Supporting Information:

Effect of Asymmetric External Reorganization Energy on Electron and Hole Transport in Organic Semiconductors

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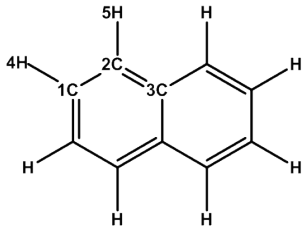
Table S1 The detailed SS-PFF parameters for molecules NAP, PEP, PFN and PFP.

	anion	cation	neutral

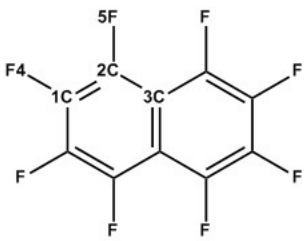
NAP



bond stretching			k_b	b_0	k_b	b_0	k_b	b_0
	1	2	392.3	1.4083	399.3	1.4036	487.7	1.3734
	1	1	452.2	1.3881	446.4	1.3892	396.8	1.4144
	1	4	385.4	1.0880	405.8	1.0830	399.1	1.0842
	2	3	372.0	1.4202	387.6	1.4116	393.7	1.4195
	2	5	385.4	1.0880	402.4	1.0844	397.5	1.0848
	3	3	285.6	1.4520	319.7	1.4299	313.5	1.4312
angle bending			k_θ	θ_0	k_θ	θ_0	k_θ	θ_0
1	1	2	24.06	120.09	24.44	120.17	25.06	120.30
2	3	3	24.13	118.33	24.45	118.01	24.91	118.83
4	1	2	24.33	119.73	25.80	119.62	25.46	120.13
2	3	2	31.04	123.33	30.62	121.98	31.09	122.34
1	2	3	24.44	121.58	24.80	120.83	25.70	120.87
4	1	1	24.57	120.18	25.68	120.22	25.41	119.58
1	2	5	24.64	119.96	25.77	119.75	25.46	120.43
5	2	3	24.97	118.47	25.75	119.43	25.63	118.71

torsional rotation				k_ϕ-anion	k_ϕ-cation	k_ϕ-neutral	γ	n
1	1	2	3	0.542	0.618	0.675	180.0	2
1	1	2	5	0.494	0.550	0.628	180.0	2
4	1	2	3	0.466	0.642	0.670	180.0	2
4	1	2	5	0.452	0.715	0.705	180.0	2
2	1	1	4	0.554	0.632	0.610	180.0	2
2	1	1	2	0.654	0.595	0.690	180.0	2
4	1	1	4	0.509	0.764	0.660	180.0	2
1	2	3	2	0.402	0.449	0.468	180.0	2
1	2	3	3	0.399	0.513	0.538	180.0	2
5	2	3	2	0.472	0.540	0.554	180.0	2
5	2	3	3	0.434	0.535	0.522	180.0	2
2	3	3	2	0.325	0.319	0.361	180.0	2

PFN



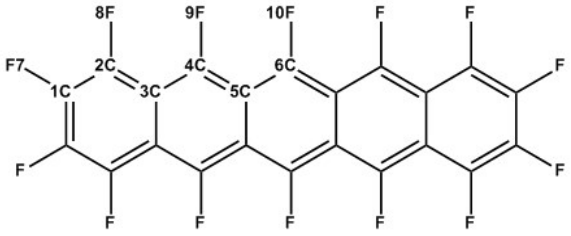
bond			k_b	b_0	k_b	b_0	k_b	b_0

stretching									
		2	3	390.6	1.4108	397.9	1.4123	404.3	1.4170
		3	3	279.0	1.4604	312.8	1.4371	306.1	1.4394
		1	2	403.4	1.4032	408.6	1.4042	494.0	1.3712
		2	5	418.1	1.3658	533.9	1.3087	477.9	1.3366
		1	1	479.8	1.3748	451.2	1.3883	414.0	1.4068
		1	4	432.8	1.3575	538.2	1.3101	488.5	1.3331
angle bending				k_θ	θ_0	k_θ	θ_0	k_θ	θ_0
	2	3	2	35.83	124.45	35.93	122.69	37.39	122.89
	2	3	3	24.35	117.78	24.80	118.65	25.63	118.56
	1	2	3	24.95	122.29	25.29	121.37	26.19	121.06
	3	2	5	41.64	120.86	43.36	121.22	43.21	120.76
	1	2	5	42.51	116.85	44.58	117.41	44.55	118.19
	1	1	2	24.88	119.94	25.18	119.98	25.89	120.39
	2	1	4	38.03	119.56	38.43	119.57	38.99	120.73
	1	1	4	37.64	120.50	38.07	120.46	38.61	118.89
torsional rotation				k_ϕ-anion		k_ϕ-cation	k_ϕ-neutral	γ	n
1	2	3	2	0.327		0.418	0.428	180.0	2
5	2	3	2	0.396		0.609	0.592	180.0	2
1	2	3	3	0.257		0.375	0.394	180.0	2
5	2	3	3	0.385		0.646	0.610	180.0	2
2	3	3	2	0.271		0.281	0.316	180.0	2
1	1	2	3	0.362		0.464	0.491	180.0	2
4	1	2	3	0.419		0.718	0.745	180.0	2
1	1	2	5	0.417		0.622	0.663	180.0	2
4	1	2	5	0.329		0.941	0.956	180.0	2
2	1	1	4	0.539		0.705	0.663	180.0	2
2	1	1	2	0.461		0.427	0.489	180.0	2
4	1	1	4	0.707		0.982	0.841	180.0	2
PEN									
bond stretching				k_b	b_0	k_b	b_0	k_b	b_0
		10	6	391.3	1.0861	402.6	1.0831	398.3	1.0842
		2	1	406.5	1.4071	410.3	1.4044	424.3	1.4004
		2	2	275.1	1.4613	285.6	1.4530	282.3	1.4553
		2	3	406.5	1.4072	414.9	1.4035	399.4	1.4132
		3	4	416.7	1.4022	417.4	1.4007	455.5	1.3861

		4	4	288.2	1.4492	292.5	1.4457	282.8	1.4530
		4	5	381.1	1.4238	386.4	1.4217	366.3	1.4351
		5	6	473.3	1.3766	480.7	1.3729	516.8	1.3617
		6	6	386.7	1.4168	385.8	1.4176	364.3	1.4317
		7	1	387.4	1.0871	398.0	1.0843	394.2	1.0856
		8	3	387.1	1.0878	398.0	1.0851	394.0	1.0856
		9	5	388.8	1.0872	400.2	1.0840	395.9	1.0852
angle bending				k_θ	θ_0	k_θ	θ_0	k_θ	θ_0
	1	2	2	23.85	119.10	23.65	118.57	24.03	119.02
	3	2	1	30.02	121.87	30.15	122.99	30.25	122.28
	10	6	5	25.66	120.03	25.00	120.21	25.36	120.22
	10	6	6	25.65	119.35	24.95	119.73	25.28	119.22
	2	1	2	24.94	121.81	24.93	122.89	25.38	121.95
	3	2	2	24.02	119.04	23.63	118.45	24.01	118.70
	4	3	2	25.07	121.69	25.11	122.72	25.40	121.95
	8	3	2	25.82	119.13	25.39	118.50	25.64	118.72
	3	4	4	23.99	119.27	23.94	118.84	24.11	119.36
	5	4	3	30.69	121.91	30.35	122.93	30.51	122.28
	4	4	5	24.66	118.83	24.19	118.24	24.31	118.37
	6	5	4	25.40	120.55	25.45	121.71	25.47	121.07
	5	6	6	24.52	120.63	24.63	120.06	24.48	120.56
	7	1	2	25.75	119.09	25.34	118.57	25.65	119.03
	8	3	4	25.85	119.19	25.36	118.79	25.65	119.34
	9	5	4	25.82	118.95	25.42	118.18	25.56	118.36
	9	5	6	25.75	120.51	25.21	120.12	25.42	120.57
torsional rotation				k_ϕ-anion		k_ϕ-cation	k_ϕ-neutral	γ	n
1	2	2	1	0.368		0.366	0.384	180.0	2
1	2	2	3	0.327		0.325	0.338	180.0	2
1	2	3	4	0.444		0.449	0.446	180.0	2
1	2	3	8	0.521		0.537	0.533	180.0	2
10	6	5	4	0.615		0.675	0.677	180.0	2
10	6	5	9	0.625		0.742	0.718	180.0	2
10	6	6	5	0.563		0.614	0.577	180.0	2
10	6	6	10	0.560		0.710	0.634	180.0	2
2	2	1	2	0.404		0.485	0.481	180.0	2
2	2	1	7	0.450		0.497	0.489	180.0	2
2	3	4	4	0.441		0.478	0.486	180.0	2
2	2	3	4	0.417		0.490	0.479	180.0	2
2	3	4	5	0.436		0.482	0.493	180.0	2
2	2	3	8	0.455		0.508	0.480	180.0	2
2	2	1	2	0.402		0.483	0.479	180.0	2

3	2	1	2	0.426	0.465	0.468	180.0	2
3	2	1	7	0.504	0.545	0.545	180.0	2
3	2	2	3	0.353	0.389	0.378	180.0	2
3	4	4	3	0.396	0.361	0.392	180.0	2
3	4	4	5	0.334	0.343	0.342	180.0	2
3	4	5	6	0.460	0.431	0.431	180.0	2
3	4	5	9	0.531	0.543	0.532	180.0	2
4	4	3	8	0.472	0.499	0.507	180.0	2
4	5	6	6	0.648	0.638	0.650	180.0	2
4	4	5	6	0.492	0.521	0.512	180.0	2
4	4	5	9	0.486	0.530	0.492	180.0	2
5	4	3	8	0.509	0.568	0.566	180.0	2
5	4	4	5	0.368	0.413	0.384	180.0	2
5	6	6	5	0.674	0.649	0.665	180.0	2
5	4	3	8	0.508	0.568	0.566	180.0	2
6	5	4	3	0.462	0.432	0.432	180.0	2
6	6	5	9	0.602	0.619	0.627	180.0	2

PFP



bond stretching			k_b	b_0	k_b	b_0	k_b	b_0
	1	7	456.6	1.3472	519.2	1.3182	488.7	1.3325
	2	8	451.2	1.3473	501.1	1.3244	477.8	1.3360
	4	9	433.0	1.3538	496.6	1.3222	467.5	1.3373
	6	10	430.3	1.3552	501.0	1.3194	469.0	1.3358
	1	2	491.5	1.3703	475.3	1.3773	523.5	1.3602
	2	3	394.4	1.4223	400.9	1.4191	379.8	1.4333
	1	1	410.4	1.4066	407.9	1.4093	387.4	1.4222
	3	4	433.3	1.4011	427.4	1.4046	467.6	1.3875
	3	3	294.4	1.4516	300.3	1.4475	289.7	1.4559
	4	5	426.6	1.4055	426.6	1.4064	414.9	1.4148
	5	6	424.7	1.4062	422.2	1.4080	438.4	1.4025
	5	5	293.0	1.4580	299.8	1.4530	298.9	1.4530
angle bending			k_θ	θ_0	k_θ	θ_0	k_θ	θ_0
1	2	8	46.33	117.17	45.92	117.97	45.94	118.27
3	2	8	44.40	121.21	44.19	121.32	44.07	120.72
1	2	3	26.05	121.63	25.88	120.72	25.98	121.02
2	1	7	39.00	120.79	39.19	120.52	39.24	121.13
1	1	7	38.44	118.90	38.82	118.90	38.80	118.13

	1	1	2	25.56	120.31	25.45	120.58	25.41	120.74
	2	3	4	39.09	123.88	39.69	122.67	39.65	123.08
	2	3	3	25.58	118.07	26.06	118.71	25.80	118.25
	3	3	4	25.76	118.07	25.84	118.63	26.04	118.68
	3	4	9	53.66	117.29	54.33	118.20	54.59	118.49
	5	4	9	53.03	118.60	53.96	118.89	54.04	118.32
	3	4	5	26.07	124.12	26.11	122.91	26.42	123.19
	4	5	6	41.25	124.30	41.52	123.01	42.27	123.40
	4	5	5	25.96	117.82	26.46	118.46	26.69	118.14
	5	5	6	26.08	117.88	26.37	118.54	26.77	118.47
	5	6	10	54.25	117.88	55.48	118.54	55.70	118.47
	5	6	5	25.89	124.24	26.09	122.92	26.47	123.06

torsional rotation				k_ϕ-anion	k_ϕ-cation	k_ϕ-neutral	γ	n
7	1	2	8	0.847	0.981	0.975	180.0	2
1	1	2	8	0.609	0.639	0.641	180.0	2
7	1	2	3	0.676	0.750	0.752	180.0	2
1	1	2	3	0.462	0.449	0.451	180.0	2
8	2	3	3	0.554	0.615	0.556	180.0	2
8	2	3	4	0.532	0.580	0.544	180.0	2
1	2	3	3	0.347	0.369	0.357	180.0	2
1	2	3	4	0.400	0.385	0.377	180.0	2
7	1	1	7	0.699	0.901	0.769	180.0	2
2	1	1	7	0.585	0.675	0.616	180.0	2
2	1	1	2	0.465	0.449	0.453	180.0	2
2	3	4	9	0.508	0.610	0.604	180.0	2
2	3	4	5	0.353	0.418	0.420	180.0	2
3	3	4	9	0.504	0.560	0.566	180.0	2
3	3	4	5	0.307	0.365	0.367	180.0	2
2	3	3	2	0.241	0.291	0.265	180.0	2
2	3	3	4	0.279	0.295	0.290	180.0	2
4	3	3	4	0.256	0.231	0.257	180.0	2
9	4	5	6	0.506	0.592	0.558	180.0	2
9	4	5	5	0.497	0.584	0.539	180.0	2
3	4	5	6	0.357	0.385	0.376	180.0	2
3	4	5	5	0.283	0.386	0.372	180.0	2
4	5	6	10	0.471	0.594	0.569	180.0	2
4	5	6	5	0.327	0.396	0.391	180.0	2
5	5	6	10	0.467	0.565	0.542	180.0	2
5	5	6	5	0.257	0.379	0.370	180.0	2
4	5	5	4	0.211	0.271	0.264	180.0	2
4	5	5	6	0.256	0.260	0.270	180.0	2
6	5	5	6	0.223	0.248	0.265	180.0	2

Table S2. The electron couplings for ET and HT reactions based on the optimized neutral supercells and containing electron/hole supercells.

The sizes of supercells are defined in main text. The electron couplings are calculated by isolated orbitals methods as our previous paper[1, 2]. The P1 , P2 and P3 pathways are the same directions described in Figure 4 of main text. The optimized center-to-center distances of the closest channels in ab-plane of crystals also are listed in Å.

		$\|H_{AD}\|$(meV)				Distance(Å)		
		Hole[a]	electron[a]	hole[b]	electron[c]	Neutral	HT	ET
NAP	P1	19.7	47.8	14.6	39.8	5.03	5.08	5.18
	P2	19.7	47.8	15.1	40.8	5.03	5.10	5.02
	P3	44.1	30.2	43.9	30.7	5.94	5.97	5.95
PEN	P1	102.2	102.9	84.7	67.5	4.69	4.75	5.05
	P2	35.1	46.6	18.8	35.2	6.24	6.38	6.47
	P3	59.5	103.6	72.4	77.2	5.16	5.35	5.34
PFN	P1	33.9	29.4	12.4	42.2	5.00	5.09	4.96
	P2	5.22	19.4	12.4	8.2	6.49	6.82	6.29
	P3	5.22	19.5	7.5	17.3	6.49	6.76	6.40
PFP	P1	155.9	93.9	80.3	129.2	4.49	4.67	4.43
	P2	1.9	3.1	4.7	3.8	6.15	6.14	6.24
	P3	1.9	3.1	3.6	2.6	6.15	6.16	6.23

[a], [b] and [c] mean that H_{AD}s are calculated on the basis of optimized supercells in neutral, hole-transfer and electron-transfer states, respectively.

Table S3. Electron-vibration couplings for some significant vibrations whose λ_i >5cm^{-1} during ET and HT processes in NAP molecule.

HT	Netrual	HT	Cation	ET	Neutral	ET	Anion
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
520	23.3	515	24.7	520	244.8	511	235.9
1184	31.3	1065	14.8	773	38.3	749	51.6
1399	274.9	1204	35.0	1184	56.7	1051	19.1
1490	37.6	1405	352.4	1399	470.3	1157	35.6
1615	419.0	1500	31.5	1615	299.7	1366	380.8
		1623	285.6	3188	6.1	1466	7.2
						1597	303.5
						3141	7.8

Table S4. Electron-vibration couplings for some significant vibrations whose λ_i >5cm^{-1} during ET and HT processes in PEN molecule.

HT	Netrual	HT	Cation	ET	Neutral	ET	Anion
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
264	8.3	263	8.0	264	164.1	263	145.1
1019	6.6	1039	4.3	616	28	616	27.0
1184	15.7	1196	26.8	762	10.3	753	8.8
1207	59.6	1218	57.0	1184	26.2	796	5.9
1411	110.7	1329	6.0	1207	71.2	1170	26.4
1435	15.5	1411	4.5	1411	154.5	1208	60.6
1558	136.2	1427	139.9	1435	47.8	1312	7.0
1577	20.6	1549	81.9	1493	6.5	1393	8.9
		1578	55.5	1558	25.3	1411	199.9
				1577	11.1	1535	33.4
						1564	8.6

Table S5. Electron-vibration couplings for some significant vibrations whose λ_i >5cm^{-1} during ET and HT processes in PFN molecule.

HT	Netrual	HT	Cation	ET	Neutral	ET	Anion
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
277	21.6	278	14.6	277	2.0	269	4.6
296	16.8	296	17.8	296	183	288	160.6
390	36.5	390	37.8	390	155.3	381	144.7
511	132.3	513	128.3	511	321.1	498	333.7
1083	52.6	1113	51.7	1083	8.8	1035	1.6
1252	142.6	1300	128	1252	283.8	1194	248.4
1386	54	1400	240.2	1386	894.5	1373	585.6
1531	358	1571	774.9	1531	230.4	1504	105.7
1653	917.8	1644	333	1653	99.2	1658	458.4

Table S6. Electron-vibration couplings for some significant vibrations whose λ_i >5cm^{-1} during ET and HT processes in PFP molecule.

HT	Netrual	HT	Cation	ET	Neutral	ET	Anion
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
177	3.7	177	3.3	177	131.3	176	128.5

281	5.2	282	5	281	19.3	278	21.1
492	76.9	494	76.6	344	8.7	344	8.8
706	28	712	29.3	454	10.4	451	12.9
1019	12.5	1027	15.2	492	14.3	487	10.4
1121	9.3	1149	9.4	706	11.1	697	13.3
1257	130.2	1285	176.3	1019	14	989	10.3
1363	100.1	1377	144	1121	6.3	1090	6.8
1401	75.4	1411	19.5	1222	10.3	1196	7.3
1503	71.5	1445	33.3	1257	233.2	1227	224.6
1572	90.4	1520	40.2	1363	448.6	1367	279.7
1628	344.6	1554	80.6	1401	21.9	1396	168.6
		1620	333	1503	22.3	1442	5.4
				1572	10.5	1514	43
				1628	30.8	1546	8.6
						1604	12.8

Table S7. The effective vibration frequency and its Huang-Ryhs factors for ET and HT reactions under the one-mode approximation.

$$\omega_{eff} = \sum \omega_i S_i / \sum S_i$$

$$S_{eff} = \lambda_{int} / h\omega_{eff} \qquad \lambda_{int} = \sum h\omega_i S_i$$

	Hole			electron		
	$\omega_{eff}(cm^{-1})$	S_{eff}	λ_{int}(meV)	$\omega_{eff}(cm^{-1})$	S_{eff}	λ_{int}(meV)
NAP	1412	1.1	191.1	1008	2.2	268.7
PEN	1328	0.58	95.6	622	1.7	134.3
PFN	1172	2.95	429.4	794	5.32	523.4
PFP	1175	1.63	238.1	660	2.98	243.6

Table S8. The reorganization energies including internal and external contributions for different CT channels.

		λ_{int}(meV)		λ_{ext} (meV)		λ_{tot}(meV)	
		Hole	Electron	hole	electron	hole	electron
NAP	P1	197.6	243.6	29.9	226.8	227.4	470.4
	P2	198.7	247.2	35.8	224.8	234.5	472.0
	P3	198.6	246.9	25.8	251.3	224.4	498.2
PEN	P1	115.3	132.8	31.1	219.0	146.5	351.8
	P2	113.1	137.5	50.4	214.3	163.4	351.8
	P3	112.1	141.9	15.3	225.8	127.4	367.7
PFN	P1	443.6	511.6	71.2	21.2	514.8	532.8
	P2	447.8	516.6	119.9	55.5	567.7	572.2

	P3	444.4	511.6	126.3	58.7	570.7	570.3
PFP	P1	277.5	272.4	161.9	131.2	439.4	403.6
	P2	272.6	279.0	157.6	143.0	430.2	422.0
	P3	276.7	294.3	137.1	122.9	413.8	417.2

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