Journal: *New Journal of Chemistry*

Electronic Supplementary Information

Fusion thienyl into backbone of electron acceptor in organic photovoltaic heterojunctions: a comparative study of BTPT-4F and BTPTT-4F

Rui-Rong Bai [1], Cai-Rong Zhang [1*], You-Zhi Wu [2], Mei-Ling Zhang [1], Yu-Hong Chen [1], Zi-Jiang Liu [3], Hong-Shan Chen [4]

[1] Department of Applied Physics, Lanzhou University of Technology, Lanzhou, Gansu 730050, China;

[2] School of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou, Gansu 730050, China;

[3] Department of Physics, Lanzhou City University, Lanzhou, Gansu 730070, China

[4] College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou, Gansu 730070, China

[*]Corresponding author: Cai-Rong Zhang;

E-mail address: zhcrxy@lut.edu.cn (C.R. Zhang).

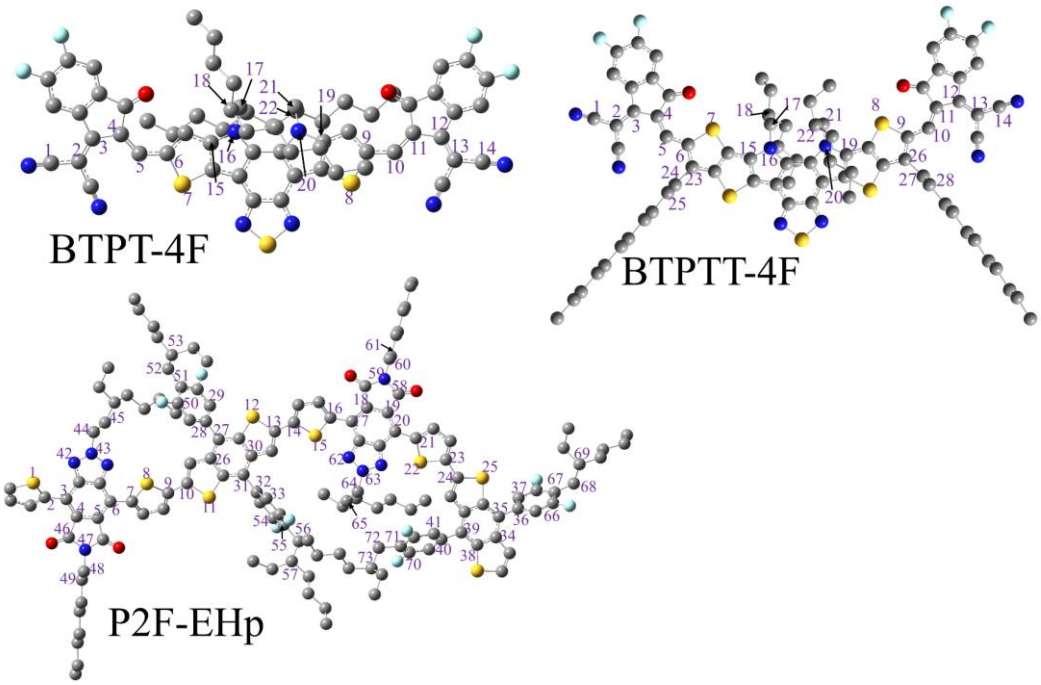


Figure S1. The optimized molecular structures of BTPT-4, BTPTT-4F and P2F-EHp in solid phase (ωB97XD/CEP-121G*). The atomic serial numbers are also labeled in order to give geometrical parameters and the hydrogen atoms are omitted for clarity.

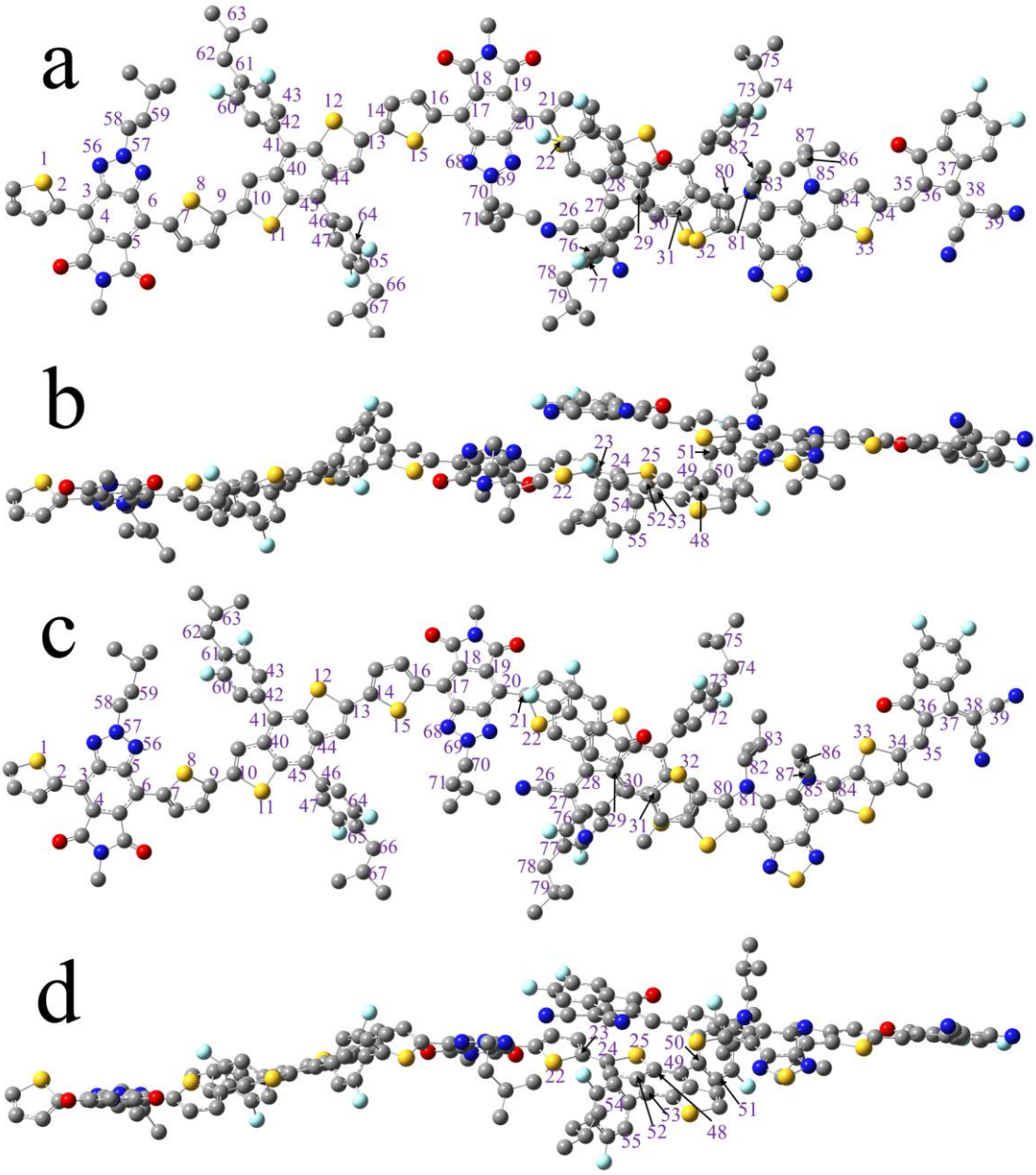
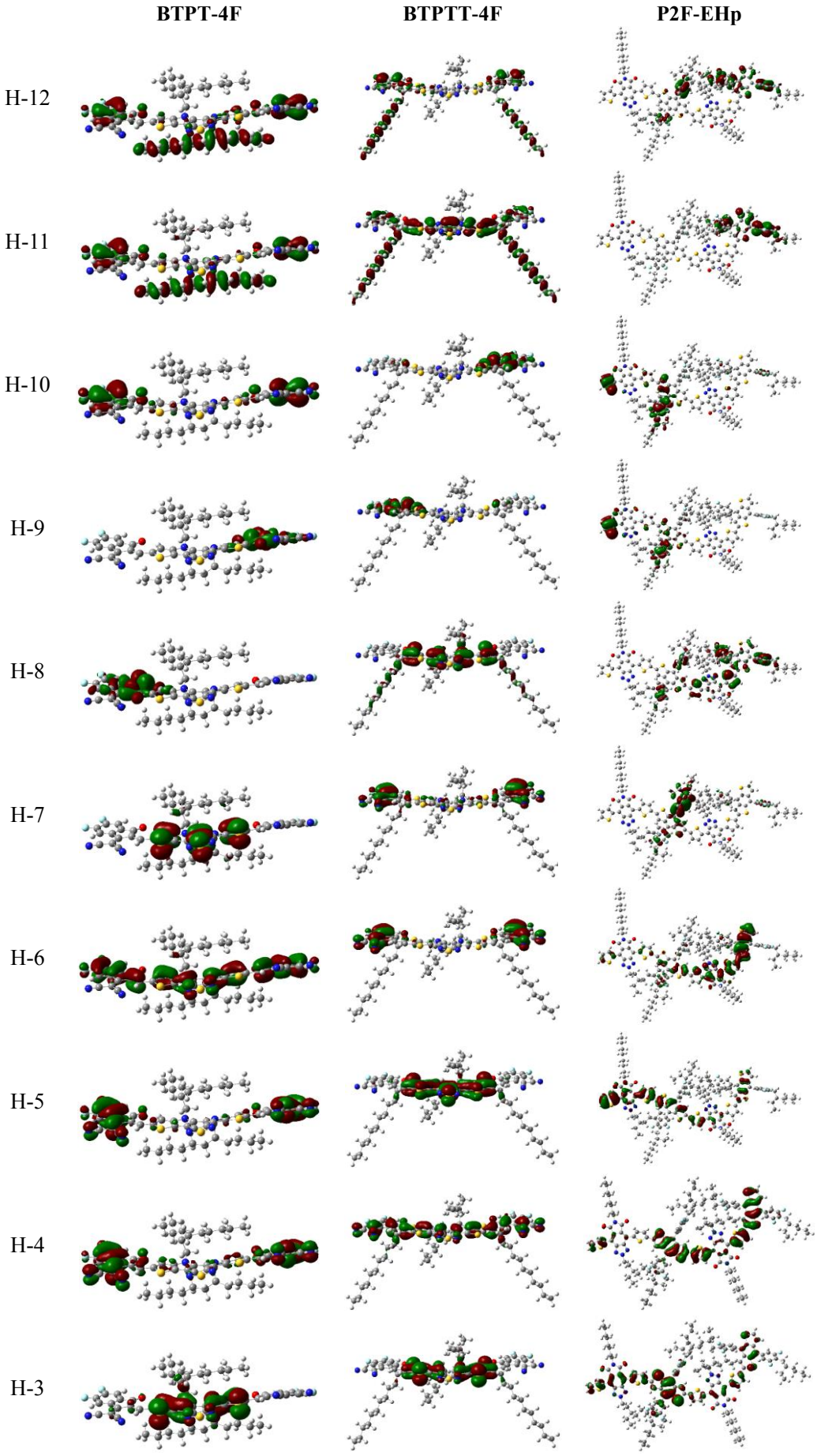


Figure S2. The optimized structures of P2F-EHp/BTPT-4F (top view (a) and side view (b)) and P2F-EHp/BTPTT-4F complexes (top view (c) and side view (d)) in solid phase (ωB97XD/CEP-121G*). The atomic serial numbers are also labeled in order to give geometrical parameters and the hydrogen atoms are omitted for clarity.


BTPT-4F
BTPTT-4F
P2F-EHp
H-12
H-11
H-10
H-9
H-8
H-7
H-6
H-5
H-4
H-3

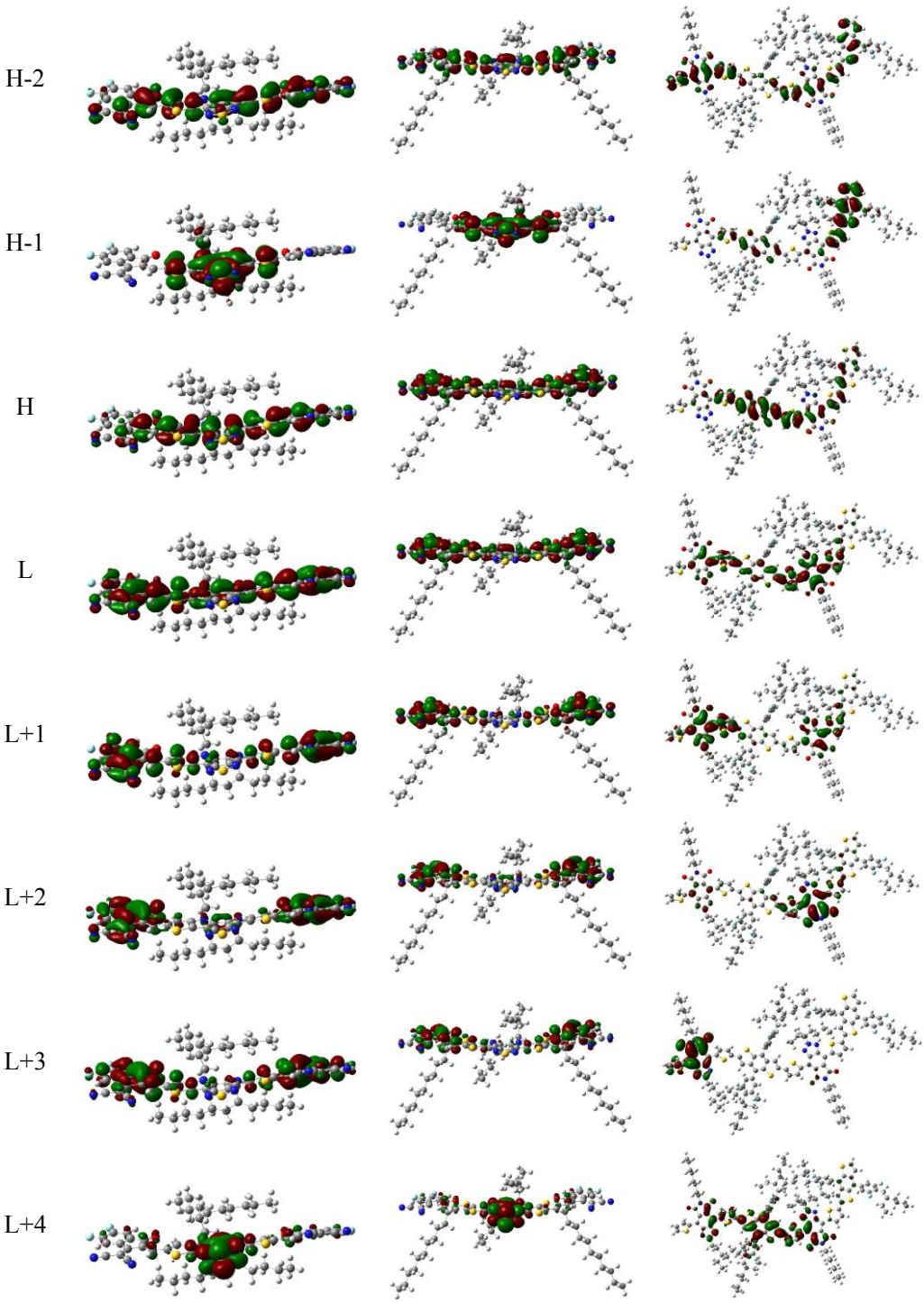


Figure S3. The selected frontier molecular orbitals for the BTPT-4F, BTPTT-4F, and P2F-EHp (H = HOMO, L = LUMO, ωB97XD/CEP-121G*, ω=0.002 $Bohr^{-1}$)

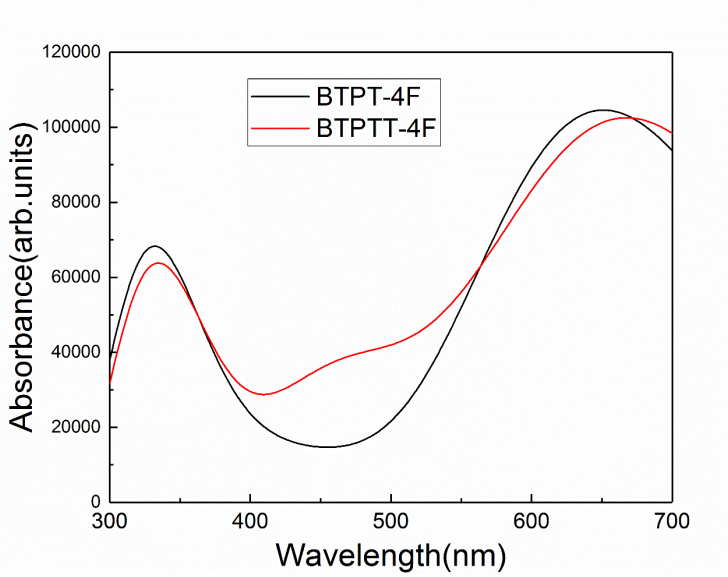


Figure S4. The Simulated absorption spectra of the electron acceptors (BTPT-4F and BTPTT-4F).

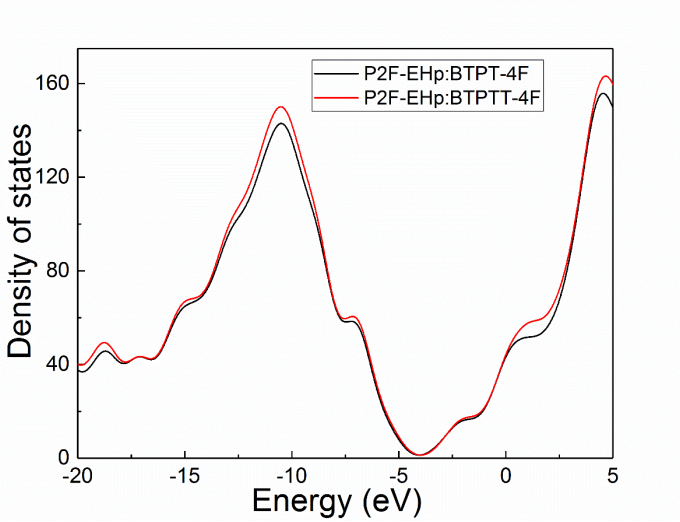


Figure S5. The density of states (DOS) of P2F-EHp/BTPT-4F and P2F-EHp/BTPTT-4F complexes, where the full width at half maximum is 0.05 a.u. .

Table S1. The selected bond length (in Å), bond angles and dihedral angles (in°) for the optimized monomers of P2F-EHp, BTPT-4F and BTPTT-4F in solid phase (ωB97XD/CEP-121G*).

Definition	Values	Definition	Values	Definition	Values
BTPT-4F					
2-3	1.377	2-3-4	128.6	1-2-3-4	179.9
4-5	1.381	3-4-5	124.8	2-3-4-5	-7.8
5-6	1.431	4-5-6	132.9	3-4-5-6	178.6
6-7	1.789	5-6-7	115.4	4-5-6-7	179.3
8-9	1.793	8-9-10	115.0	8-9-10-11	177.3
9-10	1.432	9-10-11	133.0	9-10-11-12	-177.8
10-11	1.379	10-11-12	124.8	10-11-12-13	-0.3
12-13	1.377	12-13-14	123.5	11-12-13-14	-179.5
16-17	1.480	15-16-17	119.3	15-16-17-18	56.7
20-21	1.487	18-19-20	119.7	19-20-21-22	76.8
BTPTT-4F					
2-3	1.379	2-3-4	128.7	1-2-3-4	179.8
4-5	1.383	3-4-5	126.1	2-3-4-5	-0.8
5-6	1.425	4-5-6	134.5	3-4-5-6	-179.3
6-7	1.784	5-6-7	127.4	4-5-6-7	-0.2
8-9	1.786	8-9-10	127.6	8-9-10-11	-1.2
9-10	1.425	9-10-11	134.5	9-10-11-12	179.2
10-11	1.382	10-11-12	126.0	10-11-12-13	-0.4
12-13	1.379	12-13-14	123.6	11-12-13-14	-179.6
16-17	1.472	15-16-17	118.3	15-16-17-18	-77.9
20-21	1.475	19-20-21	119.3	19-20-21-22	-101.3
23-24	1.511	6-23-24	126.3	6-23-24-25	-82.2
26-27	1.510	9-26-27	126.3	9-26-27-28	81.2
P2F-EHp					
2-3	1.477	2-3-4	125.6	1-2-3-4	133.1
6-7	1.475	6-7-8	120.9	5-6-7-8	-149.6
9-10	1.467	9-10-11	120.6	8-9-10-11	143.2
13-14	1.465	13-14-15	118.2	12-13-14-15	-162.4
16-17	1.476	16-17-18	127.6	15-16-17-18	139.4
20-21	1.476	20-21-22	118.2	19-20-21-22	-147.2
23-24	1.468	23-24-25	124.3	22-23-24-25	148.1
27-28	1.494	26-27-28	121.1	26-27-28-29	57.6
31-32	1.495	30-31-32	120.1	30-31-32-33	64.5
35-36	1.495	34-35-36	121.6	34-35-36-37	116.1
39-40	1.496	38-39-40	125.0	38-39-40-41	121.6
43-44	1.479	42-43-44	122.6	42-43-44-45	-126.0
47-48	1.467	46-47-48	123.8	46-47-48-49	88.9
51-52	1.513	50-51-52	122.1	50-51-52-53	74.5
55-56	1.513	54-55-56	123.5	54-55-56-57	-105.9
59-60	1.467	58-59-60	123.3	58-59-60-61	86.5
63-64	1.477	62-63-64	121.5	62-63-64-65	63.1
67-68	1.515	66-67-68	122.4	66-67-68-69	-76.6
71-72	1.514	70-71-72	123.0	70-71-72-73	82.3

Table S2. The selected bond length (in Å), bond angles and dihedral angles (in°) for the optimized complexes of P2F-EHp/BTPT-4F and P2F-EHp/BTPTT-4F in solid phase (ωB97XD/CEP-121G*).

Definition	Values	Definition	Values	Definition	Values
P2F-EHp/BTPT-4F					
2-3	1.477	2-3-4	125.7	1-2-3-4	132.9
6-7	1.475	6-7-8	120.5	5-6-7-8	-149.6
9-10	1.467	9-10-11	121.4	8-9-10-11	144.4
13-14	1.468	13-14-15	120.3	12-13-14-15	-141.1
16-17	1.474	16-17-18	125.8	15-16-17-18	140.9
20-21	1.474	20-21-22	120.1	19-20-21-22	-143.7
23-24	1.464	23-24-25	120.7	22-23-24-25	175.5
27-28	1.378	26-27-28	123.4	26-27-28-29	-177.7
29-30	1.381	28-29-30	124.6	27-28-29-30	15.0
30-31	1.430	29-30-31	132.4	28-29-30-31	179.8
31-32	1.788	30-31-32	115.8	29-30-31-32	-172.8
33-34	1.790	33-34-35	115.3	33-34-35-36	170.4
34-35	1.433	34-35-36	132.4	34-35-36-37	179.4
35-36	1.378	35-36-37	124.5	35-36-37-37	-15.5
37-38	1.376	36-37-38	127.9	36-37-38-39	179.5
41-42	1.495	40-41-42	120.4	40-41-42-43	-115.9
45-46	1.495	44-45-46	121.4	44-45-46-47	-116.1
49-50	1.494	48-49-50	121.6	48-49-50-51	-125.6
53-54	1.494	52-53-54	120.3	52-53-54-55	116.0
57-58	1.478	56-57-58	121.8	56-57-58-59	-121.0
61-62	1.514	60-61-62	122.2	60-61-62-63	79.9
65-66	1.515	64-65-66	122.3	64-65-66-67	77.3
69-70	1.476	68-69-70	121.1	68-69-70-71	81.4
73-74	1.515	72-73-74	123.8	72-73-74-75	102.7
77-78	1.514	76-77-78	123.4	76-77-78-79	-99.0
81-82	1.483	80-81-82	120.3	80-81-82-83	51.3
85-86	1.485	84-85-86	120.6	84-85-86-87	66.1
P2F-EHp/BTPTT-4F					
2-3	1.479	2-3-4	125.9	1-2-3-4	-130.2
6-7	1.475	6-7-8	120.7	5-6-7-8	31.5
9-10	1.467	9-10-11	121.6	8-9-10-11	145.5
13-14	1.464	13-14-15	119.8	12-13-14-15	-170.8
16-17	1.475	16-17-18	126.4	15-16-17-18	135.6
20-21	1.474	20-21-22	120.8	19-20-21-22	-137.5
23-24	1.463	23-24-25	119.6	22-23-24-25	177.1
27-28	1.380	26-27-28	123.5	26-27-28-29	179.8
29-30	1.381	28-29-30	125.4	27-28-29-30	13.5
30-31	1.421	29-30-31	134.8	28-29-30-31	-177.3
31-32	1.780	30-31-32	127.8	29-30-31-32	7.2
33-34	1.784	33-34-35	127.8	33-34-35-36	0.4
34-35	1.424	34-35-36	134.5	34-35-36-37	-178.8
35-36	1.382	35-36-37	126.1	35-36-37-38	-0.2
37-38	1.379	36-37-38	128.7	36-37-38-39	179.3
41-42	1.495	40-41-42	120.5	40-41-42-43	-118.0
45-46	1.495	44-45-46	120.5	44-45-46-47	-117.3
49-50	1.493	48-49-50	121.0	48-49-50-51	-119.6
53-54	1.493	52-53-54	120.5	52-53-54-55	-97.9
57-58	1.477	56-57-58	121.1	56-57-58-59	61.3
61-62	1.514	60-61-62	122.1	60-61-62-63	77.3
65-66	1.515	64-65-66	122.1	64-65-66-67	78.8
69-70	1.477	68-69-70	120.6	68-69-70-71	67.3
73-74	1.514	72-73-74	124.0	72-73-74-75	99.0
77-78	1.514	76-77-78	123.3	76-77-78-79	-97.9
81-82	1.478	80-81-82	120.4	80-81-82-83	-117.5
85-86	1.474	84-85-86	119.3	84-85-86-87	-66.7

Table S3. The components of the electric dipole moment (Debye) and quadrupole moment (Debye-Ang) of BTPT-4F and BTPTT-4F molecules.

	Dipole moment			Quadrupole moment					
	X	Y	Z	XX	YY	ZZ	XY	XZ	YZ
BTPT-4F	-0.0349	12.1684	1.4482	-723.7970	-532.3592	-472.0758	6.0897	-29.3682	-2.7674
BTPTT-4F	0.0954	-2.1116	-0.9502	-907.7403	-637.5367	-620.4592	3.7497	-0.1615	-14.6708

Table S4. The selected excitation energies, excitation wavelengths, oscillator strengths (f), and the corresponding main transition configurations for singlet excited states of BTPT-4F and BTPTT-4F molecules in solid phase with a separation parameter of ω=0.002. (H=HOMO, L=LUMO).

States	Main Transition configurations	E(eV/nm)	f
	BTPT-4F		
S1	H→L(97.56%)	1.9008/652.28	2.5671
S2	H→L+1(91.18%)	2.3471/528.24	0.0034
S3	H-1→L(91.74%)	2.3907/518.60	0.0370
S4	H→L+2(93.93%)	2.5766/481.20	0.0738
S5	H-1→L+1(71.66%);H-3→L(21.86%)	2.7069/458.02	0.0058
S6	H→L+3(91.02%)	2.7305/454.07	0.0910
S7	H-2→L(91.23%)	2.8677/432.35	0.0402
S8	H-3→L(73.19%);H-1→L+1(21.10%)	2.8910/428.86	0.0605
S9	H→L+4(94.73%)	3.0696/403.91	0.0252
S10	H-1→L+2(91.81%)	3.1338/395.63	0.0113
S11	H-1→L+3(86.57%)	3.2189/385.18	0.0009
S12	H-3→L+1(62.65%);H-2→L+1(25.46%)	3.2406/382.60	0.0241
S13	H-2→L+1(64.00%);H-3→L+1(25.65%)	3.2635/379.91	0.1283
S14	H-4→L(82.98%)	3.3846/366.32	0.0111
S15	H-5→L(64.00%);H-2→L+2(18.06%)	3.4062/364.00	0.1667
S16	H-8→L(46.19%);H-8→L+3(25.95%);H-8→L+2(20.62%)	3.4870/355.56	0.0023
S17	H-9→L(45.85%);H-9→L+3(24.69%);H-9→L+2(19.84%)	3.4995/354.29	0.0048
S18	H-2→L+2(65.66%);H-5→L(21.15%)	3.5504/349.22	0.3750
S19	H-3→L+2(63.21%);H-2→L+3(19.14%)	3.6108/343.37	0.0499
S20	H-1→L+4(84.10%)	3.6182/342.67	0.1481
S21	H-8→L+1(14.42%);H-6→L(13.92%);H-8→L+2(13.13%); H-8→L(12.05%)	3.6400/340.62	0.0009
S22	H-8→L(13.57%);H-9→L+1(12.78%);H-8→ L+1(12.68%);H-8→L+2(12.61%);H-9→ L+2(11.59%);H-9→L(10.01%)	3.6477/339.90	0.0003
S23	H-2→L+3(19.94%);H-6→L(12.92%);H-3→L+2(12.68%); H-9→L(12.32%);H-9→L+1(10.31%)	3.6652/338.27	0.0006
S24	H-3→L+3(48.60%);H-7→L(29.50%)	3.7082/334.35	0.0084
S25	H-6→L(46.76%);H-2→L+3(21.34%)	3.7216/333.14	0.0959
S26	H-7→L(58.44%);H-3→L+3(30.67%)	3.7581/329.92	0.0007
S27	H-4→L+1(52.52%);H-5→L+2(19.43%)	3.8121/325.24	0.7055
S28	H-5→L+1(36.52%);H-4→L+2(25.39%); H-5→L+3(10.33%);H-2→L+3(10.11%)	3.8332/323.45	0.0373
S29	H-10→L(35.62%);H-4→L+1(29.47%)	3.9154/316.66	0.0025
S30	H-5→L+1(33.79%);195→L(22.96%);194→L(10.06%)	3.9525/313.68	0.0267
S31	H-5→L+2(24.68%);H-6→L+1(23.62%); H-10→L(21.75%);H-4→L+3(13.83%)	3.9909/310.66	0.0759
S32	H-3→L+4(77.74%)	3.9982/310.10	0.0395

S33	H-11→L(58.07%);H-4→L+2(14.27%)	4.0312/307.56	0.0680
S34	H-12→L(64.27%);H-4→L+2(13.56%)	4.0500/306.13	0.1042
S35	H-2→L+4(75.48%)	4.0810/303.81	0.0179
S36	H-7→L+1(79.92%)	4.1092/301.72	0.0483
S37	H-6→L+1(51.91%);196→L(12.24%);H-2→L+4(11.91%)	4.1223/300.76	0.0267
S38	H→L+5(75.56%)	4.1274/300.39	0.0285
S39	H-13→L(92.61%)	4.1744/297.01	0.0019
S40	H→L+6(72.27%)	4.2855/289.31	0.0050
	BTPTT-4F		
S1	H→L(96.53%)	1.8309/677.19	2.3682
S2	H→L+1(97.32%)	2.1533/575.78	0.2483
S3	H→L+2(93.69%)	2.4581/504.39	0.1001
S4	H-1→L(93.60%)	2.4659/502.80	0.0165
S5	H→L+3(92.40%)	2.5600/484.32	0.1743
S6	H-1→L+1(57.77%);H-3→L(37.49%)	2.6145/474.23	0.0926
S7	H-2→L(92.06%)	2.6495/467.95	0.3567
S8	H-3→L(48.39%);H-1→L+1(35.29%)	2.8164/440.23	0.0286
S9	H→L+4(81.34%)	2.8473/435.44	0.0236
S10	H-2→L+1(75.51%);H→L+4(12.26%)	2.8963/428.08	0.1259
S11	H-3→L+1(87.86%)	2.9737/416.93	0.0074
S12	H-1→L+2(87.35%)	3.1362/395.33	0.0002
S13	H-1→L+3(81.00%);H-3→L+2(12.76%)	3.1829/389.53	0.0536
S14	H-2→L+2(82.31%)	3.2247/384.48	0.0610
S15	H-2→L+3(56.74%);H-4→L(25.98%)	3.3024/375.44	0.0247
S16	H-4→L(66.81%);H-2→L+3(24.08%)	3.3345/371.82	0.0048
S17	H-5→L(86.69%)	3.3597/369.04	0.0040
S18	H-3→L+2(73.63%);H-1→L+3(13.62%)	3.4411/360.30	0.0004
S19	H-3→L+3(45.21%);H-1→L+4(40.38%)	3.4701/357.29	0.0663
S20	H-6→L(50.73%);H-4→L+1(20.30%);H-1→L+4(13.11%)	3.5188/352.35	0.6086
S21	H-5→L+1(58.11%);H-8→L(17.49%)	3.5326/350.97	0.0585
S22	H-1→L+4(33.20%);H-3→L+3(32.66%);H-4→L+1(15.91%)	3.5390/350.33	0.0108
S23	H-7→L(58.78%);H-6→L+1(15.08%)	3.5726/347.04	0.0195
S24	H-9→L+3(37.38%);H-9→L+2(35.24%);H-9→L(10.79%)	3.5768/346.63	0.0009
S25	H-10→L+3(40.74%);H-10→L+2(39.22%);H-10→L(10.95%)	3.5795/346.37	0.0004
S26	H-4→L+1(52.17%);H-6→L(17.93%)	3.5855/345.79	0.0629
S27	H-9→L(52.94%);H-9→L+1(34.28%)	3.6268/341.85	0.0002
S28	H-10→L(53.62%);H-10→L+1(34.97%)	3.6284/341.70	0.0001
S29	H-3→L+4(82.24%)	3.7199/333.30	0.0404
S30	H-2→L+4(88.89%)	3.7456/331.01	0.0256
S31	H-8→L(49.67%);H→L+5(29.67%);H-5→L+1(11.23%)	3.7886/327.26	0.0156
S32	H→L+5(53.52%);H-8→L(23.68%);H-5→L+1(10.94%)	3.7968/326.55	0.0750
S33	H-6→L+1(35.88%);H-7→L+2(19.43%);H-6→L+3(15.14%)	3.8628/320.97	0.2673
S34	H-6→L+2(28.93%);H-7→L+1(26.42%);H-7→L+3(16.22%)	3.8708/320.30	0.3864
S35	H-7→L+1(22.26%);251→L(21.80%);H-6→L(14.15%)	3.9173/316.50	0.0023
S36	H-4→L+2(49.32%);H-7→L(16.78%);H-6→L+1(16.35%)	3.9329/315.25	0.0548
S37	H-8→L+1(59.87%);H-11→L(13.11%)	3.9562/313.39	0.0901
S38	H-4→L+2(31.00%);H-6→L+1(18.96%);H-7→L+2(11.91%)	3.9846/311.15	0.0083
S39	H→L+6(74.02%)	4.0008/309.90	0.0171
S40	H-5→L+2(61.74%)	4.0214/308.31	0.0762

Table S5. Calculated ionization potentials of the donors IP_D, electron affinities of the acceptor EA_A, fundamental gaps defined as the difference between the ionization energy of donor and the electron affinity of acceptor ($IP_D - EA_A$), first adiabatic excitation energy of donor E_{S1A}, and exciton binding energy E_b (in eV)

Complex	IP_D	EA_A	IP_D - EA_A	E_{S1A}	E_b
P2F-EHp/BTPT-4F	5.7069	3.5191	2.1878	2.0856	0.4528
P2F-EHp/BTPTT-4F	5.7069	3.2106	2.4963	2.0909	0.4582

Table S6. The calculated relaxation energies (eV) of monomer BTPT-4F, BTPTT-4F and P2F-EHp molecules for the three electron transfer processes (ETP, charge transfer, exciton dissociation and charge recombination).

ETP	P2F-EHp				BTPT-4F	BTPTT-4F
CT	$E^{D+}(Q_R) \rightarrow E^{D+}(Q_P)$	0.2260	$E^{A-}(Q_R) \rightarrow E^{A-}(Q_P)$		0.3539	0.2766
ED	$E^{D+}(Q_R) \rightarrow E^{D+}(Q_P)$	0.2260	$E^{A-}(Q_R) \rightarrow E^{A-}(Q_P)$		0.3539	0.2766
	$E^{D}(Q_P) \rightarrow E^{D}(Q_R)$	0.2179	$E^{A*}(Q_P) \rightarrow E^{A*}(Q_R)$		0.1513	0.0306
CR	$E^{D+}(Q_G) \rightarrow E^{D+}(Q_P)$	0.2260	$E^{A-}(Q_G) \rightarrow E^{A-}(Q_P)$		0.3539	0.2766
	$E^{D}(Q_P) \rightarrow E^{D}(Q_G)$	0.2179	$E^{A}(Q_P) \rightarrow E^{A}(Q_G)$		0.2726	0.2162

Table S7. The GMH mode method is used to calculate the parameters required for the electronic coupling of the CT and CR processes.

	E_{S1}(eV)	Δμ(Debye)	μ_{tr}(Debye)	V(eV)
P2F-EHp/BTPT-4F	1.6869	27.7861	4.4865	0.2592
P2F-EHp/BTPTT-4F	1.7697	14.5706	13.8760	0.7834

Table S8. The parameters required for calculating electronic coupling of the ED processes. The selected molecular orbital are HOMO orbitals for both donor and acceptor.

Complex	H_{if} (meV)	S_{if}(meV)	E_i(eV)	E_f(eV)	V(meV)
P2F-EHp/BTPT-4F	42.04206	-0.00382	-5.18418	-5.52649	21.57899
P2F-EHp/BTPTT-4F	32.73044	-0.00303	-5.14478	-5.28057	16.94398