et)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1700	63	-2	L	-1700	63	2
H-1	2565	77	2	H	975	77	-7
H-2	3203	57	-1	H-1	1076	57	1
H-4	4350	112	3	H-3	1993	112	6
Total			2				2

(g) (perylene)(OS-Et)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
L+1	-2706	50	-1	L+1	-3271	70	-2
H	1697	85	4	L	-1697	85	4
H-2	3203	62	1	H	-975	37	-1
H-3	3651	66	-1	H-2	1219	37	1
Total			2				2

(h) (perylene)(**OS-Pr**)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1309	77	5	L+1	-2924	70	-2
H-4	3155	70	-2	L	-1309	77	5
Total			2				2

(i) (pyrene)(**SO-Et**)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1503	35	1	L	-1503	35	1
H-1	2371	91	-3	H-2	1276	58	3
H-2	3010	94	3	H-3	1950	63	2
Total			0				5

(j) (perylene)(**SO-Et**)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1433	124	11	L	-1433	124	11
H-1	2301	73	-2	H-3	1939	75	3
H-3	3388	92	-2				
Total			6				13

(k) (coronene)(**SO-Et**)

Electron				Hole			
A L→	$E_i - E_0$	t	$t^2/(E_i - E_0)$	D H→	$E_i - E_0$	t	$t^2/(E_i - E_0)$
H	1445	105	8	L	-1445	105	8
H-1	1585	56	2	H	1052	94	-8
H-3	2809	115	-5	H-2	1276	59	3
Total			5				2

The observed mobilities taken from Table 3 are roughly correlated with the largest t_{AA} , t_{DD} , or t_e^{eff} taken from Table 4 (Fig. S4).

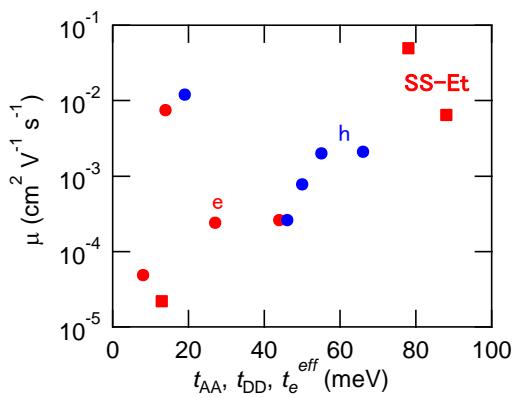


Figure S5. Correlation of observed mobilities and calculated transfers.

References

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