Electronic Supplementary Information

Single Crystal Biphenyl End-Capped Furan-Incorporated Oligomers: Influence of Unusual Packing Structure on Carrier Mobility and Luminescence

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1. Crystal data

Table S1. Crystallographic Data for BPFT and BP2F

	BPFT	BP2F
Empirical Formula	$C_{32}H_{22}OS$	$C_{32}H_{22}O_2$
Formula Weight	454.59	438.52
T / K	100	100
Wavelength / Å	1.54186(Cu Kα)	1.54187(Cu Kα)
Crystal Color, Habit	yellow, platelet	yellow, block
Crystal Dimensions	0.170 X 0.150 X 0.001 mm	1.000 X 0.300 X 0.100 mm
Crystal System	triclinic	monoclinic
Lattice Type	Primitive	Primitive
a / Å	5.7894(2)	5.7294(2)
b / Å	7.6083(4)	7.4822(2)
c / Å	49.676(3)	25.6222(7)
α	87.332(4)	90.000
β	89.233(3)	97.803(2)
γ	89.946(4)	90.000
V / Å	2185.54(19)	1088.21(6)
Space Group	P-1 (#2)	$P2_1/n$ (#14)
Z value	4	2
D_{calc}	1.381 g/cm^3	1.338 g/cm^3
F_{000}	952.00	460.00
Reflection collected	16347	12070
Unique reflections	6134	1958
Refined parameters	613	155
GOF on F^2	1.078	1.088
R1 (I>2.00σ(I))	0.1010	0.0402
wR2 (all data)	0.2954	0.1081

2. Theoretical calculation

2.1. Computational details

Calculations of monomer molecule were performed at the DFT level, by means of the hybrid B3LYP functional as implemented in Gaussian 09W.[1] The 6-31G++(d, p) basis set was used for the all atoms. Geometry optimization, single point, and time-dependent density functional theory (TDDFT) calculations were performed at the same level.

2-2. Full computational details

Cartesian Coordinates and Total Electron Energies

BP2T

SCF Done: E(RB3LYP) = -2029.12215952 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.209467	11.798618	0.000000
2	6	0	-1.335373	10.972325	0.000000
3	6	0	-1.194904	9.584828	0.000000
4	6	0	0.073501	8.969725	0.000000
5	6	0	1.194901	9.823804	0.000000
6	6	0	1.057753	11.211711	0.000000
7	6	0	0.221861	7.485921	0.000000
8	6	0	1.486414	6.862228	0.000000
9	6	0	1.629347	5.480487	0.000000
10	6	0	0.510165	4.624445	0.000000
11	6	0	-0.755188	5.240675	0.000000
12	6	0	-0.892156	6.624321	0.000000
13	6	0	0.670703	3.169807	0.000000
14	6	0	1.834845	2.425214	0.000000
15	6	0	1.626181	1.024530	0.000000
16	6	0	0.292293	0.660786	0.000000
17	16	0	-0.718942	2.094386	0.000000
18	6	0	-0.292289	-0.660785	0.000000
19	6	0	-1.626178	-1.024529	0.000000
20	6	0	-1.834841	-2.425213	0.000000
21	6	0	-0.670700	-3.169807	0.000000
22	16	0	0.718945	-2.094386	0.000000
23	6	0	-0.510162	-4.624445	0.000000
24	6	0	0.755190	-5.240675	0.000000
25	6	0	0.892158	-6.624321	0.000000
26	6	0	-0.221860	-7.485921	0.000000
27	6	0	-1.486412	-6.862227	0.000000
28	6	0	-1.629345	-5.480486	0.000000
29	6	0	-0.073502	-8.969725	0.000000
30	6	0	1.194901	-9.584831	0.000000
31	6	0	1.335366	-10.972329	0.000000
32	6	0	0.209458	-11.798618	0.000000
33	6	0	-1.057760	-11.211708	0.000000

34	6	0	-1.194905	-9.823801	0.000000
35	1	0	-0.317516	12.879080	0.000000
36	1	0	-2.331031	11.406861	0.000000
37	1	0	-2.095787	8.982537	0.000000
38	1	0	2.197340	9.412104	0.000000
39	1	0	1.947573	11.834943	0.000000
40	1	0	2.391472	7.458071	0.000000
41	1	0	2.631130	5.064153	0.000000
42	1	0	-1.655164	4.632521	0.000000
43	1	0	-1.898035	7.027170	0.000000
44	1	0	2.822931	2.869370	0.000000
45	1	0	2.434608	0.301902	0.000000
46	1	0	-2.434604	-0.301902	0.000000
47	1	0	-2.822928	-2.869369	0.000000
48	1	0	1.655166	-4.632522	0.000000
49	1	0	1.898036	-7.027171	0.000000
50	1	0	-2.391471	-7.458070	0.000000
51	1	0	-2.631128	-5.064151	0.000000
52	1	0	2.095786	-8.982543	0.000000
53	1	0	2.331023	-11.406868	0.000000
54	1	0	0.317504	-12.879081	0.000000
55	1	0	-1.947582	-11.834938	0.000000
56	1	0	-2.197342	-9.412098	0.000000

BPFT

SCF Done: E(RB3LYP) = -1706.15195306 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	10.010990	5.519881	0.000000
2	6	0	8.804521	6.223367	0.000000
3	6	0	7.587846	5.541711	0.000000
4	6	0	7.529145	4.133330	0.000000
5	6	0	8.759230	3.445021	0.000000
6	6	0	9.977626	4.123775	0.000000
7	6	0	6.227251	3.406158	0.000000

8	6	0	6.158473	1.997935	0.000000
9	6	0	4.947671	1.316783	0.000000
10	6	0	3.716869	2.002861	0.000000
11	6	0	3.778736	3.408933	0.000000
12	6	0	4.993507	4.085239	0.000000
13	6	0	2.446102	1.277185	0.000000
14	6	0	2.223645	-0.086715	0.000000
15	6	0	0.855203	-0.453198	0.000000
16	6	0	0.000000	0.631974	0.000000
17	16	0	0.906658	2.128541	0.000000
18	6	0	-1.438184	0.633563	0.000000
19	6	0	-2.393405	1.625424	0.000000
20	6	0	-3.657797	0.975801	0.000000
21	6	0	-3.416380	-0.379390	0.000000
22	8	0	-2.058628	-0.589432	0.000000
23	6	0	-4.275194	-1.551092	0.000000
24	6	0	-3.745153	-2.853921	0.000000
25	6	0	-4.579366	-3.966536	0.000000
26	6	0	-5.983547	-3.851151	0.000000
27	6	0	-6.501245	-2.538824	0.000000
28	6	0	-5.676696	-1.421183	0.000000
29	6	0	-6.873332	-5.048254	0.000000
30	6	0	-6.349906	-6.357239	0.000000
31	6	0	-7.180296	-7.477673	0.000000
32	6	0	-8.569072	-7.330596	0.000000
33	6	0	-9.110702	-6.043376	0.000000
34	6	0	-8.277521	-4.924904	0.000000
35	1	0	10.958921	6.049514	0.000000
36	1	0	8.806477	7.309721	0.000000
37	1	0	6.676492	6.128067	0.000000
38	1	0	8.780583	2.361579	0.000000
39	1	0	10.903764	3.555910	0.000000
40	1	0	7.065360	1.404786	0.000000
41	1	0	4.964320	0.232019	0.000000
42	1	0	2.862853	3.992902	0.000000
43	1	0	4.962998	5.168320	0.000000
44	1	0	3.024354	-0.816473	0.000000
45	1	0	0.500095	-1.476292	0.000000

46	1	0	-2.207755	2.690034	0.000000
47	1	0	-4.626958	1.452636	0.000000
48	1	0	-2.669761	-2.992780	0.000000
49	1	0	-4.110303	-4.943273	0.000000
50	1	0	-7.571829	-2.371940	0.000000
51	1	0	-6.129761	-0.434530	0.000000
52	1	0	-5.278371	-6.518658	0.000000
53	1	0	-6.736773	-8.469381	0.000000
54	1	0	-9.216739	-8.202165	0.000000
55	1	0	-10.188227	-5.904936	0.000000
56	1	0	-8.741362	-3.945574	0.000000

BP2F

SCF Done: E(RB3LYP) = -1383.18074423 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.659368	11.157717	0.000000
2	6	0	-1.698276	10.224402	0.000000
3	6	0	-1.421827	8.857443	0.000000
4	6	0	-0.099175	8.369921	0.000000
5	6	0	0.932511	9.330529	0.000000
6	6	0	0.659369	10.698298	0.000000
7	6	0	0.193835	6.907362	0.000000
8	6	0	1.514915	6.412719	0.000000
9	6	0	1.792470	5.051752	0.000000
10	6	0	0.757203	4.098113	0.000000
11	6	0	-0.565068	4.577196	0.000000
12	6	0	-0.832344	5.941965	0.000000
13	6	0	1.051476	2.675461	0.000000
14	6	0	2.218072	1.944732	0.000000
15	6	0	1.853797	0.569602	0.000000
16	6	0	0.478955	0.533137	0.000000
17	6	0	-0.478955	-0.533137	0.000000
18	6	0	-1.853797	-0.569602	0.000000
19	6	0	-2.218072	-1.944732	0.000000

20	6	0	-1.051476	-2.675462	0.000000
21	8	0	0.016515	-1.809162	0.000000
22	6	0	-0.757203	-4.098113	0.000000
23	6	0	0.565068	-4.577196	0.000000
24	6	0	0.832343	-5.941965	0.000000
25	6	0	-0.193835	-6.907362	0.000000
26	6	0	-1.514915	-6.412719	0.000000
27	6	0	-1.792470	-5.051752	0.000000
28	6	0	0.099175	-8.369921	0.000000
29	6	0	1.421827	-8.857443	0.000000
30	6	0	1.698277	-10.224401	0.000000
31	6	0	0.659369	-11.157716	0.000000
32	6	0	-0.659368	-10.698298	0.000000
33	6	0	-0.932511	-9.330529	0.000000
34	1	0	-0.873251	12.222305	0.000000
35	1	0	-2.731947	10.558684	0.000000
36	1	0	-2.259109	8.169532	0.000000
37	1	0	1.970714	9.019911	0.000000
38	1	0	1.483651	11.405976	0.000000
39	1	0	2.356005	7.095830	0.000000
40	1	0	2.828553	4.727195	0.000000
41	1	0	-1.388667	3.871876	0.000000
42	1	0	-1.871952	6.247448	0.000000
43	1	0	3.221643	2.344523	0.000000
44	1	0	2.510561	-0.287428	0.000000
45	1	0	-2.510561	0.287428	0.000000
46	1	0	-3.221644	-2.344522	0.000000
47	1	0	1.388667	-3.871876	0.000000
48	1	0	1.871952	-6.247448	0.000000
49	1	0	-2.356005	-7.095830	0.000000
50	1	0	-2.828553	-4.727194	0.000000
51	1	0	2.259109	-8.169531	0.000000
52	1	0	2.731947	-10.558683	0.000000
53	1	0	0.873252	-12.222305	0.000000
54	1	0	-1.483651	-11.405976	0.000000
55	1	0	-1.970714	-9.019912	0.000000
56	8	0	-0.016515	1.809162	0.000000

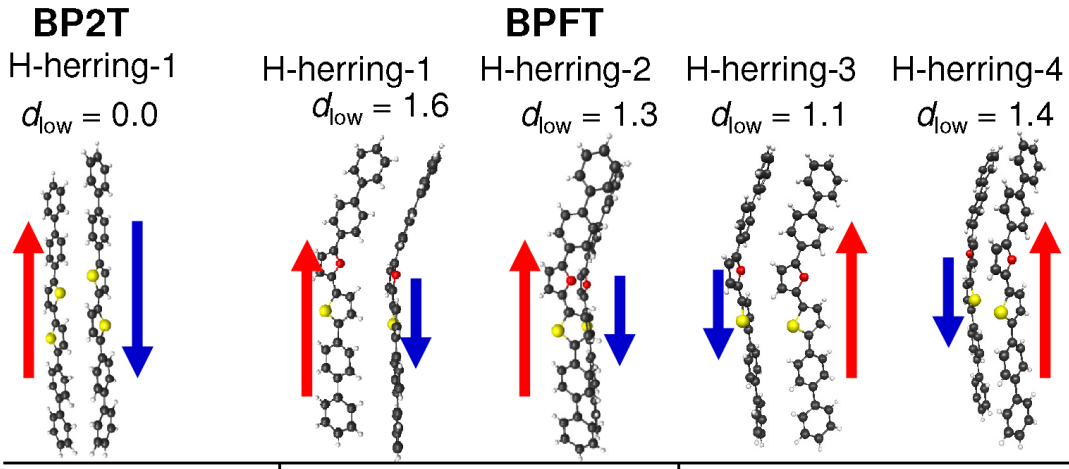
2.3. TDDFT results

Table S2. Summarized excitation state both lower singlet and triplet.

	S_1 / eV	T_1 / eV	$2T_1 - S_1$ / eV
BP2T	2.63	1.66	0.70
BPFT	2.69	1.74	0.79
BP2F	2.77	1.85	0.93

2.4. Calculation for the exciton coupling and the transition dipole moment of the aggregates of BP2T and BPFT.

Table S3. Summarized the exciton coupling (h_{ij}), and the transition dipole moment (d)[a]



	BP2T			BPFT		
	h_{ij} (eV)	d_{low}	d_{high} (a.u.)	h_{ij} (eV)	d_{low}	d_{high} (a.u.)
H-herring-1	0.091	0.0	6.4	0.091	1.6	5.9
H-herring-2	0.091	0.0	6.4	0.095	1.3	6.0
H-herring-3	0.091	0.0	6.4	0.096	1.1	6.0
H-herring-4	0.091	0.0	6.4	0.098	1.4	6.0
H-parallel	0.070	0.0	6.4	0.069	0.0	6.1
H-bent		—		0.067	0.0	6.1
J-herring	0.019	7.0	0.0	0.018	5.5	3.7
J-parallel-1	0.020	7.0	0.3	~0.022	~6.7	~0.1
J-parallel-2	0.014	6.9	0.3	~0.012	~6.5	~0.6

[a] Exciton coupling (hij) for the H- and J-aggregates in the BP2T and BPFT crystals, together with transition dipole moments of the lower and higher exciton states (dlow and dhigh), where the

LC-BLYP functional is used. Schematic illustrations of the transition dipoles of the H-aggregates are shown, where the red and blue arrows indicate the single molecule transition dipoles.

2.5. Calculated excitation energy and transition dipole moment of the BP2T and BPFT single molecules.

Table S4. Calculated excitation energy (and transition dipole moment

	BP2T	BPFT flat	BPFT bent
$\Delta E_{absorption}$ [eV (nm)]	2.883 (430)	2.930 (423)	2.983 (415)
d [a.u]	5.33	5.04	4.92

2.6. Reorganization energy

The reorganization energies (λ) were calculated by following equation;

$$\lambda = \lambda_1 + \lambda_2 = (E_{\pm}^{*} - E_{\pm}) + (E^{*} - E)$$

where E and $E_{\pm}$ represent the energies of neutral and cationic/anionic species in their lowest-energy geometry, respectively, and E^{*} and $E_{\pm}^{*}$ are the energies of the neutral and cationic/anionic species with geometry of the cationic/anionic and neutral species, respectively.

Table S5. Summarized reorganization energy

	λ_h / meV	λ_e / meV
BP2T	215	205
BPFT	219	207
BP2F	213	204

2.7. Charge transfer integrals

Table S6. Summarized charge transfer integrals (t)

Direction[a]	BP2T		BPFT		BP2F	
	t_h (meV)	t_e (meV)	t_h (meV)	t_e (meV)	t_h (meV)	t_e (meV)
d1	45.0	74.8	24.4	94.9	27.0	23.5
d2	14.4	55.9	6.0	65.5	38.8	40.9
d3	12.8	127.4	37.5	92.5	59.4	66.7
d4	-	-	40.5	71.3	-	-
d5	-	-	1.4	43.4	-	-
d6	-	-	37.1	94.1	-	-

[a] Directions are shown in Figure 2.

3. Thin film FETs (TFTs) Device fabrication and characterization

3.1. Device fabrication

A highly doped silicon wafer with a 200 nm thermally grown SiO_2 layer was covered with a 60 nm thick film of PMMA by spin coating using toluene as a solvent. The resulting films were annealed at 90 °C 50 h in the glove box under an Ar atmosphere. These substrates used for the thin film deposition. Thin film transistors were made by evaporating the highly pure molecules under the high vacuum (10^{-6} Torr) with a thickness of 45 nm, as measured in situ by a quartz crystal microbalance. The thin film deposition rate maintained at 0.2 Å/sec. The top contact symmetric electrodes were realized by thermal evaporating gold metal through a shadow mask on top of the thin film. The electrical characterization of thin film transistors were analyzed similar to the single crystal devices.

3.2. Device performance of TFTs

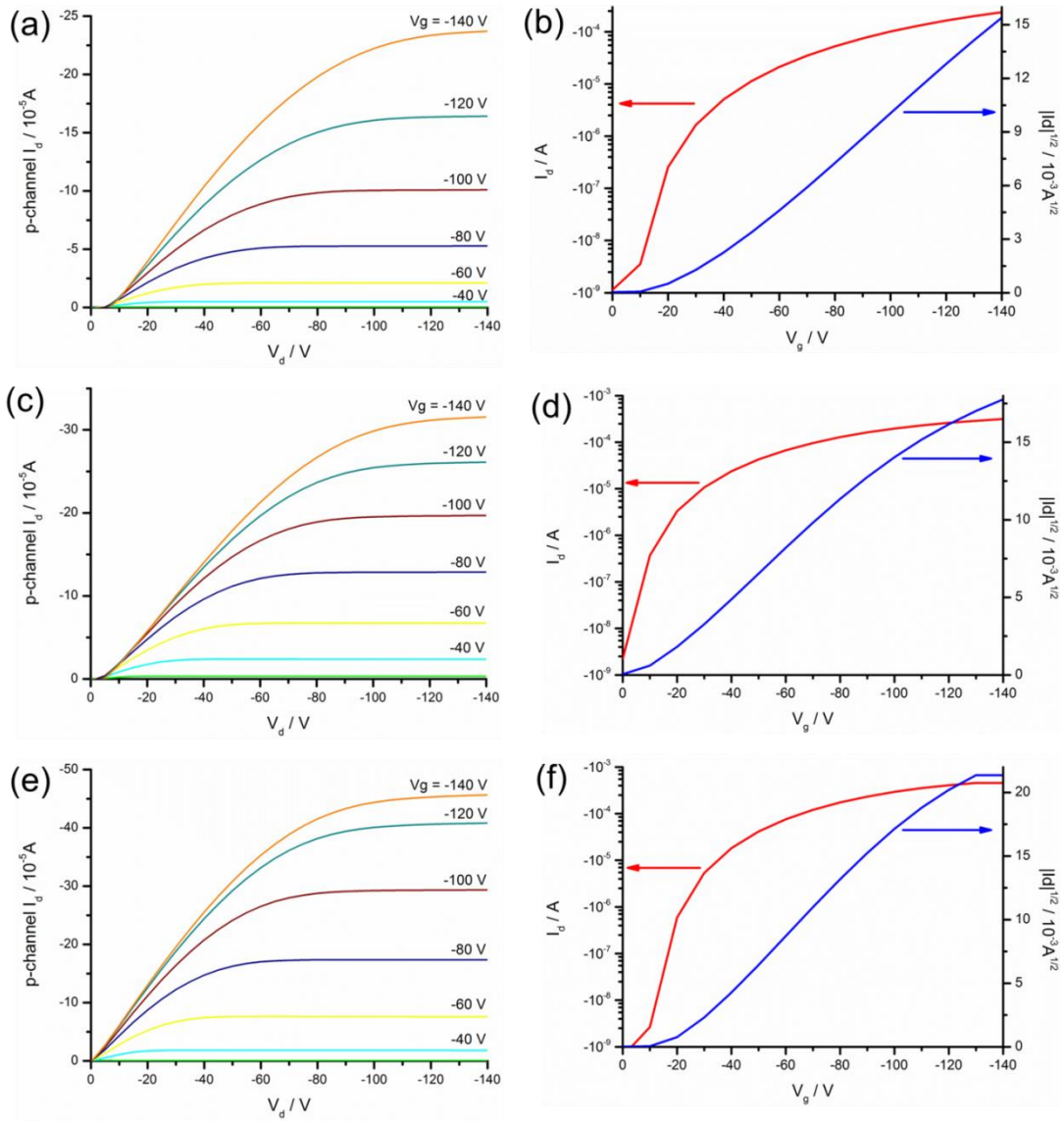


Figure S1. TFT characteristics for I_d-V_d and I_d-V_g graph, BP2T (a and b), BPFT (c and d) and BP2F (e and f). All I_d-V_g characteristics were measured under V_d = -140V.

Table S7. TFT performances

	μ_h	I_{on}/I_{off} ($\times 10^5$)	V_{th} (V)
BP2T	0.023	2.1	-26
BPFT	0.031	1.4	-10
BP2F	0.047	7.3	-21

4. Device performance of SC-FETs of BP2T and BPFT

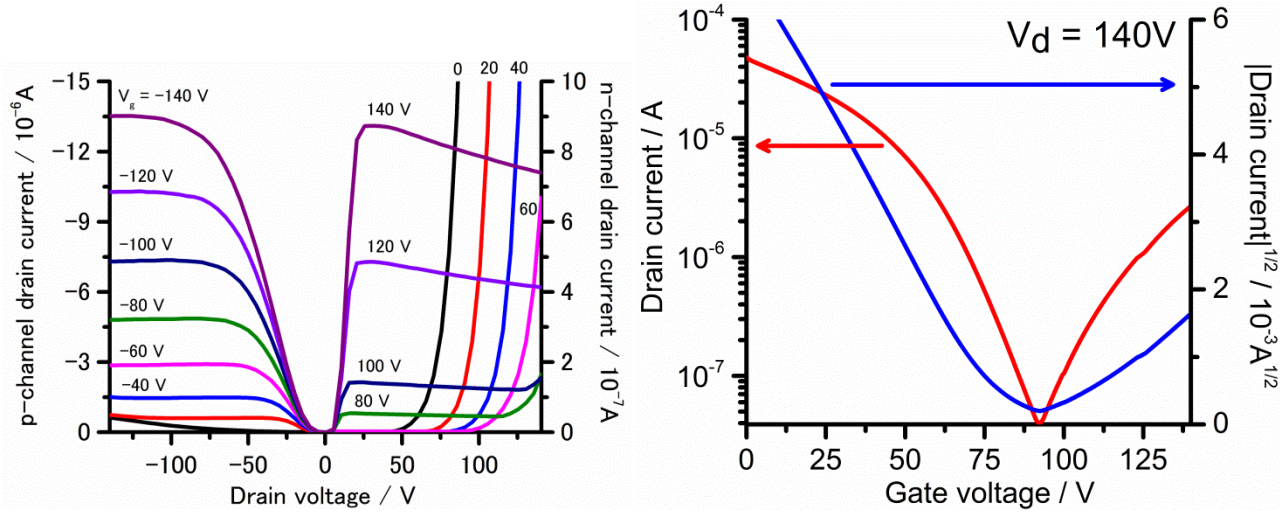


Figure S2. SC-FET characteristics of **BP2T**.

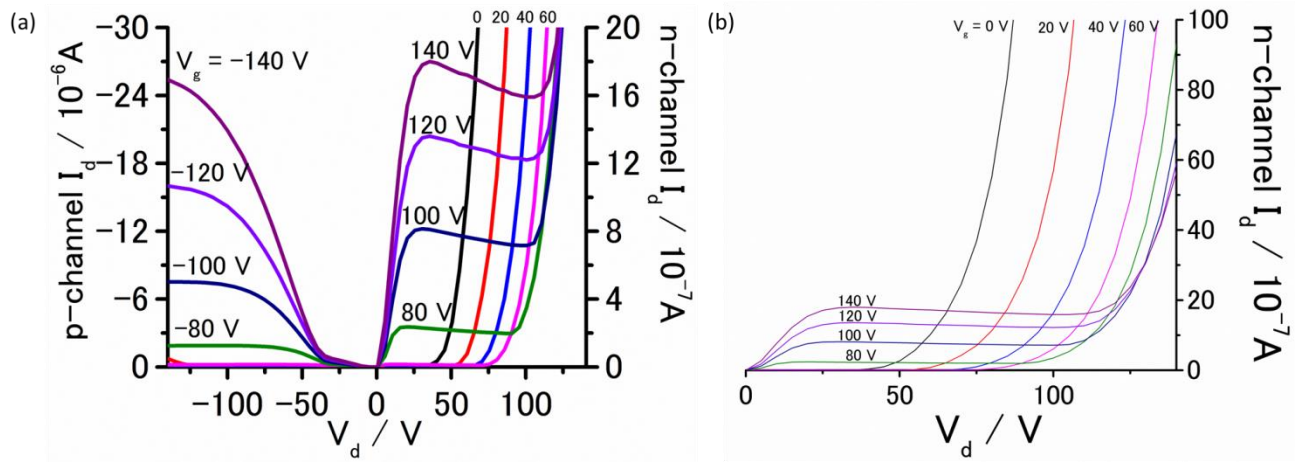


Figure S3. (a) Output characteristic of **BPFT**. (b) Magnified I_d-V_d characteristic of n-channel drain current of **BPFT**.

References

[1] Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.;

Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J., Gaussian, Inc., Wallingford CT, 2010.