Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Effect of Dynamic Disorder on Charge Carrier Dynamics in Ph4DP and Ph4DTP Molecules

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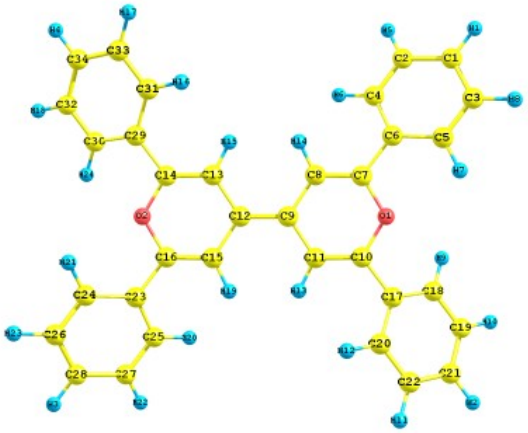
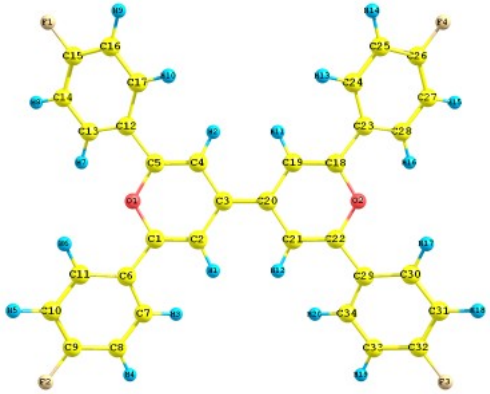
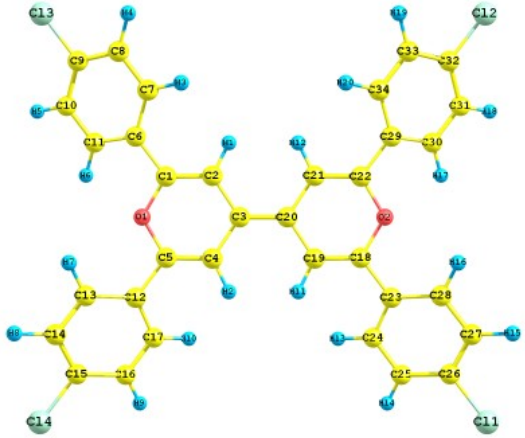
Fig. S1: The optimized structure of Ph4DP and their derivatives and Ph4DTP molecules calculated at B3LYP/6-31G(d,p) level of theory.



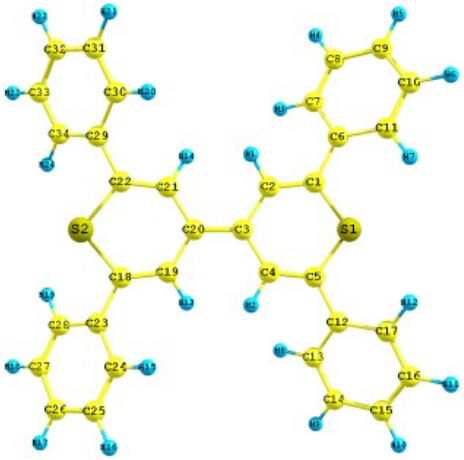
Ph4DP



F-Ph4DP

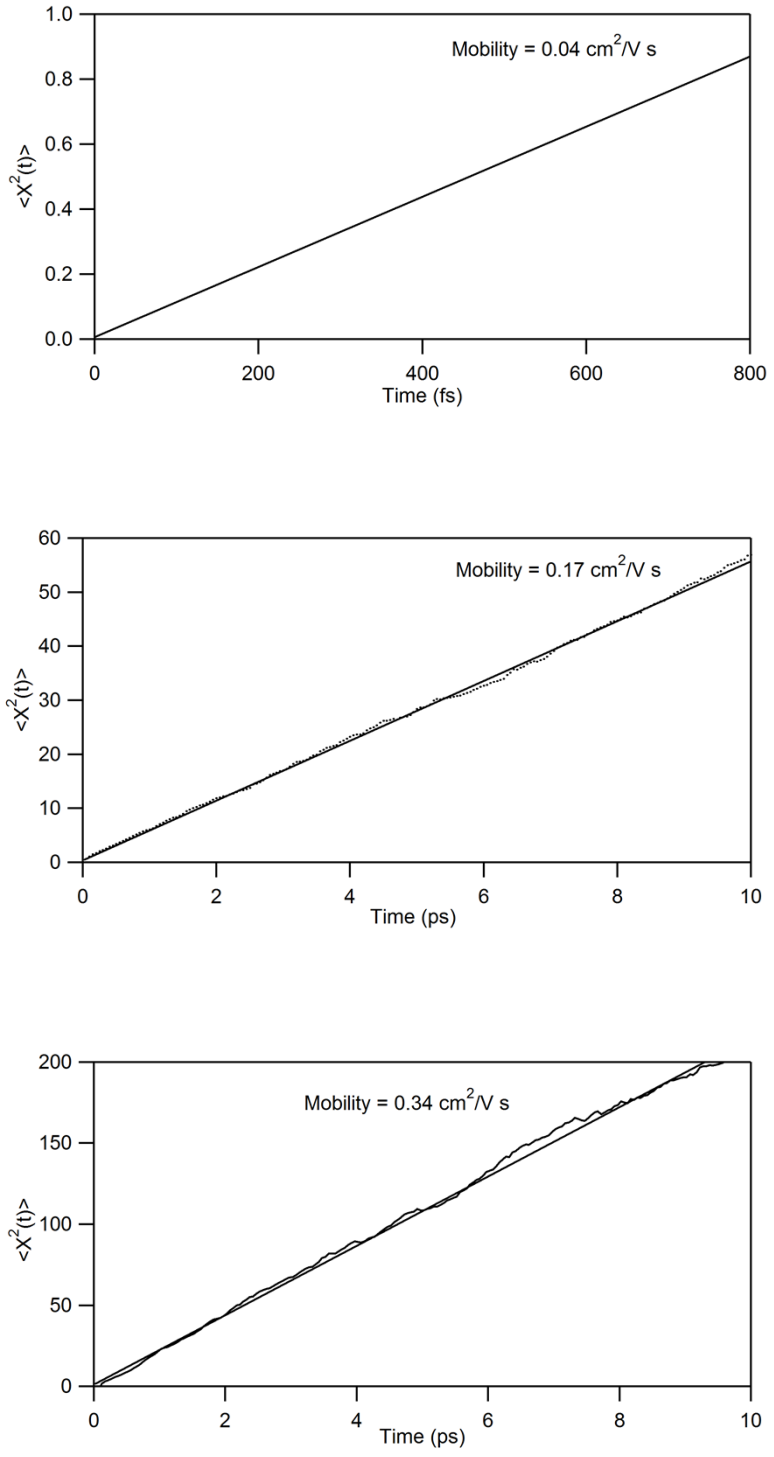


Cl-Ph4DP



Ph4DTP

Fig. S2: Mean squared displacement of hole in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules



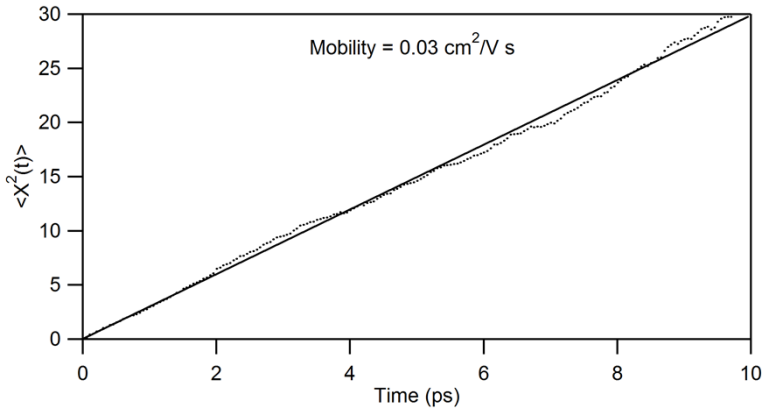
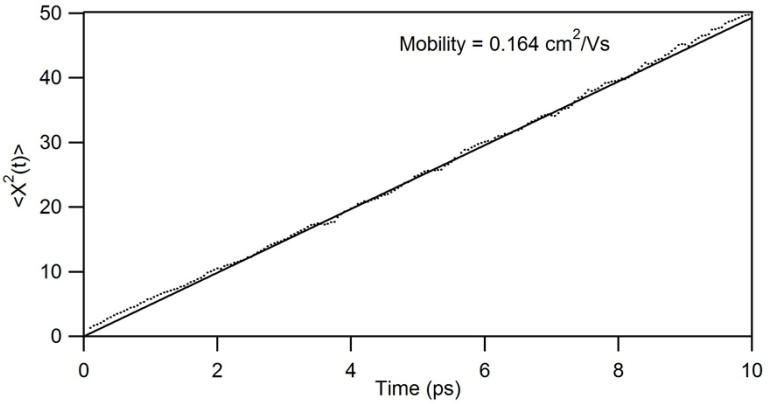
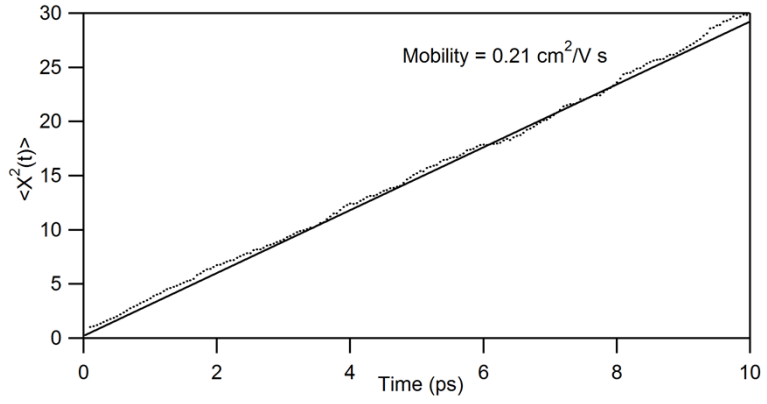


Fig. S2: Mean squared displacement of electron in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules





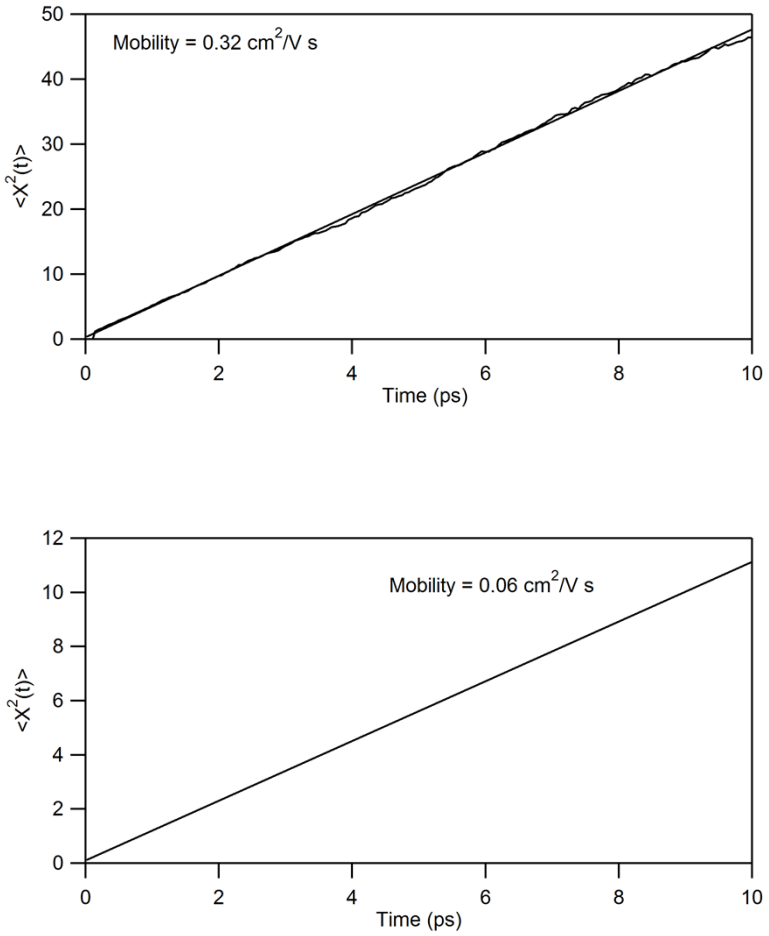
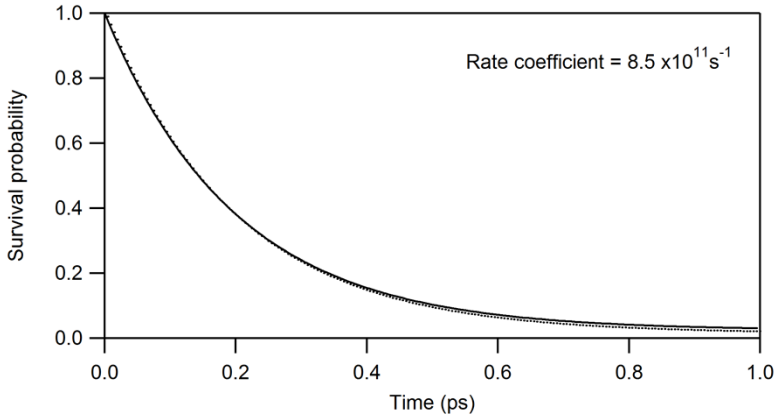
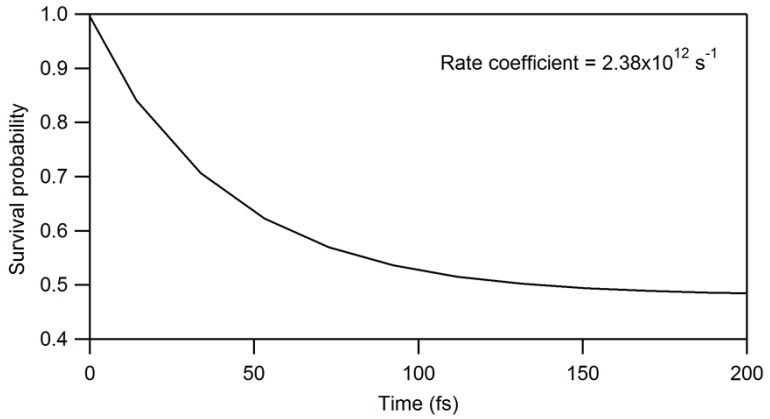
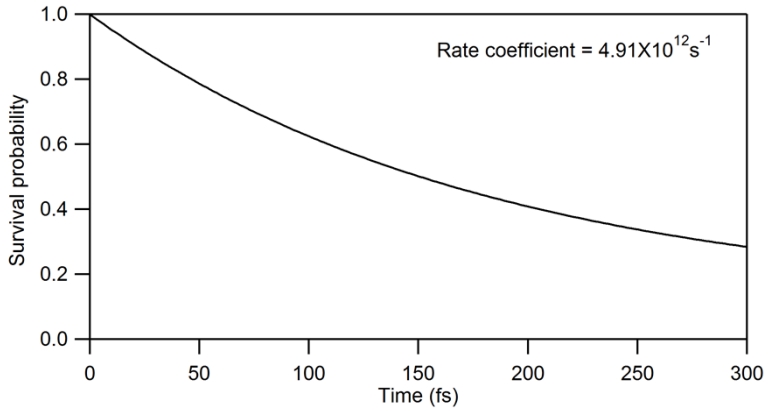


Fig. S2: Survival probability of positive charge in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules with respect to time




Rate coefficient = 2.38x10^12 s^-1
Survival probability
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0
50
100
150
200
Time (fs)


Rate coefficient = 4.91X10^12s^-1
Survival probability
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0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Time (fs)

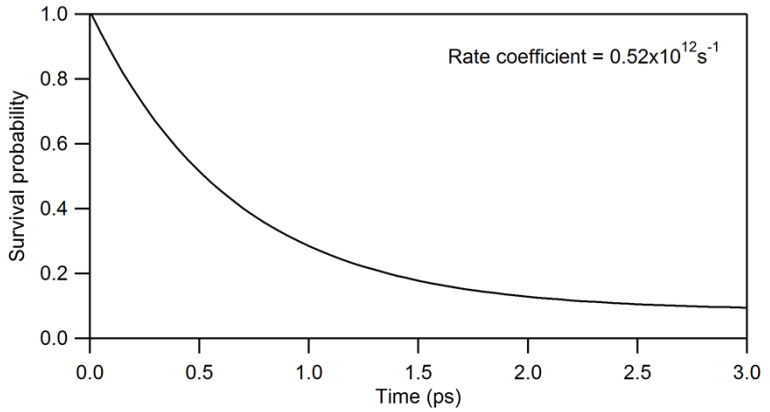
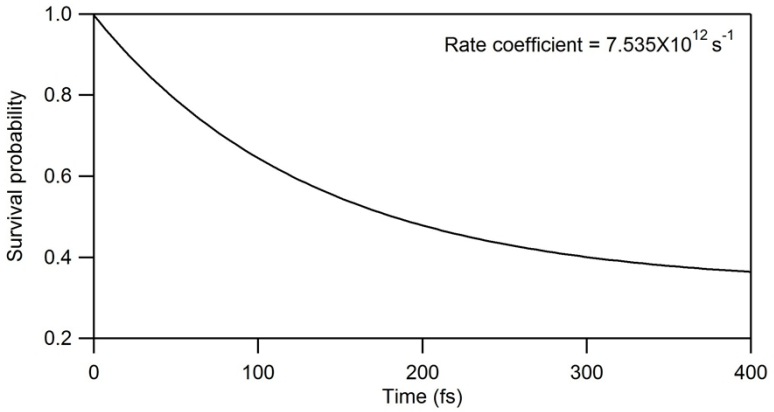
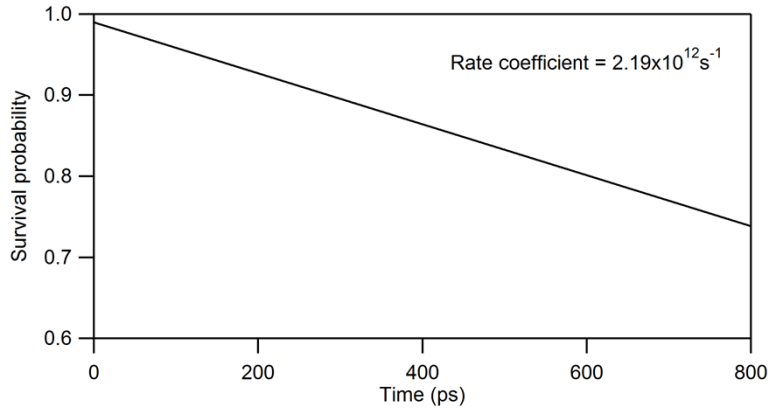
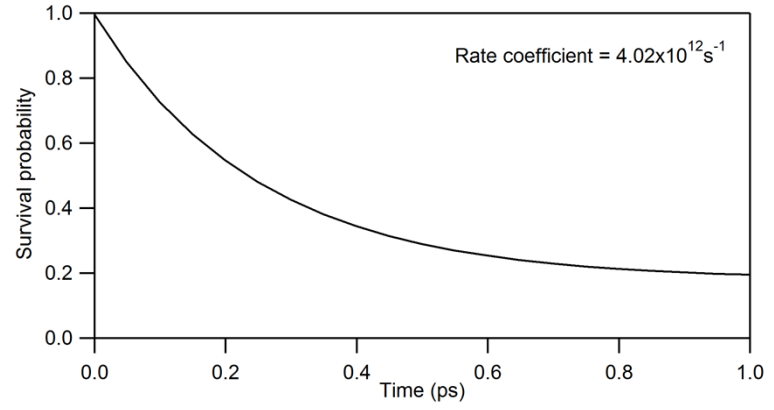

Rate coefficient = 0.52x10^12s^-1
Survival probability
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time (ps)

Fig. S2: Survival probability of negative charge in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules with respect to time







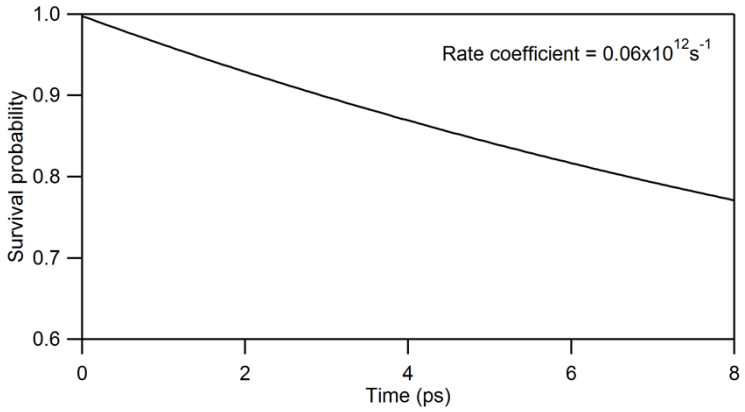
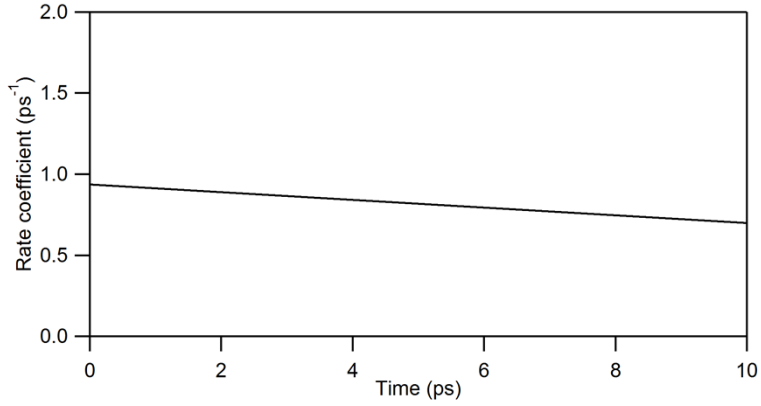
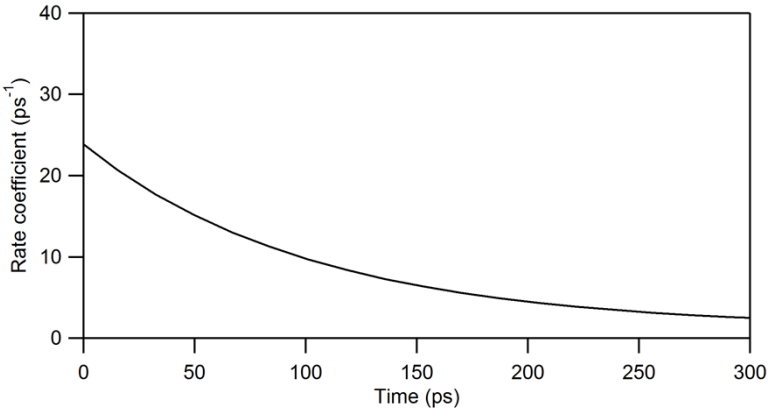


Fig. S2: Time evolution of the rate coefficient for hole transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules





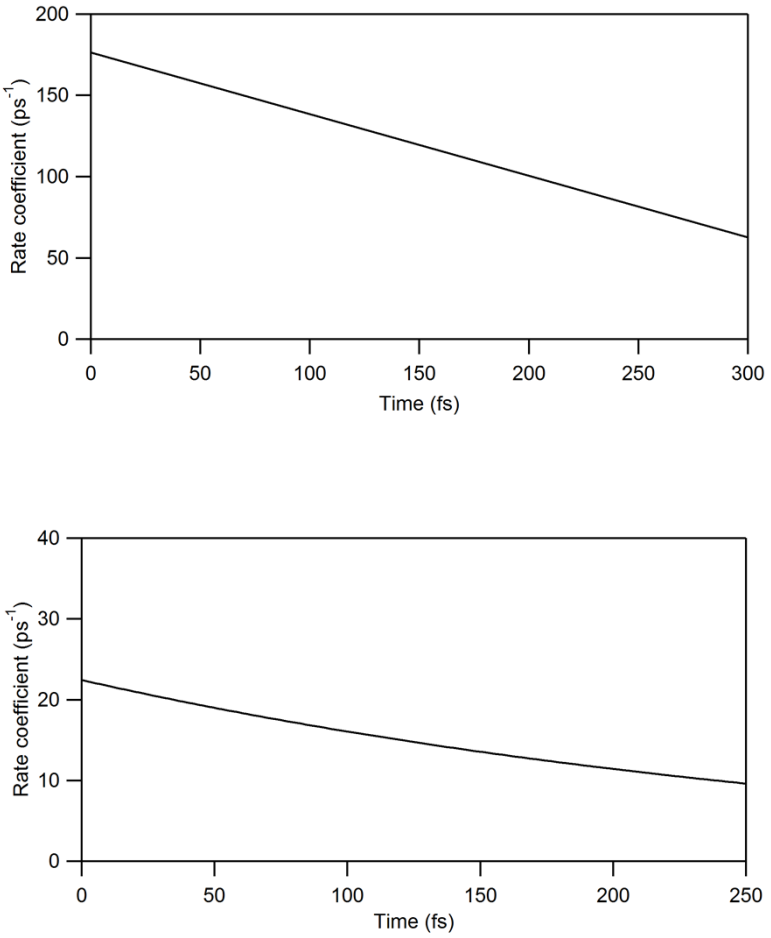
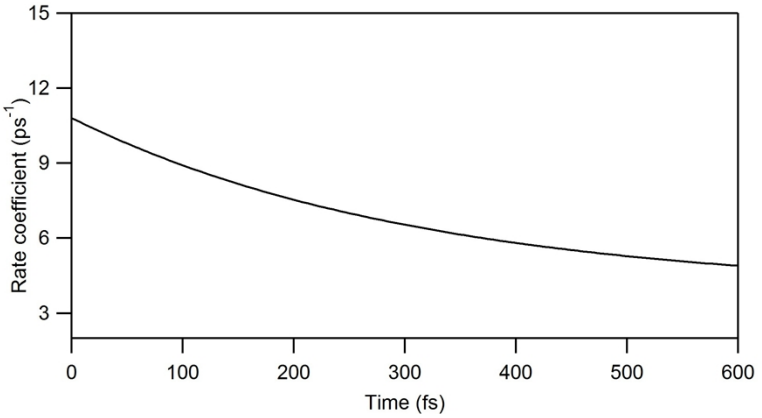
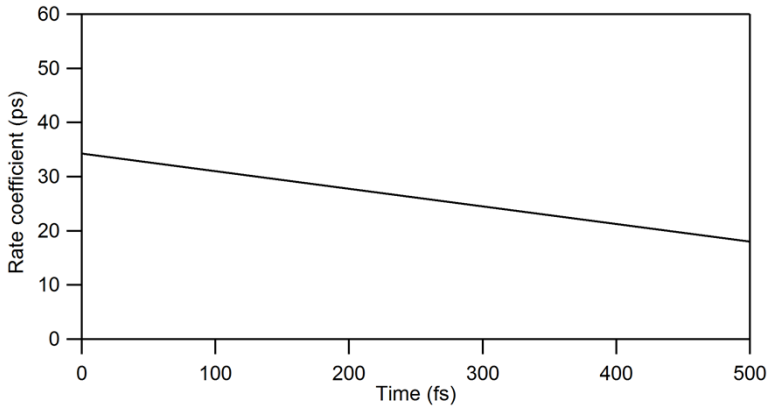
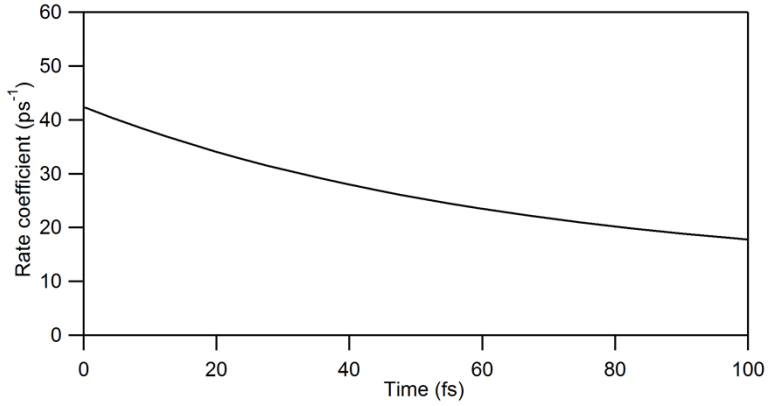


Fig. S2: Time evolution of the rate coefficient for electron transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules




Rate coefficient (ps)
60
50
40
30
20
10
0
0
100
200
300
400
500
Time (fs)


Rate coefficient (ps-1)
60
50
40
30
20
10
0
0
20
40
60
80
100
Time (fs)

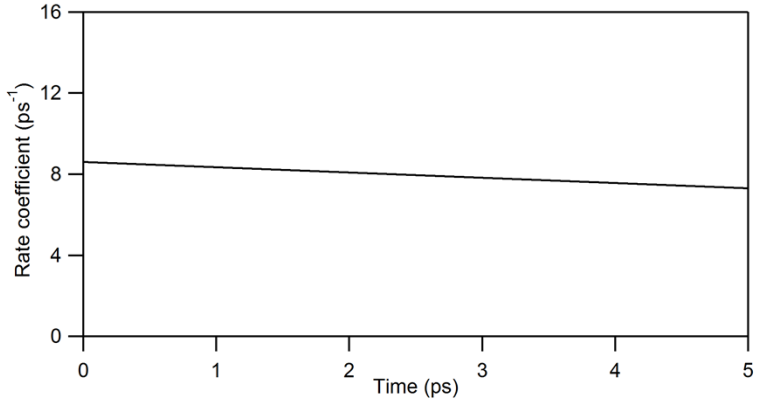
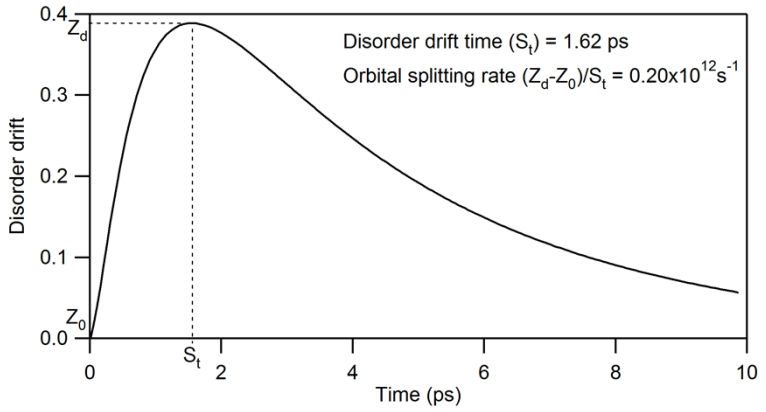
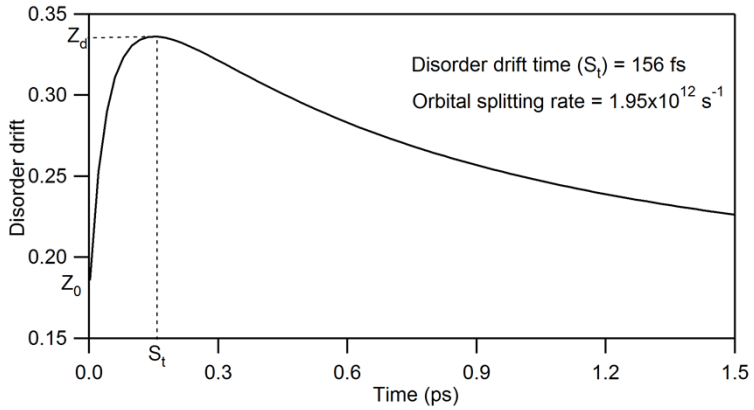
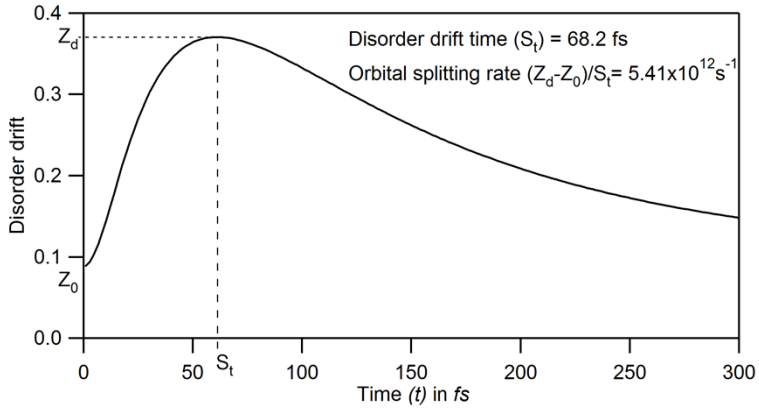

Rate coefficient (ps-1)
16
12
8
4
0
0
1
2
3
4
5
Time (ps)

Fig. S2: Disorder drift with in time scale of simulation for hole transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules







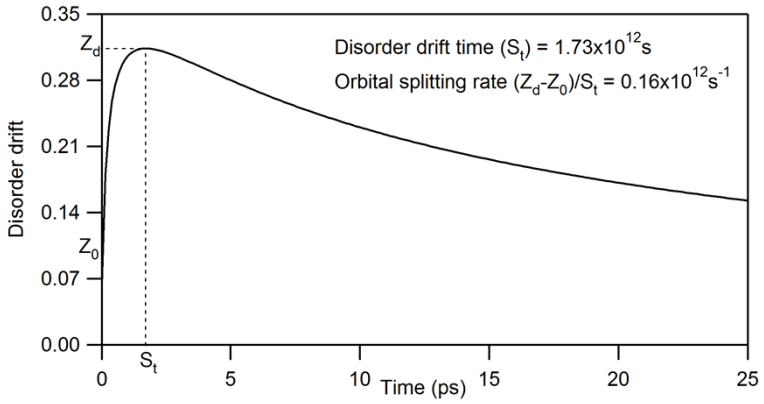
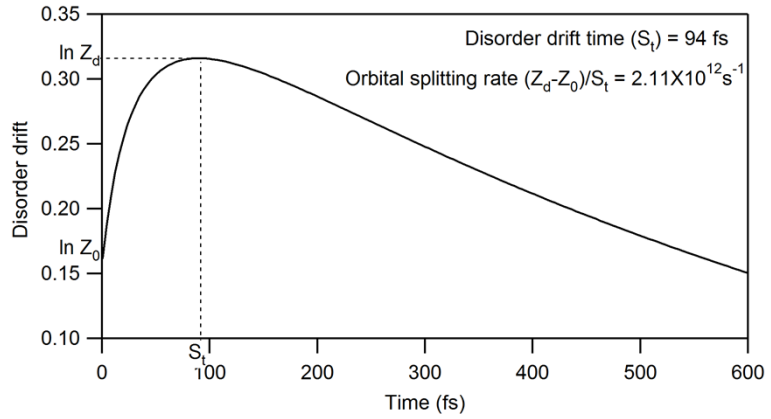
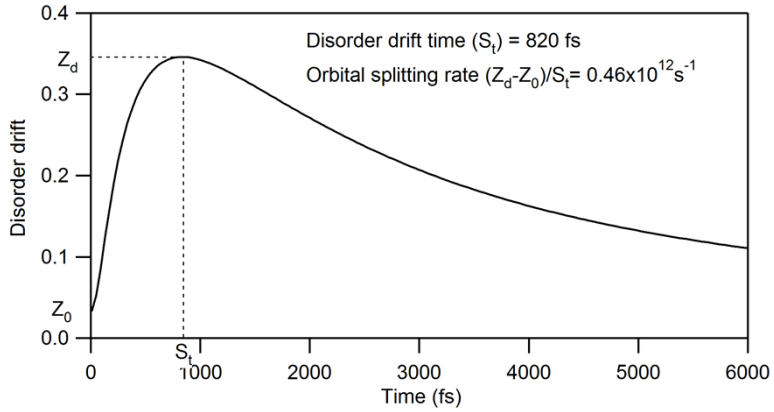


Fig. S2: Disorder drift with in time scale of simulation for electron transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules





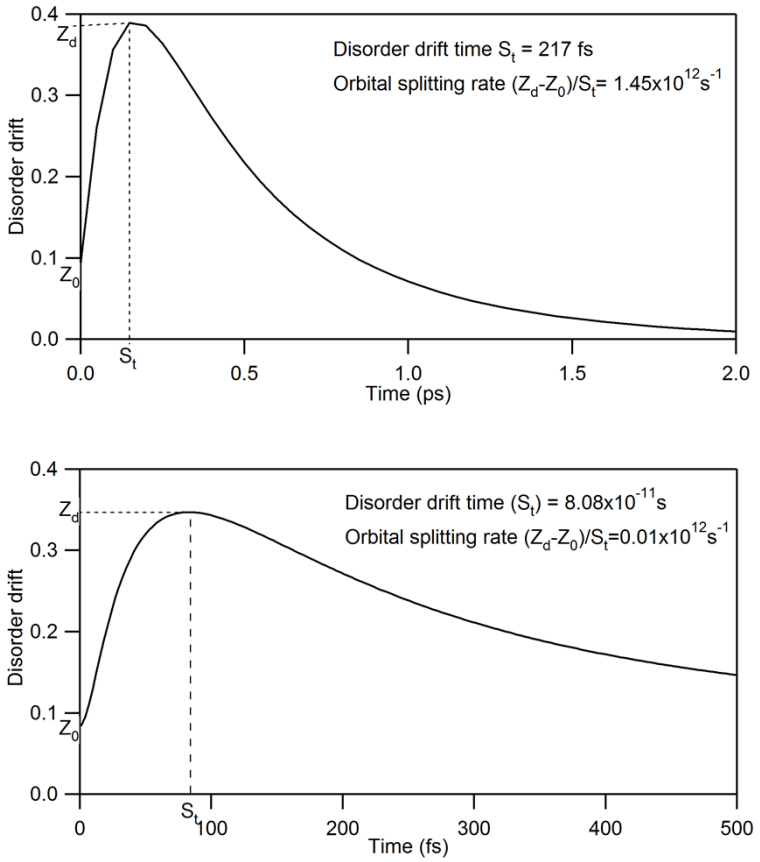
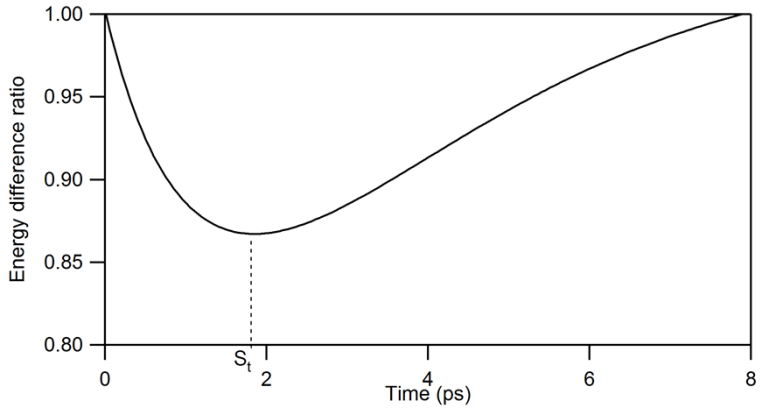
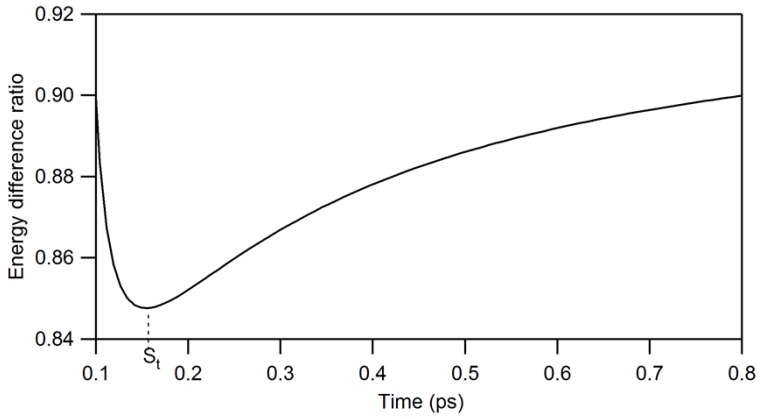
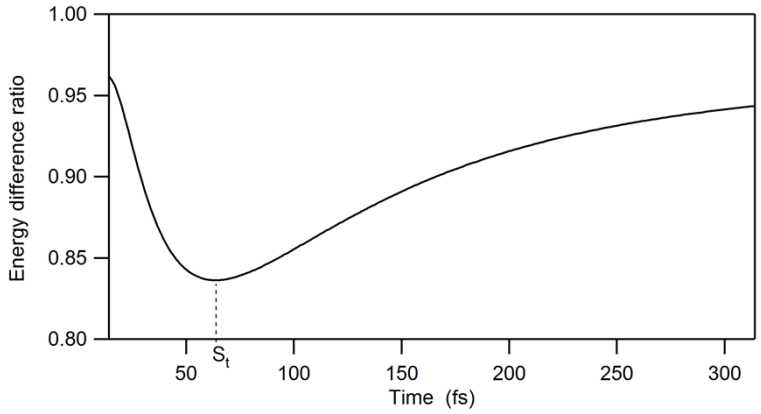


Fig. S2: Time evolution of dispersal energy difference ratio for hole transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules




0.92
0.90
0.88
0.86
0.84
Energy difference ratio
S_t
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Time (ps)


1.00
0.95
0.90
0.85
0.80
Energy difference ratio
S_t
50
100
150
200
250
300
Time (fs)

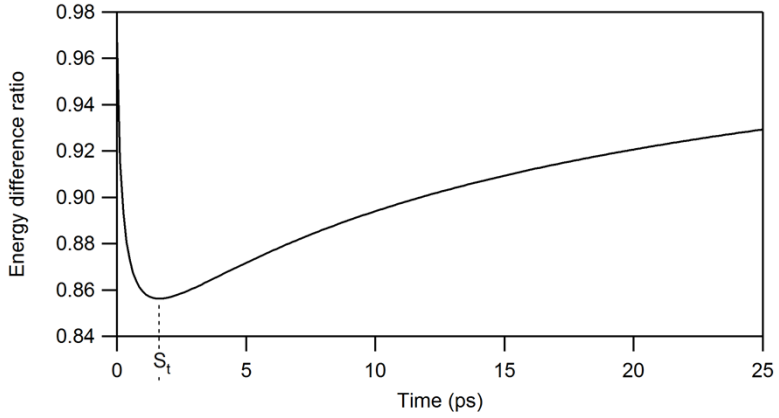
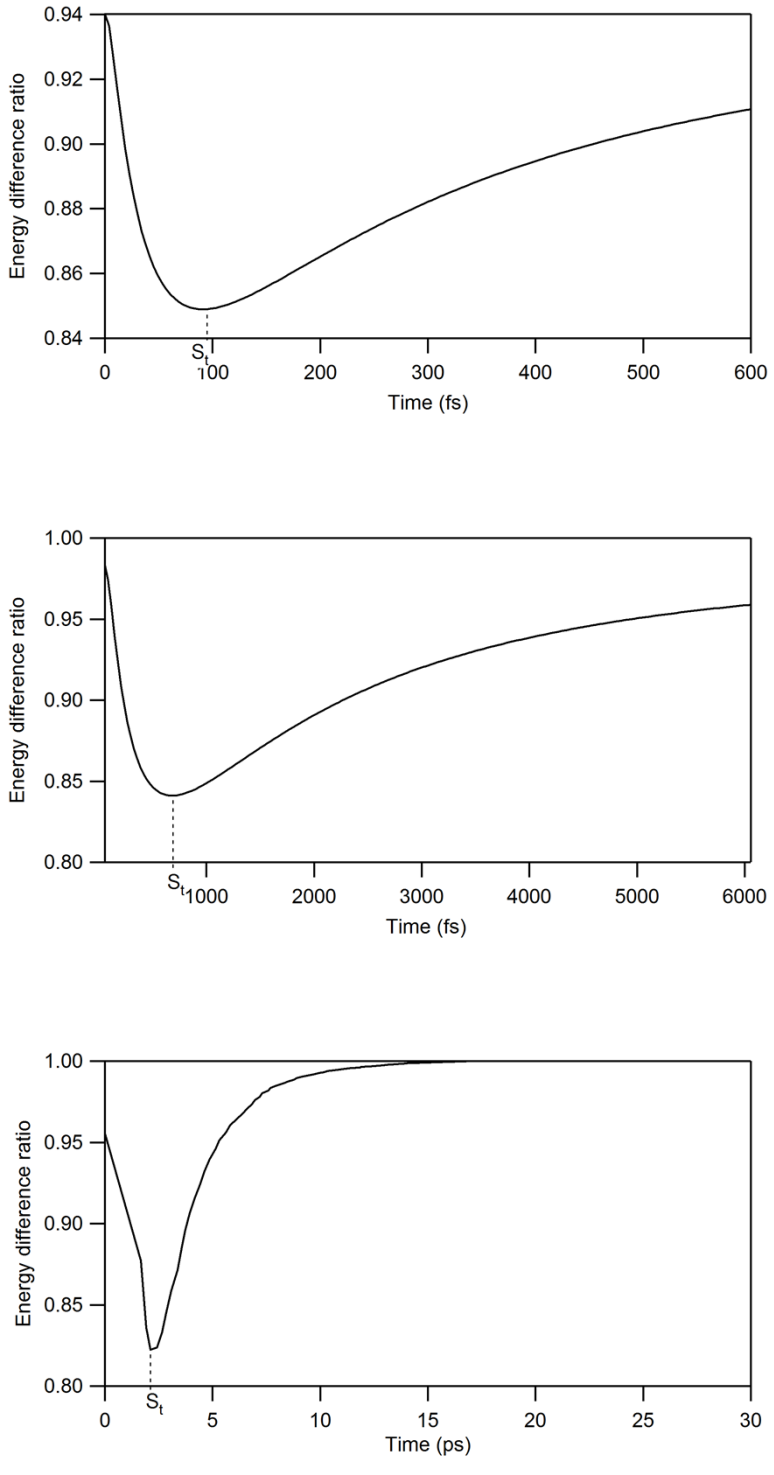

0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
Energy difference ratio
S_t
0
5
10
15
20
25
Time (ps)

Fig. S2: Time evolution of dispersal energy difference ratio for electron transport in Ph4DP, F-Ph4DP, Cl-Ph4DP and Ph4DTP molecules



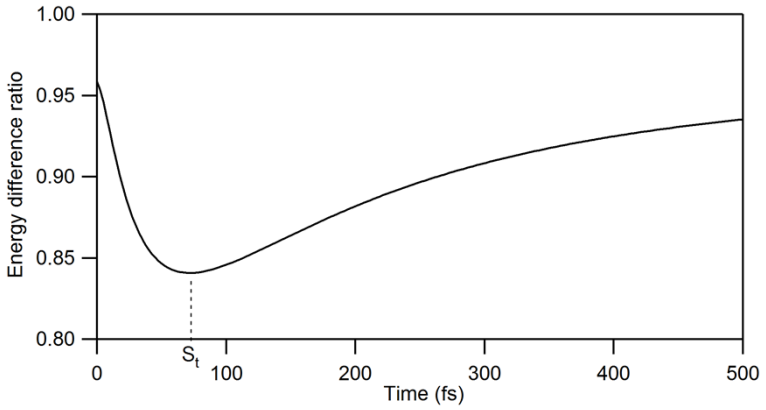


Table S1. (a) Calculated bond lengths for neutral, cationic and anionic geometries for the studied Ph4DP and Ph4DTP derivatives.

Molecules	Atomic specification	Bond length in Å		
		Neutral geometry	Cationic geometry	Anionic geometry
Ph4DP	C3-C20	1.39	1.43	1.43
	O1-C5	1.38	1.36	1.40
	C5-C12	1.47	1.46	1.45
F-Ph4DP	C3-C20	1.39	1.44	1.43
	O1-C5	1.38	1.37	1.40
	C5-C12	1.47	1.46	1.45
	C15-F1	1.35	1.34	1.36
Cl-Ph4DP	C3-C20	1.39	1.44	1.42
	O1-C5	1.38	1.36	1.40
	C5-C12	1.47	1.46	1.45
	C15-Cl2	1.76	1.74	1.77
Ph4DTP	C3-C20	1.40	1.45	1.44
	S1-C5	1.78	1.75	1.80
	C5-C12	1.48	1.48	1.47

Table S1. (b) Calculated bond angles for neutral, cationic and anionic geometries for the studied Ph4DP and Ph4DTP derivatives.

Molecules	Atomic specification	Bond angle *(θ)* in degree		
		Neutral geometry	Cationic geometry	Anionic geometry
Ph4DP	C3-C20-C19	123.44	122.28	123.32
	O1-C5-C12	112.16	113.21	112.55
	C4-C5-C12	126.39	126.77	126.78
F-Ph4DP	C3-C20-C19	123.45	122.28	123.34
	O1-C5-C12	112.02	113.12	112.33
	C4-C5-C12	126.48	126.87	126.92
Cl-Ph4DP	C3-C20-C19	123.42	122.28	123.28
	O1-C5-C12	112.16	113.13	112.48
	C4-C5-C12	126.39	126.83	126.80
Ph4DTP	C3-C20-C19	121.67	120.82	121.16
	S1-C5-C12	114.71	114.94	116.70
	C4-C5-C12	126.39	122.70	124.04

Table S1. (c) Calculated dihedral angle *(φ)* in neutral, cationic and anionic geometries of the studied Ph4DP and Ph4DTP derivatives.

Molecules	Atomic specification of adjacent rings	Torsion angle *(φ)* in degree		
		Neutral geometry	Cationic geometry	Anionic geometry
Ph4DP	C4-C3-C20-C19	0	0	0
	C4-C5-C12-C17	22.69	23.12	9.91
	O1-C5-C12-C13	20.92	21.88	8.51
F-Ph4DP	C4-C3-C20-C19	0.02	0	0.03
	C4-C5-C12-C17	23.38	22.83	10.72
	O1-C5-C12-C13	21.57	21.56	9.16
Cl-Ph4DP	C4-C3-C20-C19	0	0	0
	C4-C5-C12-C17	22.5	22.4	10
	O1-C5-C12-C13	20.6	21.1	8.58
Ph4DTP	C4-C3-C20-C19	4.4	2.75	10.23
	C4-C5-C12-C17	142.5	141.65	155.62
	S1-C5-C12-C13	141.35	139.75	153

Table S2: Calculated effective charge transfer integral (J_{eff}, in eV) for hole and electron transport in Ph4DP and Ph4DTP molecules.

θ (degrees)	$\lvert J_{eff} \rvert$ (eV)							
	Ph4DP		F-Ph4DP		Cl-Ph4DP		Ph4DTP	
	Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron
12	0.007	0.020	0.019	0.034	0.313	0.139	0.0	0.002
9	0.009	0.029	0.044	0.035	0.202	0.071	0.006	0.001
6	0.012	0.042	0.068	0.026	0.168	0.008	0.018	0.016
3	0.017	0.062	0.089	0.003	0.092	0.018	0.028	0.053
0	0.019	0.070	0.103	0.033	0.033	0.015	0.005	0.096
-3	0.002	0.096	0.106	0.083	0.004	0.014	0.112	0.077
-6	0.096	0.031	0.091	0.141	0.007	0.022	0.377	0.152
-9	0.120	0.020	0.054	0.200	0.008	0.010	0.624	0.630
-12	0.122	0.013	0.013	0.248	0.010	0.008	0.401	0.530