Supporting Information

Contents

Table S1. The crystal structure data of the four compounds from the Cambridge Crystallographic Database [a]

Compound	Space group	a/Å	b/Å	c/Å	α/º	β/º	γ/º
DP-DTT	P21/c	7.47	5.92	34.72	90.00	94.01	90.00
DP-BDTT	P-1	5.96	7.51	50.36	90.00	92.86	90.00
FPP-DTT	P21/c	5.87	36.12	7.50	90.00	91.67	90.00
FPP-BDTT	P-1	3.83	5.83	26.04	86.15	87.92	87.04

[a] The data are based on the experimental crystal structure from CCDC No.1005153–1005156.

Table S2. The crystal structure data of the optimized four compounds and the predicted two compounds

Compound	Space group	a/Å	b/Å	c/Å	α/º	β/º	γ/º
DP-DTT [a]	P21/c	7.75	5.24	33.28	90.00	96.59	90.00
DP-BDTT	P-1	5.55	7.57	47.79	90.00	91.25	90.00
FPP-DTT	P21/c	5.62	35.60	7.03	90.00	89.66	90.00
FPP-BDTT [b]	P-1	3.59	5.64	25.23	86.34	87.89	90.34
DFP-DTT	P21/c	6.15	36.88	7.41	90.00	83.06	90.00
DFP-BDTT	P-1	3.69	5.84	26.17	86.15	88.85	87.58

[a] the optimized crystal structures based on the experimental crystallizes

[b] the predicted crystal structures based on the precursor crystallizes FPP-DTT and FPP-BDTT

Table S3. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **DP-DTT** in the neutral and ionic states together with experimental values at the B3LYP/6-311G(d,p) level

	Ground state	Expt.	Anion state	Cation state
R(1,2)	1.087	0.951	1.089	1.085
R(2,3)	1.392	1.370	1.387	1.387
R(3,4)	1.086	0.953	1.086	1.085
R(3,5)	1.408	1.411	1.425	1.417
R(5,6)	1.466	1.435	1.436	1.446
R(6,7)	1.378	1.395	1.404	1.404
R(7,8)	1.418	1.399	1.394	1.390
R(8,9)	1.761	1.754	1.777	1.760
R(9,10)	1.761	1.763	1.777	1.760
R(10,11)	1.418	1.393	1.394	1.390
R(11,12)	1.378	1.380	1.404	1.404
R(12,13)	1.466	1.460	1.436	1.446
R(13,14)	1.408	1.412	1.425	1.417
R(14,15)	1.086	0.950	1.086	1.085
R(14,16)	1.392	1.369	1.387	1.387
R(16,17)	1.087	0.951	1.089	1.085
R(16,18)	1.397	1.396	1.402	1.400
R(18,19)	1.086	0.950	1.087	1.086
R(18,20)	1.396	1.385	1.400	1.400
R(20,21)	1.087	0.949	1.089	1.085
R(20,23)	1.393	1.372	1.389	1.387
R(22,23)	1.087	0.951	1.087	1.086
R(13,23)	1.407	1.394	1.423	1.415
R(12,24)	1.773	1.767	1.800	1.774
R(24,25)	1.739	1.734	1.755	1.740

R(25,26)	1.418	1.392	1.395	1.388
R(26,27)	1.739	1.748	1.755	1.740
R(6,27)	1.773	1.759	1.800	1.774
R(5,28)	1.407	1.405	1.423	1.415
R(28,29)	1.087	0.952	1.087	1.086
R(28,30)	1.393	1.352	1.389	1.387
R(30,31)	1.087	0.951	1.089	1.085
R(30,32)	1.396	1.407	1.400	1.400
R(32,33)	1.086	0.950	1.087	1.086
R(2,32)	1.397	1.379	1.402	1.400
R(8,26)	1.394	1.371	1.413	1.423
R(10,25)	1.394	1.368	1.413	1.423
A(H4-C3-C5)	119.50	119.58	119.39	120.27
A(H15-C14-C13)	119.50	119.08	119.39	120.27
D(C7-C6-C5-C28)	179.19	172.95	167.78	179.96
D(C11-C12-C13-C23)	179.20	173.16	167.64	179.98

Table S4. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **FPP-DTT** in the neutral and ionic states together with experimental values at the B3LYP/6-311G(d,p) level

	Ground state	Expt.	Anion state	Cation state
R(1,2)	1.087	1.119	1.089	1.085
R(2,3)	1.392	1.382	1.388	1.386
R(3,4)	1.086	0.897	1.086	1.084
R(3,5)	1.408	1.408	1.422	1.419
R(5,6)	1.467	1.468	1.441	1.443
R(6,7)	1.378	1.379	1.400	1.407
R(7,8)	1.418	1.404	1.396	1.388
R(8,9)	1.760	1.742	1.775	1.759
R(9,10)	1.761	1.734	1.776	1.760
R(10,11)	1.412	1.410	1.390	1.390
R(11,12)	1.384	1.383	1.413	1.406
R(12,13)	1.412	1.461	1.390	1.390
R(13,14)	1.411	1.409	1.431	1.419
R(14,15)	1.345	1.349	1.357	1.338
R(14,16)	1.390	1.370	1.384	1.388
R(16,17)	1.337	1.335	1.349	1.329
R(16,18)	1.392	1.386	1.395	1.396
R(18,19)	1.335	1.330	1.351	1.322
R(18,20)	1.391	1.377	1.395	1.396
R(20,21)	1.337	1.345	1.349	1.328
R(20,23)	1.390	1.374	1.384	1.387
R(22,23)	1.345	1.354	1.356	1.340
R(13,23)	1.384	1.403	1.413	1.406
R(12,24)	1.781	1.756	1.808	1.778
R(24,25)	1.734	1.722	1.750	1.738

R(25,26)	1.418	1.417	1.396	1.389
R(26,27)	1.739	1.722	1.753	1.739
R(6,27)	1.772	1.748	1.796	1.775
R(5,28)	1.407	1.403	1.420	1.417
R(28,29)	1.087	0.953	1.087	1.086
R(28,30)	1.393	1.388	1.390	1.386
R(30,31)	1.087	0.864	1.089	1.085
R(30,32)	1.396	1.388	1.399	1.401
R(32,33)	1.086	0.983	1.087	1.086
R(2,32)	1.397	1.401	1.401	1.400
R(8,26)	1.395	1.394	1.412	1.426
R(10,25)	1.394	1.393	1.412	1.420
A(H4-C3-C5)	119.52	120.33	119.47	120.34
A(H15-C14-C13)	120.58	119.85	120.30	120.84
D(C7-C6-C5-C28)	179.44	179.14	171.66	179.98
D(C11-C12-C13-C23)	179.47	177.98	173.65	179.98

Table S5. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **DFP-DTT** in the neutral and ionic states at the B3LYP/6-311G(d,p) level

	Ground state	Anion state	Cation state
R(1,2)	1.337	1.348	1.328
R(2,3)	1.390	1.385	1.387
R(3,4)	1.344	1.355	1.337
R(3,5)	1.411	1.428	1.420
R(5,6)	1.465	1.434	1.449
R(6,7)	1.384	1.410	1.409
R(7,8)	1.413	1.391	1.388
R(8,9)	1.760	1.774	1.760
R(9,10)	1.760	1.774	1.760
R(10,11)	1.413	1.391	1.388
R(11,12)	1.384	1.410	1.409
R(12,13)	1.465	1.434	1.449
R(13,14)	1.411	1.428	1.420
R(14,15)	1.344	1.355	1.337
R(14,16)	1.390	1.385	1.387
R(16,17)	1.337	1.348	1.328
R(16,18)	1.392	1.394	1.397
R(18,19)	1.334	1.349	1.320
R(18,20)	1.391	1.394	1.397
R(20,21)	1.337	1.347	1.327
R(20,23)	1.390	1.385	1.386
R(22,23)	1.345	1.354	1.339
R(13,23)	1.408	1.425	1.417
R(12,24)	1.780	1.805	1.779
R(24,25)	1.734	1.749	1.738

R(25,26)	1.418	1.396	1.388
R(26,27)	1.734	1.749	1.738
R(6,27)	1.780	1.805	1.779
R(5,28)	1.408	1.425	1.417
R(28,29)	1.345	1.354	1.339
R(28,30)	1.390	1.385	1.386
R(30,31)	1.337	1.347	1.327
R(30,32)	1.391	1.394	1.397
R(32,33)	1.334	1.349	1.320
R(2,32)	1.392	1.394	1.397
R(8,26)	1.395	1.412	1.423
R(10,25)	1.395	1.412	1.423
A(H4-C3-C5)	120.58	120.40	120.84
A(H15-C14-C13)	120.57	120.40	120.85
D(C7-C6-C5-C28)	177.87	174.99	179.98
D(C11-C12-C13-C23)	177.67	175.03	179.95

Table S6. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **DP-BDTT** in the neutral and ionic states together with experimental values at the B3LYP/6-311G(d,p) level

	Ground state	Expt.	Anion state	Cation state
R(1,2)	1.087	0.930	1.088	1.086
R(2,3)	1.392	1.392	1.389	1.390
R(3,4)	1.086	0.930	1.086	1.085
R(3,5)	1.408	1.394	1.418	1.412
R(5,6)	1.466	1.476	1.448	1.457
R(6,7)	1.378	1.375	1.393	1.392
R(7,8)	1.417	1.419	1.401	1.401
R(8,9)	1.760	1.730	1.771	1.759
R(9,10)	1.760	1.752	1.771	1.760
R(10,11)	1.416	1.411	1.398	1.391
R(11,12)	1.381	1.360	1.405	1.405
R(12,13)	1.443	1.443	1.411	1.413
R(13,14)	1.775	1.764	1.796	1.781
R(14,15)	1.741	1.704	1.754	1.738
R(15,16)	1.417	1.456	1.400	1.396
R(16,17)	1.740	1.728	1.748	1.741
R(17,18)	1.773	1.749	1.790	1.771
R(18,19)	1.466	1.471	1.448	1.457
R(19,21)	1.407	1.401	1.416	1.410
R(21,22)	1.087	0.931	1.087	1.087
R(21,23)	1.393	1.388	1.391	1.390
R(22,23)	1.087	0.931	1.088	1.086
R(23,24)	1.396	1.375	1.398	1.398
R(24,25)	1.086	0.927	1.087	1.086
R(24,26)	1.397	1.372	1.400	1.398

R(26,27)	1.087	0.933	1.088	1.086
R(26,28)	1.392	1.384	1.389	1.390
R(28,29)	1.086	0.930	1.086	1.085
R(19,28)	1.408	1.369	1.418	1.412
R(18,30)	1.378	1.370	1.393	1.392
R(30,31)	1.418	1.445	1.401	1.401
R(31,32)	1.760	1.734	1.771	1.759
R(32,33)	1.760	1.759	1.771	1.760
R(33,34)	1.416	1.428	1.398	1.391
R(13,34)	1.381	1.360	1.405	1.405
R(12,35)	1.775	1.747	1.796	1.781
R(35,36)	1.741	1.731	1.754	1.738
R(36,37)	1.417	1.425	1.400	1.396
R(37,38)	1.740	1.728	1.748	1.741
R(6,38)	1.773	1.757	1.790	1.771
R(5,40)	1.407	1.372	1.416	1.410
R(40,39)	1.087	0.930	1.087	1.087
R(40,42)	1.393	1.391	1.391	1.390
R(41,42)	1.087	0.932	1.088	1.086
R(42,43)	1.396	1.374	1.398	1.398
R(43,44)	1.086	0.932	1.087	1.086
R(2,43)	1.397	1.396	1.400	1.398
R(8,37)	1.395	1.408	1.407	1.412
R(10,36)	1.395	1.382	1.408	1.419
R(15,33)	1.395	1.375	1.408	1.419
R(16,31)	1.395	1.381	1.407	1.412
A(H4-C3-C5)	119.50	119.96	119.59	120.00
A(H20-C21-C19)	119.64	119.71	119.48	120.01
D(C7-C6-C5-C40)	179.62	172.44	157.03	179.57

D(C21-C19-C18-C30)	179.91	173.07	157.02	179.90
D(C11-C12-C13-C34)	179.87	179.32	179.91	179.97

Table S7. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **FPP-BDTT** in the neutral and ionic states together with experimental values at the B3LYP/6-311G(d,p) level

	Ground state	Expt.	Anion state	Cation state
R(1,2)	1.087	1.326	1.088	1.086
R(2,3)	1.392	1.369	1.390	1.389
R(3,4)	1.086	1.362	1.086	1.085
R(3,5)	1.408	1.389	1.416	1.412
R(5,6)	1.466	1.465	1.452	1.455
R(6,7)	1.378	1.365	1.390	1.394
R(7,8)	1.417	1.411	1.404	1.400
R(8,9)	1.760	1.729	1.769	1.759
R(9,10)	1.760	1.745	1.769	1.760
R(10,11)	1.415	1.406	1.400	1.390
R(11,12)	1.381	1.369	1.403	1.406
R(12,13)	1.443	1.447	1.412	1.413
R(13,14)	1.775	1.749	1.794	1.780
R(14,15)	1.741	1.719	1.754	1.737
R(15,16)	1.416	1.424	1.398	1.399
R(16,17)	1.734	1.722	1.744	1.737
R(17,18)	1.781	1.758	1.800	1.778
R(18,19)	1.464	1.465	1.440	1.460
R(19,21)	1.409	1.402	1.421	1.412
R(21,22)	1.345	1.338	1.352	1.342
R(21,23)	1.390	1.365	1.387	1.389
R(22,23)	1.337	1.314	1.345	1.331
R(23,24)	1.391	1.382	1.392	1.393
R(24,25)	1.335	1.289	1.346	1.326
R(24,26)	1.392	1.372	1.393	1.394

R(26,27)	1.337	1.326	1.345	1.331
R(26,28)	1.390	1.369	1.386	1.389
R(28,29)	1.345	1.362	1.353	1.341
R(19,28)	1.411	1.389	1.424	1.414
R(18,30)	1.384	1.365	1.404	1.395
R(30,31)	1.412	1.411	1.394	1.401
R(31,32)	1.761	1.729	1.772	1.759
R(32,33)	1.759	1.746	1.770	1.759
R(33,34)	1.415	1.406	1.396	1.391
R(13,34)	1.382	1.369	1.405	1.405
R(12,35)	1.775	1.749	1.795	1.781
R(35,36)	1.741	1.719	1.753	1.739
R(36,37)	1.417	1.424	1.402	1.394
R(37,38)	1.740	1.722	1.747	1.741
R(6,38)	1.773	1.758	1.788	1.771
R(5,40)	1.407	1.402	1.414	1.411
R(40,39)	1.087	1.338	1.087	1.087
R(40,42)	1.393	1.365	1.391	1.390
R(41,42)	1.087	1.314	1.088	1.086
R(42,43)	1.396	1.382	1.397	1.398
R(43,44)	1.086	1.289	1.087	1.086
R(2,43)	1.397	1.372	1.399	1.398
R(8,37)	1.395	1.393	1.405	1.414
R(10,36)	1.396	1.382	1.406	1.421
R(15,33)	1.396	1.382	1.411	1.418
R(16,31)	1.395	1.393	1.409	1.408
A(H4-C3-C5)	119.51	120.09	119.55	120.04
A(H20-C21-C19)	120.08	118.77	119.79	119.88
D(C7-C6-C5-C40)	179.32	179.20	178.04	179.89

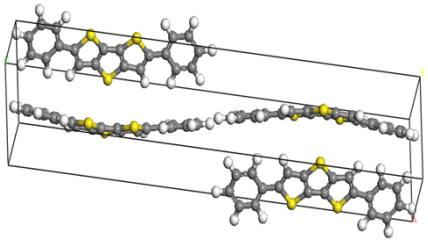
D(C21-C19-C18-C30)	177.94	179.19	175.92	178.32
D(C11-C12-C13-C34)	179.14	180.00	179.58	179.11

Table S8. The optimized bond length (in Å), bond angel (°) and dihedral angles (°) of **DFP-BDTT** in the neutral and ionic states at the B3LYP/6-311G(d,p) level

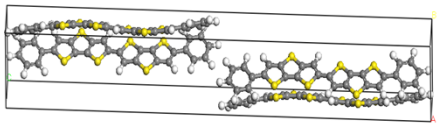
	Ground state	Anion state	Cation state
R(1,2)	1.337	1.344	1.331
R(2,3)	1.390	1.387	1.389
R(3,4)	1.345	1.352	1.340
R(3,5)	1.411	1.422	1.415
R(5,6)	1.464	1.444	1.459
R(6,7)	1.385	1.401	1.396
R(7,8)	1.412	1.396	1.400
R(8,9)	1.761	1.771	1.759
R(9,10)	1.759	1.769	1.759
R(10,11)	1.415	1.397	1.390
R(11,12)	1.382	1.404	1.406
R(12,13)	1.442	1.413	1.413
R(13,14)	1.775	1.793	1.780
R(14,15)	1.741	1.753	1.737
R(15,16)	1.416	1.399	1.397
R(16,17)	1.734	1.743	1.737
R(17,18)	1.781	1.798	1.778
R(18,19)	1.464	1.444	1.459
R(19,21)	1.409	1.419	1.412
R(21,22)	1.345	1.351	1.342
R(21,23)	1.390	1.387	1.388
R(22,23)	1.337	1.344	1.331
R(23,24)	1.391	1.392	1.394
R(24,25)	1.334	1.345	1.325
R(24,26)	1.392	1.393	1.395

R(26,27)	1.337	1.344	1.331
R(26,28)	1.390	1.387	1.389
R(28,29)	1.345	1.352	1.340
R(19,28)	1.411	1.422	1.415
R(18,30)	1.385	1.401	1.396
R(30,31)	1.412	1.396	1.400
R(31,32)	1.761	1.771	1.759
R(32,33)	1.759	1.769	1.759
R(33,34)	1.415	1.397	1.390
R(13,34)	1.382	1.404	1.406
R(12,35)	1.775	1.793	1.780
R(35,36)	1.741	1.753	1.737
R(36,37)	1.416	1.399	1.397
R(37,38)	1.734	1.743	1.737
R(6,38)	1.781	1.798	1.778
R(5,40)	1.409	1.419	1.412
R(40,39)	1.345	1.351	1.342
R(40,42)	1.390	1.387	1.388
R(41,42)	1.337	1.344	1.331
R(42,43)	1.391	1.392	1.394
R(43,44)	1.334	1.345	1.325
R(2,43)	1.392	1.393	1.395
R(8,37)	1.395	1.408	1.410
R(10,36)	1.396	1.409	1.420
R(15,33)	1.396	1.409	1.420
R(16,31)	1.395	1.408	1.410
A(H4-C3-C5)	120.60	120.55	120.75
A(H20-C21-C19)	120.06	119.86	119.85
D(C7-C6-C5-C40)	178.46	175.59	177.97

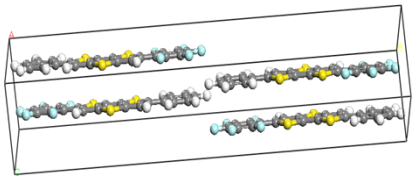
D(C21-C19-C18-C30)	178.46	175.59	177.97
D(C11-C12-C13-C34)	180.00	180.00	180.00



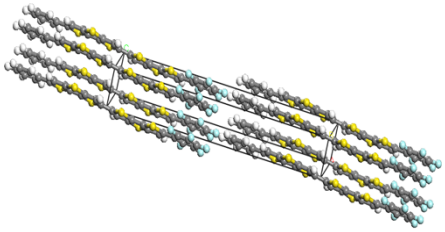
DP-DTT



DP-BDTT



FPP-DTT



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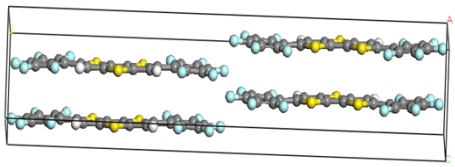
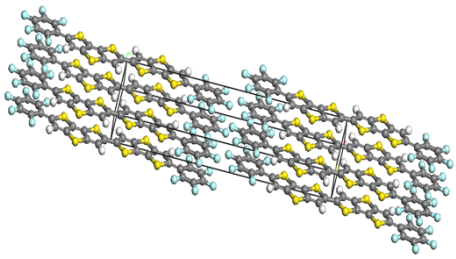
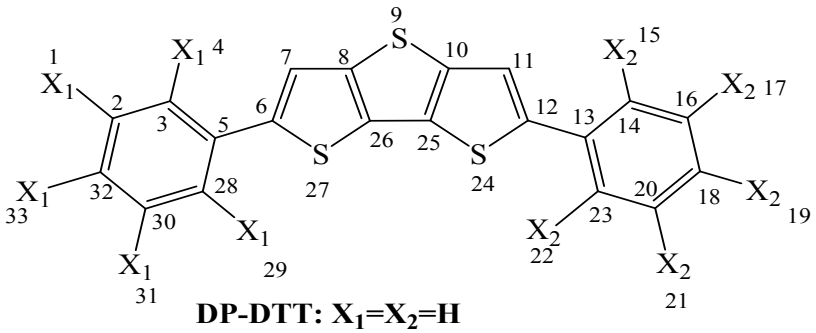


DFP-DTT

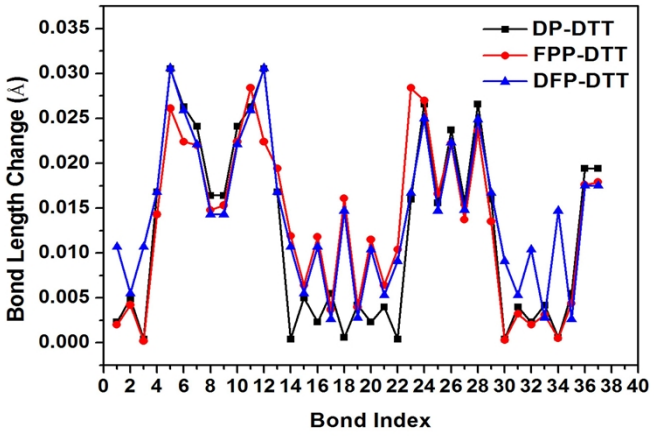


DFP-BDTT

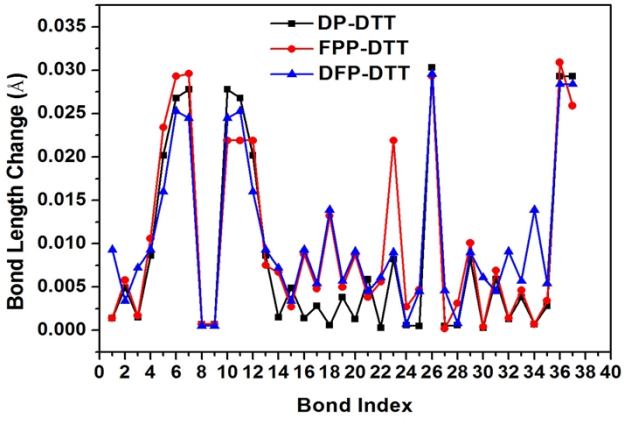
Figure S1. The crystal structures of the studied six compounds



(a)

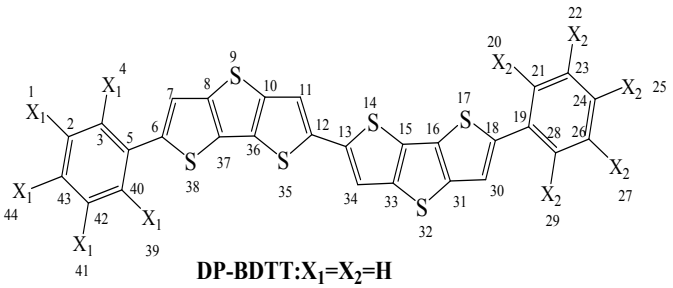


(b)



(c)

Figure S2. (a) The bond index of the bond lengths; the absolute values of bond length changes between the neutral and ionized geometries, (b) for hole and (c) for electron of the **DTT** derivatives

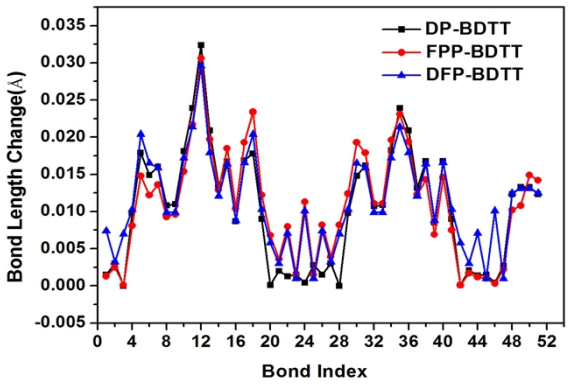


DP-BDTT:X_1=X_2=H

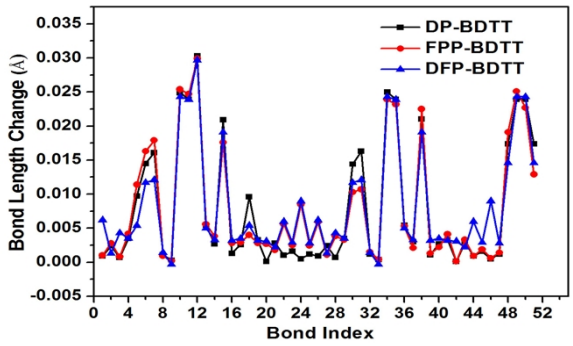
FPP-BDTT:X_1=H, X_2=F

DFP-BDTT:X_1=X_2=F

(a)



(b)



(c)

Figure S3. (a) The bond index of the bond lengths; the absolute values of bond length changes between the neutral and ionized geometries, (b) for hole and (c) for electron of the **BDTT** derivatives

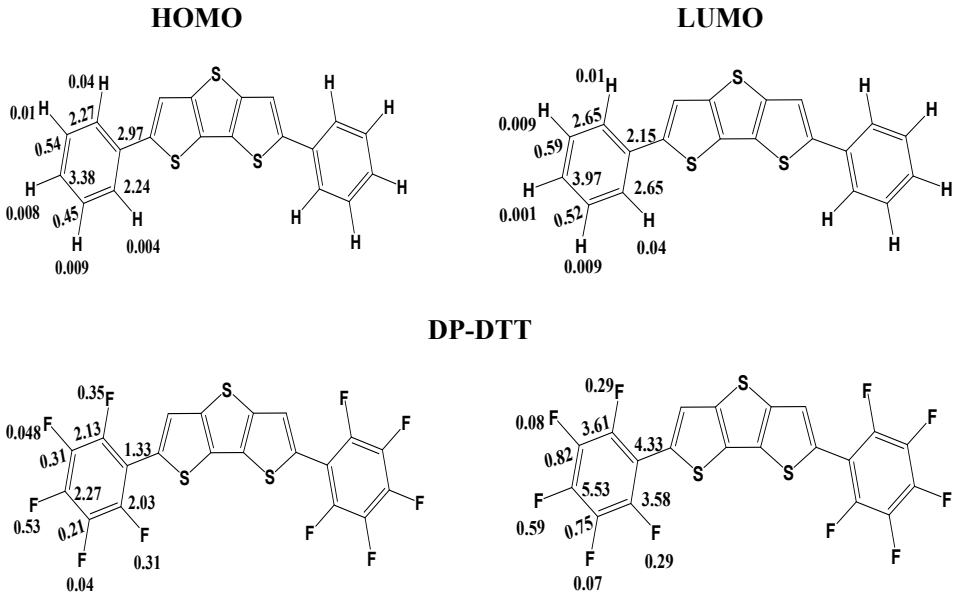
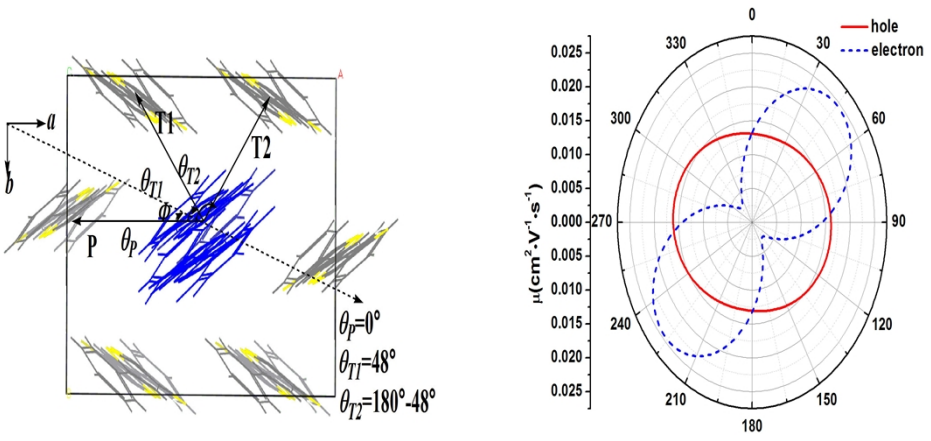
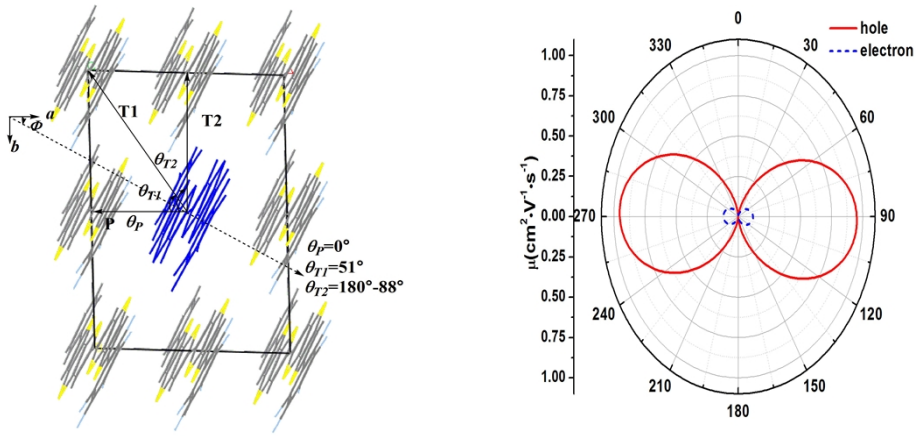


Figure S4. Contribution (%) of part atom to their HOMOs and LUMOs for compounds **DP-DTT** and **DFP-DTT**



(a) (b)

Figure S5. (a) Illustration of projecting different hopping pathways to a transistor channel in *a*-*b* plane of **DP-BDTT** crystal; $\boldsymbol{\theta_P}$, $\boldsymbol{\theta_{T1}}$ and $\boldsymbol{\theta_{T2}}$ are the angles of P, T1 and T2 dimers relative to the reference crystallographic axis *a*. Φ is the angle along a transistor channel relative to the reference crystallographic axis *a*. (b) the simulated hole and electron anisotropic mobilities in the *a*-*b* plane of **DP-BDTT**.



(a) (b)

Figure S6. (a) Illustration of projecting different hopping pathways to a transistor channel in *a*-*b* plane of **FPP-BDTT** crystal; $\boldsymbol{\theta_P}$, $\boldsymbol{\theta_{T1}}$ and $\boldsymbol{\theta_{T2}}$ are the angles of P, T1 and T2 dimers relative to the reference crystallographic axis *a*. Φ is the angle along a transistor channel relative to the reference crystallographic axis *a*. (b) and (c) the simulated hole and electron anisotropic mobilities in the *a*-*b* plane of **FPP-BDTT**.