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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 Mo$K\alpha$ radiation (λ = 0.71069 Å). 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.

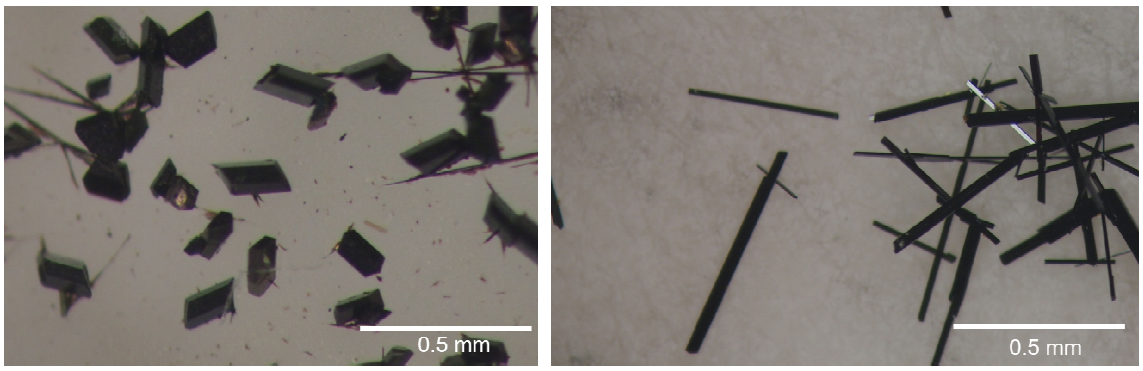
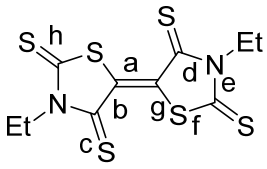


Figure S1. Crystals of (a) (perylene)(**SS-Et**) and (b) (perylene)(**OS-Et**).

By comparing bond lengths with those of neutral **SS-Et** and **SS-Et**$^{-}$ in [Fe(Cp*)$_2$][**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 (Å) for **SS-Et,** (pyrene)(**SS-Et**), (perylene)(**SS-Et**), (coronene)(**SS-Et**), and **SS-Et**$^{\cdot -}$ in [Fe(Cp*)$_2$][**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)

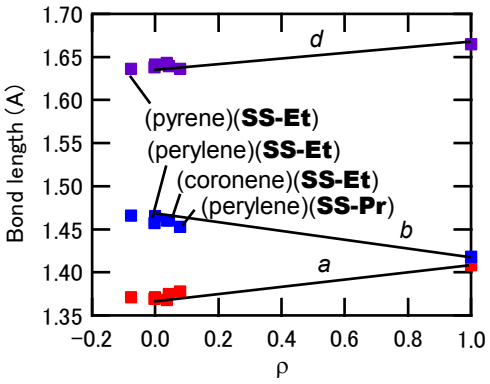
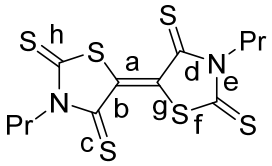


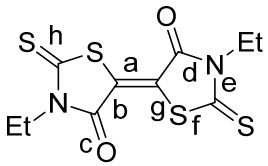
Figure S2. Estimation of charge-transfer degree ρ from the bond lengths.

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



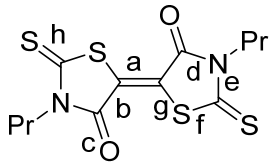
	SS-Pr	(pyrene)(**SS-Pr**)	(perylene)(**SS-Pr**)
a : C–C	1.374	1.375	1.378
b : C–C	1.460	1.460	1.453
c : C–S	1.644	1.641	1.636
d : C–N	1.386	1.379	1.394
e : N–C	1.374	1.365	1.373
f : C–S	1.756	1.748	1.742
g : C–S	1.750	1.744	1.745
h : C–S	1.636	1.639	1.636

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



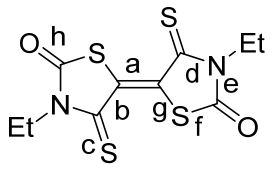
	OS-Et	(pyrene)(**OS-Et**)	(perylene)(**OS-Et**)
a : C–C	1.348	1.344	1.354
b : C–C	1.479	1.485	1.483
c : C–O	1.212	1.202	1.208
d : C–N	1.381	1.381	1.389
e : N–C	1.371	1.374	1.377
f : C–S	1.755	1.741	1.756
g : C–S	1.733	1.737	1.720
h : C–S	1.626	1.630	1.612

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.

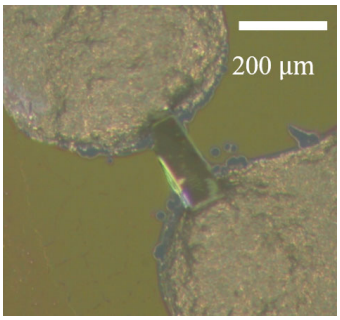


Figure S3. Single-crystal transistor of (coronene)(**SS-Et**).

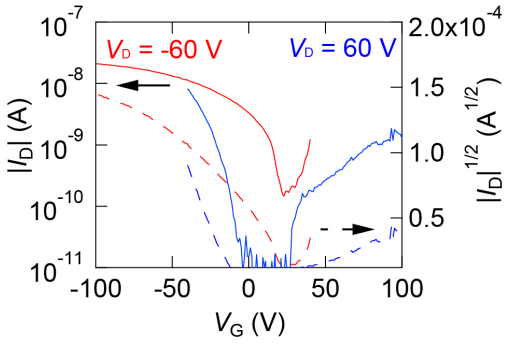


Figure S4. Transfer characteristics of a (perylene)(**SO-Et**) single-crystal transistor measured under vacuum, where L/W = 73/23 µm.

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).

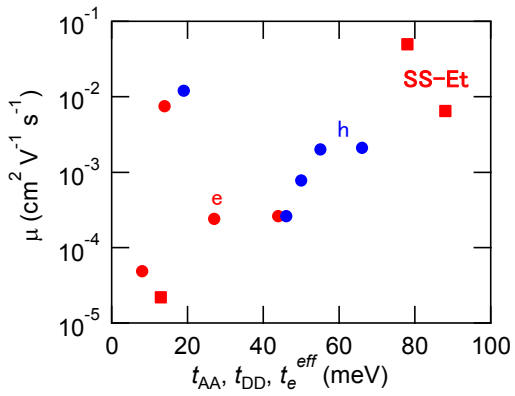


Figure S5. Correlation of observed mobilities and calculated transfers.

References

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