SUPPORTING INFORMATION

A Hammett's Analysis of the Substituent Effect in Functionalized Diketopyrrolopyrrole (DPP) Systems: Optoelectronic Properties and Intramolecular Charge Transfer Effects

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Table S1. Different Hammett's constants for a set of different substituents.*

X	σ_m	σ_p	σ_R	σ_I	σ_p^+	σ_p^-	σ_m^0	σ_p^0
–H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
–Br	0.39	0.23	-0.25	0.47	0.15	0.25	0.39	0.23
–Ph	0.06	-0.01	-0.11	0.12	0.18	0.53	0.06	0.04
–CCH	0.21	0.23	-0.04	0.29	0.18	0.53	0.21	0.23
$-CF_3$	0.43	0.54	0.11	0.40	0.61	0.65	0.43	0.54
–Me	-0.07	-0.17	-0.16	-0.01	-0.31	-0.17	-0.07	-0.12
$-CHF_2$	0.32	0.35	0.03	0.32			0.32	0.35
–CHO	0.35	0.42	0.15	0.27	0.73	1.03	0.35	0.54
–Cl	0.37	0.23	-0.25	0.47	0.11	0.19	0.37	0.23
–CN	0.56	0.66	0.08	0.57	0.66	1.00	0.56	0.66
–COMe	0.38	0.50	0.20	0.30		0.84	0.38	0.50
–COOMe	0.37	0.45	0.11	0.32	0.49	0.75	0.37	0.45
–COOH	0.37	0.45	0.11	0.30	0.42	0.77	0.37	0.45
–F	0.34	0.06	-0.48	0.54	-0.07	-0.03	0.34	0.21
$-NMe_2$	-0.16	-0.83	-0.88	0.17	-1.70	-0.12	-0.16	-0.48
$-NH_2$	-0.16	-0.66	-0.80	0.17	-1.30	-0.15	-0.16	-0.38
–NHMe	-0.21	-0.70	-0.83	0.13	-1.81		-0.21	-0.33
$-NO_2$	0.71	0.78	0.10	0.67	0.79	1.27	0.71	0.81
–OMe	0.12	-0.27	-0.58	0.30	-0.78	-0.26	0.12	0.11
–OH	0.12	-0.37	-0.62	0.24	-0.92	-0.37	0.12	-0.13
$-SO_2Me$	0.64	0.73	0.11	0.59		1.13	0.64	0.75

* Ref. [1]–[9].

Table S2. Coordinates of all DPP-X derivatives. Calculations at the B3LYP-D3/Def2-TZVP level.

DPP-H

N	-2.78800	-0.14707	-0.14459
C	-2.49910	-1.02751	-1.23663
C	-2.83959	-0.80695	1.06138
C	-2.59539	-2.12700	0.84674
C	-2.37710	-2.31884	-0.56551
C	-2.13295	-3.63890	-0.78015
C	-2.47328	-3.41831	1.51788
N	-2.18452	-4.29877	0.42582
O	-2.40430	-0.66962	-2.38826
O	-2.56818	-3.77621	2.66950
H	-3.04710	-0.27725	1.97809
H	-1.92550	-4.16861	-1.69686
H	-2.04224	-5.28547	0.56181
H	-2.93038	0.83962	-0.28059

DPP-X_1 derivatives

DPP-Br

N	-2.79178	-0.13869	-0.12515
C	-2.50091	-1.02341	-1.21217
C	-2.84661	-0.79001	1.08457
C	-2.60216	-2.11211	0.87969
C	-2.38243	-2.30906	-0.53408
C	-2.14248	-3.63137	-0.72697
C	-2.48177	-3.39591	1.56310
N	-2.19092	-4.29088	0.47794
O	-2.40033	-0.67599	-2.36583
O	-2.57709	-3.74429	2.71543
Br	-1.78740	-4.55733	-2.30659
H	-2.04713	-5.27882	0.60595
H	-2.93350	0.84722	-0.26801
H	-3.05731	-0.25675	1.99814

DPP-Ph

N	-2.89161	-0.08368	-0.15049
C	-2.59684	-0.88419	-1.28945
C	-2.97124	-0.80920	1.02724
C	-2.72842	-2.12890	0.70447
C	-2.48947	-2.21940	-0.71063
C	-2.23529	-3.51718	-1.02702
C	-2.61206	-3.46684	1.26982
N	-2.30186	-4.26133	0.12879
O	-2.48786	-0.45009	-2.41396
O	-2.72719	-3.92315	2.39281
C	-3.25765	-0.18744	2.30579
C	-3.36531	-0.98603	3.45577
C	-3.63961	-0.40575	4.68344
C	-3.80956	0.97102	4.79171
C	-3.70205	1.77168	3.65925
C	-3.42932	1.19957	2.42733
H	-3.34538	1.84624	1.56396
H	-3.23067	-2.05721	3.37708
H	-3.72048	-1.03288	5.56173
H	-4.02353	1.41925	5.75344
H	-3.83040	2.84340	3.73672
H	-2.16997	-5.25621	0.19792
H	-3.04108	0.90609	-0.23872
H	-2.01014	-3.97378	-1.97746

DPP-CCH

N	-2.78307	-0.13977	-0.19330
C	-2.49483	-1.03201	-1.26576
C	-2.84069	-0.78252	1.03645
C	-2.59519	-2.11418	0.82503
C	-2.37588	-2.31677	-0.57812
C	-2.13148	-3.64127	-0.78224
C	-2.47629	-3.39812	1.51096
N	-2.18574	-4.29006	0.42713
O	-2.39560	-0.69557	-2.42357
O	-2.57449	-3.74351	2.66526
C	-3.11130	-0.08443	2.22517
H	-2.04479	-5.27555	0.57315
H	-2.92527	0.84721	-0.33030
C	-3.34346	0.51787	3.23966
H	-3.54739	1.03702	4.14463
H	-1.92260	-4.17551	-1.69581

DPP-CF_3

N	-2.76392	-0.55016	-0.99333
C	-2.49541	-1.59908	-1.92977
C	-2.77345	-1.00771	0.30536
C	-2.50293	-2.34009	0.31394
C	-2.31902	-2.75478	-1.05395
C	-2.04229	-4.08672	-1.06052
C	-2.31716	-3.51208	1.18169
N	-2.04087	-4.54737	0.23215
O	-2.45457	-1.44593	-3.12729
O	-2.35896	-3.68371	2.37385
C	-3.01218	-0.06100	1.44245
H	-1.84351	-4.74862	-1.88918
H	-1.85621	-5.49371	0.52046
H	-2.98868	0.38801	-1.28281
F	-1.91332	0.68005	1.69766
F	-3.34550	-0.70671	2.55712
F	-4.00336	0.80645	1.13631

DPP-Me

N	-2.66828	-0.14623	-0.16548
C	-2.37858	-1.05130	-1.23551
C	-2.80828	-0.79088	1.04439
C	-2.62286	-2.12261	0.84791
C	-2.35239	-2.33568	-0.55101
C	-2.16181	-3.66898	-0.76697
C	-2.59350	-3.41744	1.52386
N	-2.30342	-4.31349	0.44698
O	-2.21618	-0.71234	-2.38889
O	-2.75298	-3.76669	2.67119
C	-1.85438	-4.40242	-2.01782
H	-2.21403	-5.30546	0.59315
H	-2.75537	0.84459	-0.31660
H	-1.77929	-3.70367	-2.84806
H	-2.63571	-5.13463	-2.24039
H	-0.91058	-4.94719	-1.92580
H	-3.02872	-0.24241	1.94663

DPP-CHF_2

N	-2.46029	-0.57222	-1.20614
C	-2.10015	-1.72152	-1.97426
C	-2.65906	-0.87327	0.12277
C	-2.44796	-2.20389	0.30852
C	-2.09811	-2.77767	-0.96292
C	-1.88493	-4.10822	-0.78500
C	-2.44414	-3.26755	1.31516
N	-2.08133	-4.41657	0.54150
O	-1.87364	-1.71020	-3.16238

O	-2.66887	-3.29102	2.50151
C	-1.49922	-5.13030	-1.79770
H	-1.99124	-5.33484	0.94524
H	-2.54846	0.34009	-1.62154
F	-2.43410	-6.13018	-1.83164
H	-1.40203	-4.70105	-2.79446
F	-0.31113	-5.71239	-1.44493
H	-2.93635	-0.10776	0.83048

DPP-CHO

N	-2.53609	-0.51798	-1.01283
C	-2.25387	-1.56770	-1.93004
C	-2.70087	-0.97233	0.27696
C	-2.53981	-2.33224	0.27983
C	-2.26227	-2.75166	-1.05952
C	-2.10277	-4.10560	-1.05557
C	-2.54723	-3.51361	1.14953
N	-2.26555	-4.56941	0.22695
O	-2.07050	-1.42028	-3.11486
O	-2.72949	-3.67219	2.33259
C	-2.99653	-0.06313	1.38482
H	-1.88412	-4.78200	-1.86742
H	-2.20088	-5.53083	0.51738
H	-2.60698	0.45312	-1.27396
O	-3.11325	1.13250	1.22588
H	-3.10506	-0.54627	2.36946

DPP-Cl

N	-2.46870	-0.50263	-1.00451
C	-2.21311	-1.58545	-1.90555
C	-2.66390	-0.92685	0.28868
C	-2.55331	-2.28186	0.32361
C	-2.27326	-2.74023	-1.01672
C	-2.16619	-4.09414	-0.96599
C	-2.61557	-3.43238	1.21881
N	-2.36027	-4.52614	0.32516
O	-2.01172	-1.45127	-3.09005
O	-2.81830	-3.56382	2.40200
Cl	-1.84891	-5.21278	-2.20730
H	-2.33433	-5.48701	0.62400
H	-2.49279	0.45281	-1.31931
H	-2.86713	-0.22650	1.08304

DPP-CN

N	-2.79251	-0.12837	-0.13594
C	-2.50447	-1.00173	-1.22871
C	-2.84153	-0.80277	1.07363
C	-2.59470	-2.12608	0.84272
C	-2.38056	-2.29831	-0.56400
C	-2.13411	-3.61952	-0.79455
C	-2.46904	-3.43076	1.50183
N	-2.18062	-4.29642	0.39652
O	-2.41034	-0.64350	-2.37820
O	-2.56248	-3.79548	2.64626
C	-3.11255	-0.12261	2.28307
H	-2.03695	-5.28519	0.51840
H	-2.93752	0.86138	-0.25252
N	-3.33630	0.46280	3.25067
H	-1.92827	-4.13213	-1.72114

DPP-COMe

N	-2.46780	-0.47928	-0.98791
C	-2.21325	-1.54523	-1.89210
C	-2.66474	-0.90943	0.30371
C	-2.55268	-2.27579	0.32524
C	-2.27383	-2.71803	-1.01149
C	-2.16301	-4.07468	-0.99955
C	-2.61188	-3.45335	1.19676
N	-2.35778	-4.52215	0.28567
O	-2.00975	-1.41495	-3.07639
O	-2.81362	-3.60735	2.38021
C	-2.94348	0.08703	1.36703
H	-2.33352	-5.48229	0.58584
H	-2.50275	0.49397	-1.24989
O	-2.99324	1.26271	1.06005
C	-3.14765	-0.41803	2.76426
H	-2.26412	-0.96086	3.10686
H	-3.96671	-1.13924	2.79532
H	-3.35488	0.42116	3.42352
H	-1.96008	-4.76269	-1.80514

DPP-COOMe

N	-2.55122	-0.50913	-0.91469
C	-2.27194	-1.53072	-1.86358
C	-2.70761	-1.00267	0.36105
C	-2.54226	-2.35942	0.33185
C	-2.26989	-2.73458	-1.02810
C	-2.10384	-4.08519	-1.07525
C	-2.53782	-3.57496	1.15698
N	-2.25699	-4.59450	0.18923
O	-2.09638	-1.34528	-3.04573
O	-2.70828	-3.79611	2.33056
C	-3.00584	-0.05831	1.45447
H	-1.88752	-4.72830	-1.91427
H	-2.18531	-5.56441	0.44706
H	-2.63002	0.46976	-1.14210
O	-3.12076	1.13263	1.27393
O	-3.12721	-0.68172	2.62343
C	-3.42706	0.14793	3.75821
H	-4.37028	0.67074	3.60370
H	-2.63263	0.87747	3.91200
H	-3.49537	-0.53349	4.60032

DPP-COOH

N	-2.51826	-0.54248	-1.07274
C	-2.28592	-1.65044	-1.95480
C	-2.64912	-0.93636	0.23148
C	-2.51547	-2.28985	0.28627
C	-2.28909	-2.79808	-1.02968
C	-2.16178	-4.14981	-0.92345
C	-2.52583	-3.38000	1.23214
N	-2.29992	-4.50741	0.40933
O	-2.13767	-1.55228	-3.14627
O	-2.68446	-3.38218	2.44346
C	-2.89469	0.02585	1.33635
H	-2.24966	-5.44573	0.77031
H	-2.57759	0.41800	-1.37518
O	-2.99031	1.20722	1.12409
O	-2.99894	-0.50293	2.55713
H	-2.90114	-1.48232	2.59377
H	-1.98370	-4.89907	-1.67809

DPP-F

N	-2.78579	-0.15605	-0.14462
C	-2.50112	-1.02581	-1.24529
C	-2.83571	-0.81834	1.05912
C	-2.59521	-2.13701	0.83808
C	-2.37804	-2.31925	-0.58323
C	-2.13524	-3.64134	-0.75866
C	-2.47492	-3.42069	1.51945
N	-2.18303	-4.31629	0.43007
O	-2.41090	-0.65919	-2.39370
O	-2.57008	-3.77194	2.66969
F	-1.87068	-4.32146	-1.85128

H	-2.03773	-5.30624	0.54340
H	-2.92601	0.83161	-0.27716
H	-3.03735	-0.29539	1.98016

DPP-NMe_2

N	-2.50271	-0.59840	-1.52864
C	-2.03417	-1.74084	-2.25391
C	-3.04212	-0.93234	-0.29531
C	-2.91734	-2.31149	-0.14110
C	-2.29250	-2.83318	-1.33130
C	-2.13294	-4.17592	-1.18581
C	-3.13714	-3.40185	0.77577
N	-2.63463	-4.51972	0.05077
O	-1.56379	-1.66916	-3.36599
O	-3.61338	-3.49129	1.90237
N	-3.54425	0.00353	0.52013
H	-1.70630	-4.90892	-1.85011
H	-2.65547	-5.44665	0.44077
H	-2.55584	0.30207	-1.97112
C	-3.61034	1.39828	0.12225
C	-4.27925	-0.37659	1.72161
H	-5.35124	-0.20805	1.57863
H	-3.93931	0.23423	2.55972
H	-4.11360	-1.42684	1.95591
H	-4.45946	1.59856	-0.54119
H	-2.68889	1.70783	-0.37063
H	-3.72639	2.00781	1.01642

DPP-NH_2

N	-2.92705	-0.15555	-0.19147
C	-2.66491	-1.05954	-1.28175
C	-2.83049	-0.78157	1.03436
C	-2.54600	-2.10953	0.81892
C	-2.44270	-2.32761	-0.59865
C	-2.21296	-3.65376	-0.80199
C	-2.37617	-3.35646	1.51279
N	-2.16666	-4.26960	0.43261
O	-2.65876	-0.71228	-2.43845
O	-2.38863	-3.66913	2.69305
N	-2.97363	-0.11649	2.19717
H	-2.00425	-5.24976	0.59097
H	-2.99171	0.83801	-0.33981
H	-2.99703	-0.67148	3.03772
H	-3.44010	0.77348	2.22269
H	-2.08515	-4.21287	-1.71438

DPP-NHMe

N	-2.63593	-0.54930	-1.20215
C	-2.29632	-1.69972	-2.00123
C	-2.69942	-0.85128	0.14293
C	-2.40586	-2.19242	0.29419
C	-2.14947	-2.75073	-1.00410
C	-1.84958	-4.07003	-0.84021
C	-2.25780	-3.20559	1.29610
N	-1.91089	-4.35008	0.50923
O	-2.19335	-1.65531	-3.20437
O	-2.37099	-3.20909	2.51425
N	-2.99833	0.05680	1.08011
H	-1.73888	-5.24897	0.92694
H	-2.81942	0.34593	-1.62149
C	-3.28132	1.45295	0.82024
H	-3.01070	-0.28591	2.02692
H	-4.16112	1.57207	0.18163
H	-2.43063	1.95419	0.34991
H	-3.48330	1.94867	1.76647
H	-1.59792	-4.82963	-1.56208

DPP-NO_2

N	-2.78693	-0.12990	-0.16556
C	-2.49785	-1.02525	-1.24027
C	-2.83824	-0.79014	1.03348
C	-2.59882	-2.11856	0.86007
C	-2.38046	-2.31031	-0.54636
C	-2.13490	-3.63498	-0.76348
C	-2.47586	-3.42615	1.53075
N	-2.18559	-4.30007	0.42895
O	-2.39495	-0.69939	-2.39754
O	-2.57056	-3.79372	2.67004
N	-3.11762	-0.05507	2.24129
H	-2.04430	-5.28801	0.56058
H	-2.93448	0.86227	-0.26468
O	-3.30709	1.15150	2.10985
O	-3.14241	-0.68170	3.28488
H	-1.92724	-4.15297	-1.68714

DPP-OMe

N	-2.93243	0.24837	-0.31795
C	-2.53268	-0.43060	-1.51192
C	-2.68095	-0.49661	0.81025
C	-2.11162	-1.69661	0.44917
C	-2.00401	-1.68828	-0.99401
C	-1.44635	-2.86078	-1.38839
C	-1.58511	-2.95796	0.94323
N	-1.19443	-3.61342	-0.26105
O	-2.65387	0.03026	-2.62209
O	-1.45446	-3.45090	2.04916
O	-3.01163	0.03919	1.96469
H	-0.78607	-4.53271	-0.24691
H	-3.34207	1.16793	-0.31277
C	-2.71316	-0.74035	3.14489
H	-3.22296	-1.70021	3.09754
H	-3.07193	-0.14739	3.98025
H	-1.64005	-0.90653	3.21677
H	-1.20720	-3.22463	-2.37424

DPP-OH

N	-2.80624	-0.19716	0.05002
C	-2.52081	-1.03245	-1.07202
C	-2.84859	-0.89974	1.23822
C	-2.59891	-2.20849	0.96670
C	-2.39074	-2.32836	-0.45401
C	-2.13855	-3.64361	-0.72554
C	-2.46296	-3.53097	1.57341
N	-2.17372	-4.36675	0.43673
O	-2.42978	-0.64674	-2.22419
O	-2.54581	-3.94752	2.70253
O	-1.88288	-4.27770	-1.86245
H	-2.02333	-5.36003	0.50415
H	-2.95261	0.79344	-0.04875
H	-1.89549	-3.63743	-2.58990
H	-3.05227	-0.40536	2.17409

DPP-SO_2Me

N	-2.36343	-0.52080	-1.40239
C	-2.11693	-1.65708	-2.24286
C	-2.73345	-0.89167	-0.13711
C	-2.75398	-2.25038	-0.04721
C	-2.36911	-2.77563	-1.33172
C	-2.35315	-4.13286	-1.24215
C	-2.99908	-3.36938	0.85942
N	-2.71965	-4.49648	0.03418
O	-1.79567	-1.58577	-3.40334
O	-3.36188	-3.43854	2.01366
S	-3.00405	0.37422	1.09281

H	-2.10374	-4.87616	-1.98306
H	-2.79886	-5.43948	0.37685
H	-2.34523	0.43407	-1.72765
O	-3.39816	1.54740	0.35010
O	-1.84523	0.40816	1.94398
C	-4.37802	-0.25952	2.01672
H	-5.25393	-0.29355	1.37272
H	-4.52705	0.44487	2.83506
H	-4.11616	-1.24677	2.39812

DPP-X_2 derivatives

DPP-Br_2

N	-2.46513	-0.49549	-1.02117
C	-2.21208	-1.59202	-1.91291
C	-2.66060	-0.91977	0.27079
C	-2.55482	-2.27344	0.32709
C	-2.27487	-2.73709	-1.01422
C	-2.16912	-4.09074	-0.95792
C	-2.61758	-3.41850	1.22579
N	-2.36459	-4.51503	0.33404
O	-2.01139	-1.46899	-3.09672
O	-2.81830	-3.54153	2.40959
Br	-3.01324	0.29985	1.63475
Br	-1.81651	-5.31035	-2.32190
H	-2.34040	-5.47378	0.63993
H	-2.48935	0.46325	-1.32707

DPP-Ph_2

N	-2.84298	-0.08400	-0.14276
C	-2.53974	-0.88128	-1.27342
C	-2.94555	-0.81069	1.03271
C	-2.71854	-2.13076	0.69825
C	-2.46838	-2.22302	-0.71091
C	-2.26547	-3.54590	-1.04949
C	-2.65868	-3.47404	1.25861
N	-2.38537	-4.27468	0.12294
O	-2.39137	-0.42764	-2.39340
O	-2.78338	-3.92536	2.38244
C	-3.24584	-0.19106	2.30768
C	-3.28957	-0.97743	3.47057
C	-3.57235	-0.39549	4.69535
C	-3.81596	0.97140	4.78960
C	-3.77729	1.75928	3.64392
C	-3.49604	1.18556	2.41459
H	-3.48171	1.82091	1.53884
H	-3.10384	-2.04151	3.40270
H	-3.60284	-1.01407	5.58293
H	-4.03637	1.42081	5.74930
H	-3.96832	2.82257	3.70830
C	-1.98526	-4.16874	-2.32738
C	-1.80864	-3.36923	-3.46844
C	-1.88452	-5.56217	-2.45797
C	-1.53570	-3.95427	-4.69405
C	-1.43506	-5.33730	-4.81086
C	-1.61248	-6.13879	-3.68795
H	-2.02771	-6.21031	-1.60346
H	-1.89037	-2.29332	-3.38400
H	-1.40128	-3.32546	-5.56461
H	-1.22165	-5.78899	-5.77106
H	-1.53984	-7.21538	-3.77115
H	-2.24896	-5.26608	0.21357
H	-2.91434	0.91514	-0.22225

DPP-$(CCH)_2$

N	-2.78141	-0.14335	-0.19706
C	-2.49292	-1.03861	-1.26789
C	-2.83921	-0.78390	1.03202
C	-2.59311	-2.11835	0.82066
C	-2.37533	-2.32114	-0.57497
C	-2.12949	-3.65562	-0.78638
C	-2.47531	-3.40085	1.51360
N	-2.18729	-4.29619	0.44271
O	-2.39301	-0.70710	-2.42621
O	-2.57544	-3.73240	2.67189
C	-3.11023	-0.08788	2.22067
C	-1.85868	-4.35167	-1.97506
H	-2.04519	-5.28289	0.58194
H	-2.92373	0.84332	-0.33633
C	-3.34277	0.51130	3.23711
H	-3.54729	1.02841	4.14316
C	-1.62631	-4.95088	-2.99152
H	-1.42195	-5.46800	-3.89760

DPP-$(CF_3)_2$

N	-2.20887	-0.64492	-1.26517
C	-2.00480	-1.85953	-1.99517
C	-2.57833	-0.87991	0.03619
C	-2.63351	-2.22149	0.25579
C	-2.28130	-2.88016	-0.97608
C	-2.29067	-4.22044	-0.74349
C	-2.87073	-3.24056	1.28547
N	-2.62625	-4.45475	0.56750
O	-1.68833	-1.90588	-3.15583
O	-3.18898	-3.19160	2.44573
C	-2.79391	0.26554	0.98630
C	-1.94273	-5.36146	-1.65594
H	-2.75844	-5.36393	0.98110
H	-2.15277	0.26316	-1.69777
F	-0.65200	-5.71684	-1.50473
F	-2.69035	-6.44625	-1.35672
F	-3.15351	1.37588	0.30569
F	-3.74366	-0.00703	1.87881
F	-2.14277	-5.04819	-2.93302
F	-1.66244	0.55829	1.65247

DPP-Me_2

N	-2.66765	-0.14265	-0.16847
C	-2.37702	-1.04427	-1.23885
C	-2.81113	-0.78141	1.05142
C	-2.62151	-2.11443	0.83926
C	-2.35011	-2.33130	-0.55787
C	-2.16116	-3.66439	-0.77014
C	-2.59401	-3.40139	1.52034
N	-2.30470	-4.30317	0.44973
O	-2.21534	-0.70315	-2.39168
O	-2.75633	-3.74259	2.67306
C	-3.11811	-0.03916	2.29762
C	-1.85474	-4.40670	-2.01646
H	-2.21712	-5.29453	0.60063
H	-2.75584	0.84864	-0.31948
H	-4.06257	0.50439	2.20404
H	-2.33719	0.69486	2.51604
H	-3.19231	-0.73232	3.13268
H	-1.78056	-3.71353	-2.85152
H	-2.63593	-5.14049	-2.23469
H	-0.91041	-4.95052	-1.92315

DPP-$(CHF_2)_2$

N	-2.46154	-0.56322	-1.21336
C	-2.10052	-1.71143	-1.98124
C	-2.65875	-0.87005	0.11544
C	-2.44652	-2.20010	0.29865
C	-2.09748	-2.77293	-0.97000

C	-1.88537	-4.10298	-0.78681
C	-2.44343	-3.26159	1.30991
N	-2.08258	-4.40983	0.54199
O	-1.87288	-1.70430	-3.16731
O	-2.67115	-3.26874	2.49596
C	-3.04444	0.15939	1.12259
C	-1.49980	-5.13246	-1.79397
H	-1.99237	-5.32782	0.94683
H	-2.55188	0.35474	-1.61823
F	-2.43755	-6.12816	-1.81993
H	-1.40039	-4.71001	-2.79343
F	-4.23013	0.73836	0.76140
H	-3.14398	-0.26309	2.12201
F	-0.31406	-5.71141	-1.43293
F	-2.10670	1.15510	1.14871

DPP-(CHO)$_2$

N	-2.54698	-0.47793	-0.97532
C	-2.26650	-1.53100	-1.88658
C	-2.71178	-0.93160	0.31300
C	-2.55158	-2.29378	0.32219
C	-2.27523	-2.71600	-1.00895
C	-2.11499	-4.07818	-0.99975
C	-2.56034	-3.47878	1.19982
N	-2.27979	-4.53183	0.28858
O	-2.08071	-1.39564	-3.07112
O	-2.74611	-3.61414	2.38437
C	-3.00839	-0.01368	1.41893
C	-1.81835	-4.99612	-2.10566
H	-2.20981	-5.50298	0.55115
H	-2.61693	0.49321	-1.23788
O	-3.12195	1.17888	1.24558
H	-3.11814	-0.48856	2.40678
O	-1.70461	-6.18865	-1.93225
H	-1.70846	-4.52124	-3.09349

DPP-Cl$_2$

N	-2.46777	-0.49338	-1.01560
C	-2.21253	-1.58572	-1.91013
C	-2.66231	-0.92209	0.27605
C	-2.55505	-2.27670	0.32782
C	-2.27465	-2.73382	-1.01496
C	-2.16740	-4.08842	-0.96319
C	-2.61717	-3.42480	1.22300
N	-2.36194	-4.51714	0.32846
O	-2.01011	-1.45766	-3.09319
O	-2.81959	-3.55287	2.40605
Cl	-2.97990	0.19503	1.51687
Cl	-1.84983	-5.20554	-2.20402
H	-2.33542	-5.47775	0.62857
H	-2.49429	0.46723	-1.31570

DPP-(CN)$_2$

N	-2.79156	-0.13017	-0.13957
C	-2.50357	-1.00313	-1.23338
C	-2.83986	-0.80612	1.06485
C	-2.59282	-2.13285	0.83597
C	-2.37971	-2.30425	-0.56454
C	-2.13274	-3.63098	-0.79343
C	-2.46889	-3.43397	1.50482
N	-2.18105	-4.30694	0.41098
O	-2.40793	-0.65311	-2.38095
O	-2.56460	-3.78399	2.65237
C	-3.11063	-0.13042	2.27689
C	-1.86205	-4.30668	-2.00549
H	-2.03574	-5.29724	0.52647
H	-2.93694	0.86011	-0.25507
N	-3.33406	0.45088	3.24667
N	-1.63868	-4.88802	-2.97526

DPP-(COMe)$_2$

N	-2.46787	-0.48340	-0.98837
C	-2.21475	-1.54636	-1.88841
C	-2.66417	-0.91561	0.30233
C	-2.55182	-2.28277	0.32246
C	-2.27406	-2.72697	-1.00905
C	-2.16209	-4.09416	-0.98899
C	-2.61072	-3.46333	1.20189
N	-2.35835	-4.52636	0.30172
O	-2.01107	-1.41489	-3.07375
O	-2.81472	-3.59483	2.38717
C	-2.94234	0.08490	1.36518
C	-1.88437	-5.09471	-2.05192
H	-2.32431	-5.49998	0.56326
H	-2.50237	0.49018	-1.25000
O	-2.99035	1.25785	1.04962
C	-3.14831	-0.41533	2.76220
O	-1.83668	-6.26769	-1.73643
C	-1.67892	-4.59449	-3.44902
H	-1.47703	-5.43560	-4.10732
H	-0.85596	-3.87753	-3.48109
H	-2.55876	-4.04530	-3.79114
H	-2.27002	-0.96720	3.10387
H	-3.97339	-1.12989	2.79417
H	-3.34790	0.42605	3.42086

DPP-(COOMe)$_2$

N	-2.56197	-0.46808	-0.86580
C	-2.28299	-1.49415	-1.81078
C	-2.72127	-0.95529	0.40814
C	-2.55981	-2.31431	0.38702
C	-2.28557	-2.70209	-0.96590
C	-2.12393	-4.06107	-0.98699
C	-2.56256	-3.52227	1.23187
N	-2.28321	-4.54828	0.28695
O	-2.10604	-1.30396	-2.98904
O	-2.73936	-3.71243	2.41016
C	-3.01859	-0.00248	1.49743
C	-1.82650	-5.01386	-2.07627
H	-2.20797	-5.52620	0.52003
H	-2.63711	0.50984	-1.09887
O	-3.12794	1.18708	1.30648
O	-3.14344	-0.61912	2.66724
C	-3.44094	0.21517	3.80007
H	-4.38261	0.73987	3.64307
H	-2.64396	0.94247	3.95073
H	-3.51104	-0.46402	4.64364
O	-1.71635	-6.20334	-1.88520
O	-1.70073	-4.39710	-3.24592
C	-1.40207	-5.23123	-4.37856
H	-0.46045	-5.75579	-4.22077
H	-1.33131	-4.55194	-5.22200
H	-2.19878	-5.95864	-4.53001

DPP-(COOH)$_2$

N	-2.51619	-0.55219	-1.07689
C	-2.28870	-1.66626	-1.92321
C	-2.65004	-0.93513	0.24301
C	-2.51834	-2.28935	0.31450
C	-2.29438	-2.78702	-0.99299
C	-2.16269	-4.14125	-0.92150
C	-2.52401	-3.41011	1.24473
N	-2.29653	-4.52417	0.39841
O	-2.13191	-1.65004	-3.12874

O	-2.68077	-3.42631	2.45026
C	-2.89571	0.04593	1.32948
C	-1.91703	-5.12232	-2.00795
H	-2.23751	-5.48353	0.70649
H	-2.57519	0.40716	-1.38496
O	-1.82445	-6.29898	-1.77457
O	-1.80877	-4.61229	-3.23692
O	-2.98815	1.22262	1.09612
O	-3.00391	-0.46410	2.55845
H	-1.90433	-3.63655	-3.28789
H	-2.90839	-1.43984	2.60940

DPP-F_2

N	-2.78670	-0.13914	-0.15393
C	-2.49813	-1.02763	-1.24958
C	-2.83495	-0.81274	1.03441
C	-2.59517	-2.13463	0.85577
C	-2.37714	-2.31118	-0.57451
C	-2.13765	-3.63311	-0.75318
C	-2.47393	-3.41814	1.53087
N	-2.18591	-4.30671	0.43516
O	-2.40619	-0.67022	-2.39759
O	-2.56613	-3.77559	2.67885
F	-3.09435	-0.13613	2.13016
F	-1.87850	-4.30976	-1.84898
H	-2.04206	-5.29725	0.54717
H	-2.93082	0.85135	-0.26598

DPP-$(NMe_2)_2$

N	-2.81194	-0.68367	-1.52713
C	-2.19071	-1.77119	-2.21898
C	-3.22771	-1.01764	-0.25096
C	-2.86090	-2.33867	-0.03872
C	-2.20443	-2.82065	-1.24355
C	-1.83650	-4.14130	-1.03078
C	-2.87399	-3.38786	0.93701
N	-2.25138	-4.47489	0.24575
O	-1.80546	-1.66759	-3.37653
O	-3.25930	-3.49117	2.09457
N	-3.84243	-0.11813	0.54893
N	-1.22117	-5.04068	-1.83040
H	-2.04224	-5.33002	0.72952
H	-3.02321	0.17050	-2.01172
C	-4.21810	1.18421	0.03566
C	-4.54679	-0.57837	1.73787
H	-5.60951	-0.74240	1.52328
H	-4.46242	0.17860	2.51886
H	-4.11639	-1.51070	2.09849
H	-5.09366	1.13966	-0.62546
H	-3.38922	1.64420	-0.50339
H	-4.46113	1.83142	0.87657
C	-0.84222	-6.34158	-1.31580
C	-0.51809	-4.58032	-3.02007
H	0.54451	-4.41469	-2.80619
H	-0.94996	-3.64889	-3.38118
H	-0.60184	-5.33799	-3.80045
H	-1.66995	-6.80336	-0.77650
H	0.03308	-6.29404	-0.65457
H	-0.59732	-6.98892	-2.15605

DPP-$(NH_2)_2$

N	-2.90438	-0.16046	-0.20001
C	-2.63549	-1.07680	-1.27898
C	-2.88575	-0.78129	1.03368
C	-2.64663	-2.11656	0.82890
C	-2.48979	-2.32751	-0.59116
C	-2.24916	-3.66250	-0.79578
C	-2.49965	-3.36699	1.51687
N	-2.22923	-4.28311	0.43805
O	-2.57246	-0.73963	-2.44756
O	-2.56258	-3.70414	2.68548
N	-3.02673	-0.08385	2.19370
N	-2.10761	-4.36035	-1.95558
H	-2.18735	-5.27714	0.59053
H	-2.94920	0.83343	-0.35240
H	-3.13882	-0.64791	3.02184
H	-3.57526	0.76059	2.17860
H	-1.99704	-3.79637	-2.78399
H	-1.55678	-5.20331	-1.94022

DPP-$(NHMe)_2$

N	-2.57267	-0.54771	-1.18317
C	-2.25734	-1.71025	-1.98232
C	-2.62833	-0.83575	0.16529
C	-2.37124	-2.18234	0.31515
C	-2.13874	-2.73708	-0.99701
C	-1.88416	-4.08392	-0.84774
C	-2.25473	-3.20950	1.29998
N	-1.94224	-4.37243	0.50043
O	-2.14943	-1.67483	-3.19759
O	-2.36140	-3.24480	2.51554
N	-2.87081	0.10298	1.10483
N	-1.64756	-5.02402	-1.78913
H	-1.80847	-5.27672	0.91872
H	-2.69775	0.35832	-1.60044
C	-3.33439	1.44054	0.80634
C	-1.14610	-6.34835	-1.48954
H	-1.52006	-4.66440	-2.72076
H	-2.98368	-0.25017	2.04045
H	-4.30337	1.44353	0.29462
H	-2.60974	1.97600	0.18748
H	-3.43816	1.99052	1.73897
H	-0.16420	-6.32746	-1.00323
H	-1.05726	-6.90556	-2.41953
H	-1.84388	-6.89117	-0.84709

DPP-$(NO_2)_2$

N	-2.78628	-0.13027	-0.16891
C	-2.49631	-1.01740	-1.25456
C	-2.83507	-0.79616	1.01776
C	-2.59488	-2.12681	0.84447
C	-2.37700	-2.31893	-0.56315
C	-2.13727	-3.64965	-0.73651
C	-2.47520	-3.42828	1.53592
N	-2.18607	-4.31554	0.45016
O	-2.39688	-0.67685	-2.39991
O	-2.57499	-3.76889	2.68122
N	-3.11610	-0.06389	2.23642
N	-1.85671	-4.38199	-1.95522
H	-2.03848	-5.30890	0.54467
H	-2.93430	0.86302	-0.26347
O	-3.30669	1.14003	2.10698
O	-3.13766	-0.69983	3.27143
O	-1.83523	-3.74606	-2.99023
O	-1.66649	-5.58598	-1.82582

DPP-$(OMe)_2$

N	-2.92746	0.23582	-0.32221
C	-2.53046	-0.43334	-1.51773
C	-2.67756	-0.50640	0.80837
C	-2.11043	-1.70054	0.44130
C	-2.00448	-1.68782	-1.01395
C	-1.43771	-2.88212	-1.38104
C	-1.58418	-2.95491	0.94510

N	-1.18781	-3.62434	-0.25046
O	-2.65995	0.05160	-2.62527
O	-1.45499	-3.43997	2.05263
O	-3.01100	0.03621	1.96529
O	-1.10458	-3.42487	-2.53798
H	-0.77814	-4.54377	-0.25346
H	-3.33743	1.15511	-0.31924
C	-2.71516	-0.73906	3.14462
C	-1.40038	-2.64957	-3.71732
H	-3.23409	-1.69495	3.10583
H	-3.06459	-0.14042	3.98031
H	-1.64333	-0.91640	3.21527
H	-2.47218	-2.47197	-3.78783
H	-1.05120	-3.24834	-4.55302
H	-0.88121	-1.69381	-3.67862

DPP-$(OH)_2$

N	-2.80877	-0.18457	0.05217
C	-2.52047	-1.02613	-1.07679
C	-2.84754	-0.89715	1.22505
C	-2.59704	-2.21281	0.96098
C	-2.38871	-2.32519	-0.46615
C	-2.13820	-3.64085	-0.73021
C	-2.46529	-3.51188	1.57162
N	-2.17695	-4.35343	0.44266
O	-2.43243	-0.62836	-2.22119
O	-2.55332	-3.90965	2.71603
O	-3.10493	-0.24374	2.35610
O	-1.88079	-4.29425	-1.86126
H	-2.02705	-5.34642	0.51610
H	-2.95865	0.80842	-0.02126
H	-3.09454	-0.87209	3.09257
H	-1.89118	-3.66590	-2.59774

DPP-$(SO_2Me)_2$

N	-2.10186	-0.60826	-1.15750
C	-1.93098	-1.75494	-1.99001
C	-2.68452	-0.92922	0.04171
C	-2.93227	-2.26832	0.08453
C	-2.48344	-2.82859	-1.16141
C	-2.73120	-4.16769	-1.11858
C	-3.48459	-3.34199	0.91320
N	-3.31386	-4.48864	0.08063
O	-1.43274	-1.73774	-3.09123
O	-3.98292	-3.35916	2.01438
S	-2.92156	0.35280	1.26534
S	-2.49422	-5.44972	-2.34223
H	-3.53958	-5.43075	0.36383
H	-1.87624	0.33385	-1.44074
O	-2.99337	1.58097	0.51180
O	-1.91423	0.17409	2.27544
C	-4.50876	-0.04784	1.94635
H	-5.26431	0.06008	1.17110
H	-4.67294	0.67221	2.74808
H	-4.47275	-1.06352	2.34082
O	-2.42304	-6.67795	-1.58874
O	-3.50123	-5.27061	-3.35259
C	-0.90670	-5.04958	-3.02277
H	-0.15141	-5.15781	-2.24732
H	-0.94225	-4.03387	-3.41719
H	-0.74254	-5.76964	-3.82449

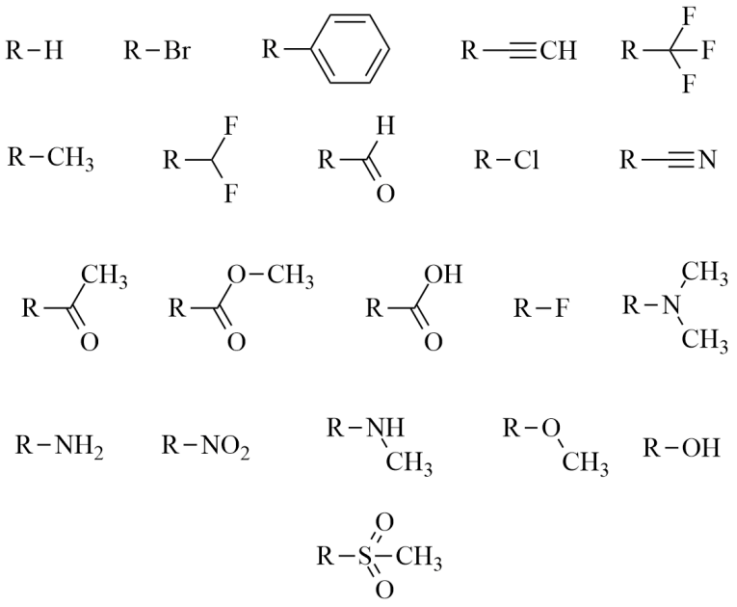


Figure S1. Structures of the substituent groups bonded to the DPP core. The letter "R" represents the bond site with the DPP core.

Excitonic and intramolecular charge transfer (ICT) analysis between molecular fragments

Table S3. Charge transfer numbers for the DPP-X_1 derivatives. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	ΔE	f	Ω	POS	PR	CT	COH	CT_{nt}	PR_{NTO}	Z_{HE}	RMS_{eh}
–H	3.56	0.26	1.03	2.00	1.02	0.02	1.02	0.00	1.06	1.19	2.75
–Br	3.54	0.27	1.03	2.05	1.12	0.10	1.12	0.01	1.06	1.19	2.87
–Ph	3.17	0.31	1.02	2.18	1.43	0.28	1.39	0.12	1.05	1.17	3.42
–CCH	3.24	0.28	1.03	2.12	1.30	0.22	1.27	0.10	1.06	1.17	3.13
–CF_3	3.46	0.24	1.03	2.04	1.10	0.09	1.10	0.04	1.06	1.17	2.87
–Me	3.60	0.27	1.03	2.04	1.10	0.09	1.09	0.03	1.06	1.19	2.84
–CHF_2	3.47	0.25	1.03	2.05	1.12	0.10	1.11	0.05	1.06	1.17	2.88
–CHO	3.04	0.24	1.03	2.14	1.35	0.27	1.30	0.19	1.05	1.14	3.14
–Cl	3.57	0.27	1.03	2.04	1.11	0.10	1.11	0.01	1.06	1.18	2.85
–CN	3.22	0.25	1.03	2.10	1.24	0.19	1.22	0.10	1.05	1.15	3.07
–COMe	3.12	0.23	1.03	2.12	1.30	0.24	1.26	0.17	1.05	1.15	3.10
–COOMe	3.17	0.24	1.03	2.10	1.26	0.20	1.23	0.13	1.05	1.15	3.06
–COOH	3.25	0.22	1.03	2.09	1.22	0.18	1.20	0.12	1.06	1.17	2.98
–F	3.76	0.27	1.03	2.02	1.06	0.06	1.06	0.01	1.07	1.20	2.79
–NMe_2	3.57	0.26	1.02	2.10	1.24	0.18	1.23	0.01	1.05	1.16	3.01
–NH_2	3.68	0.26	1.02	2.06	1.15	0.13	1.15	0.01	1.05	1.17	2.88
–NHMe	3.59	0.28	1.02	2.08	1.19	0.16	1.19	0.01	1.05	1.16	2.97
–NO_2	2.94	0.20	1.03	2.18	1.45	0.34	1.36	0.28	1.05	1.14	3.22
–OMe	3.71	0.24	1.02	2.05	1.13	0.11	1.13	0.02	1.06	1.18	2.85
–OH	3.75	0.26	1.02	2.04	1.10	0.09	1.10	0.01	1.06	1.18	2.83
–SO_2Me	3.36	0.23	1.03	2.05	1.12	0.10	1.11	0.05	1.06	1.18	2.92

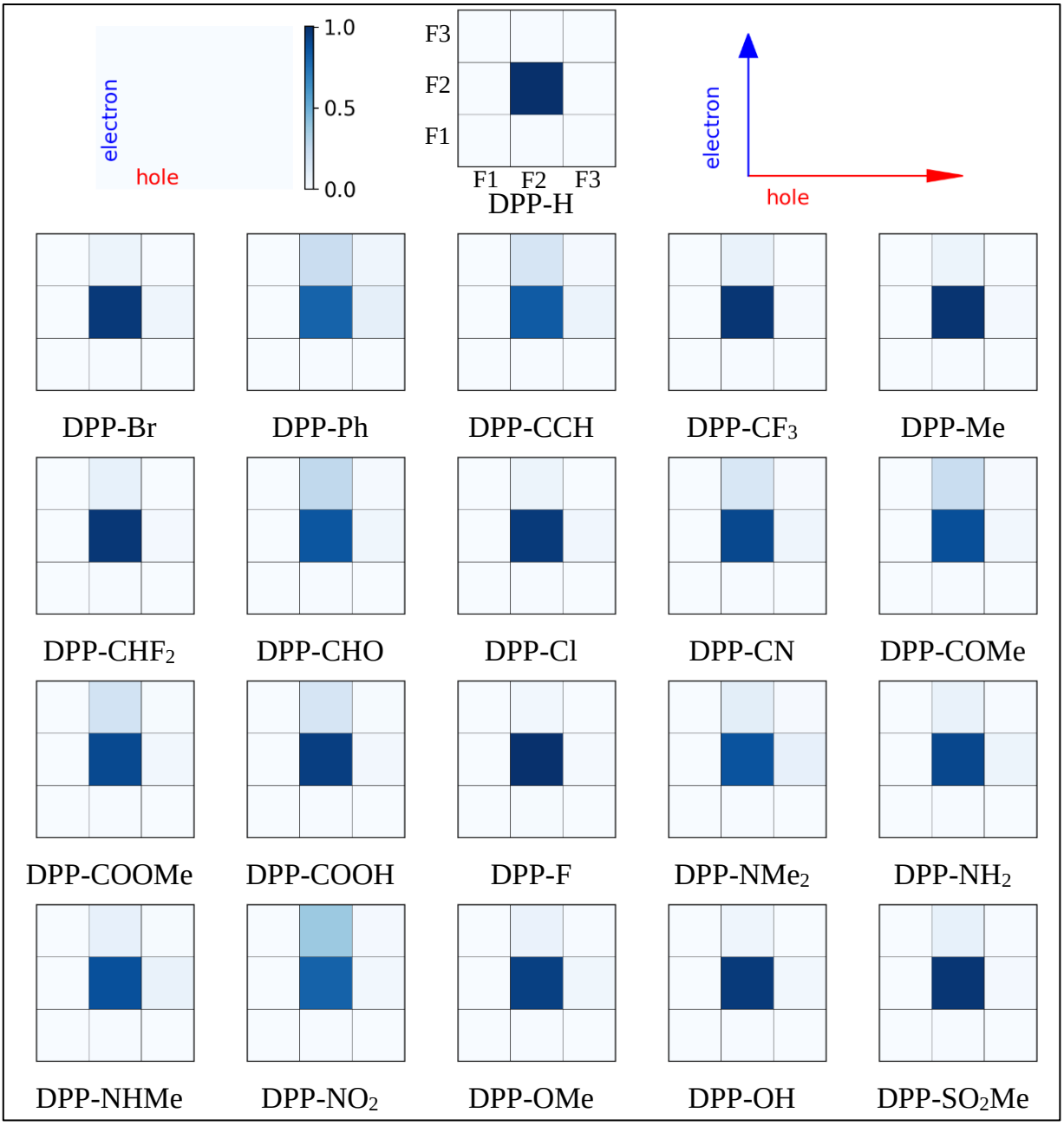


Figure S2. Transition density matrices (TDMs) of the DPP-X_1 derivatives obtained from the TheoDORE software.

Table S4. Charge transfer calculations for the DPP-X_2 derivatives. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	ΔE	f	Ω	POS	PR	CT	COH	CT_{nt}	PR_{NTO}	Z_{HE}	RMS_{eh}
–H	3.56	0.26	1.03	2.00	1.02	0.02	1.02	0.00	1.06	1.19	2.75
–Br	3.52	0.30	1.02	2.00	1.23	0.18	1.23	0.00	1.06	1.19	3.00
–Ph	2.84	0.55	1.02	2.00	1.87	0.43	1.79	0.00	1.05	1.17	4.00
–CCH	2.99	0.37	1.03	2.00	1.61	0.36	1.54	0.00	1.05	1.16	3.47
–CF_3	3.38	0.25	1.03	2.00	1.19	0.15	1.17	0.00	1.06	1.17	2.97
–Me	3.64	0.29	1.02	2.00	1.18	0.15	1.17	0.00	1.06	1.19	2.94
–CHF_2	3.42	0.26	1.03	2.00	1.22	0.17	1.20	0.00	1.06	1.17	2.99
–CHO	2.76	0.28	1.03	2.00	1.64	0.39	1.51	0.00	1.04	1.12	3.38
–Cl	3.57	0.29	1.03	2.00	1.21	0.17	1.21	0.00	1.06	1.18	2.96
–CN	3.01	0.29	1.03	2.00	1.46	0.31	1.41	0.00	1.05	1.15	3.32
–COMe	2.88	0.26	1.03	2.00	1.54	0.34	1.44	0.00	1.05	1.14	3.31
–COOMe	2.92	0.26	1.03	2.00	1.47	0.31	1.39	0.00	1.05	1.14	3.27
–COOH	3.07	0.23	1.03	2.00	1.39	0.27	1.34	0.00	1.05	1.16	3.16
–F	3.97	0.29	1.02	2.00	1.11	0.10	1.11	0.00	1.07	1.20	2.83
–NMe_2	3.54	0.38	1.02	2.00	1.55	0.34	1.52	0.00	1.05	1.18	3.21
–NH_2	3.79	0.32	1.02	2.00	1.33	0.24	1.32	0.00	1.06	1.19	2.97
–NHMe	3.65	0.41	1.02	2.00	1.44	0.29	1.42	0.00	1.06	1.18	3.13
–NO_2	2.73	0.24	1.03	2.00	1.72	0.42	1.53	0.00	1.04	1.12	3.38
–OMe	3.84	0.25	1.02	2.00	1.27	0.20	1.26	0.00	1.06	1.20	2.93
–OH	3.94	0.29	1.02	2.00	1.20	0.16	1.20	0.00	1.07	1.20	2.88
–SO_2Me	3.22	0.24	1.03	2.00	1.22	0.17	1.20	0.00	1.06	1.18	3.06

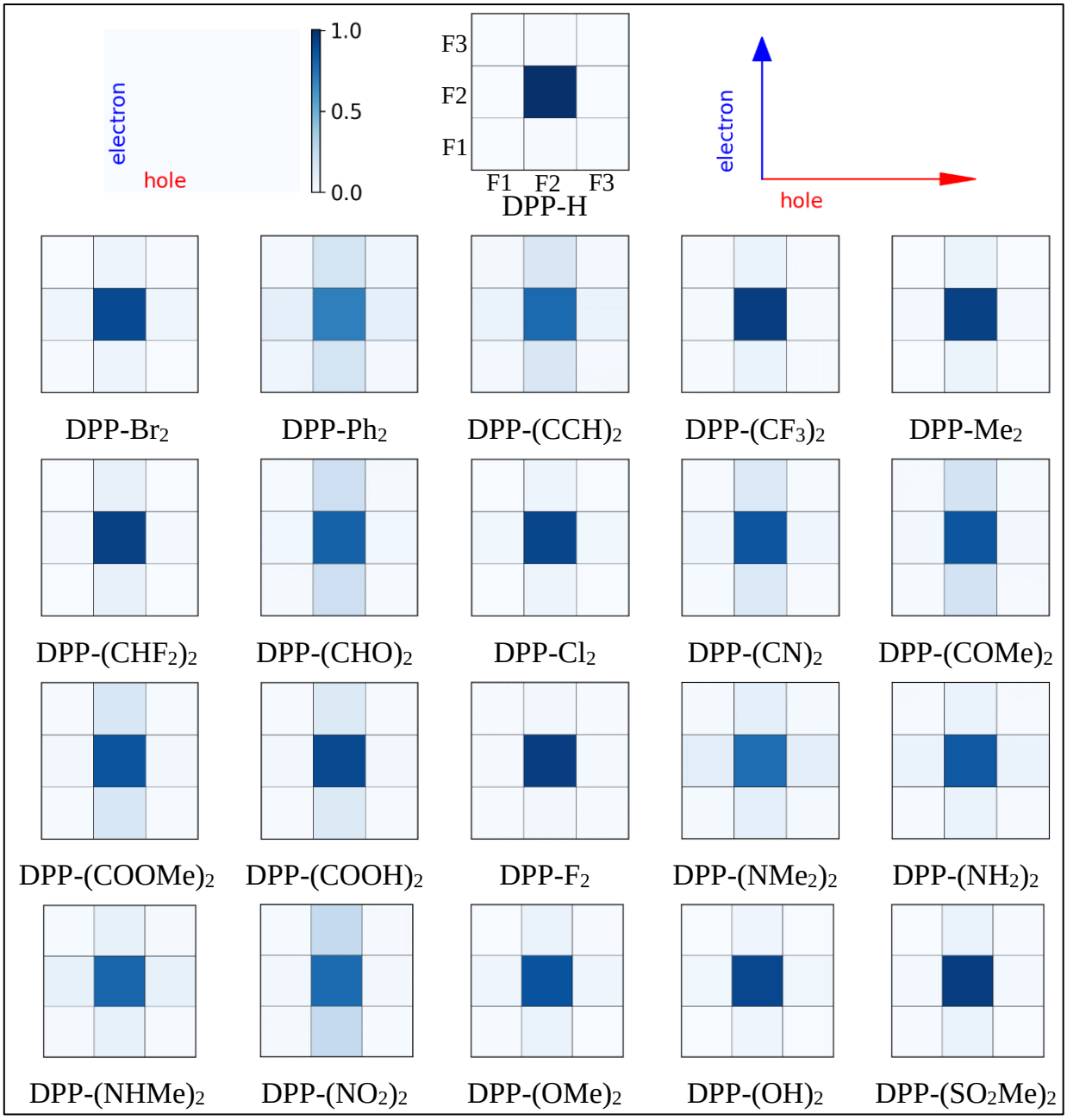


Figure S3. Transition density matrices (TDMs) of the DPP-X_2 derivatives obtained from the TheoDORE software.

Table S5. Charge transfer calculations for the DPP-X_1 derivatives. Calculations at the ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	ΔE	f	Ω	POS	PR	CT	COH	CT_{nt}	PR_{NTO}	Z_{HE}	RMS_{eh}
–H	3.36	0.29	0.96	2.00	1.02	0.02	1.02	0.00	1.00	1.04	2.71
–Br	3.34	0.30	0.96	2.07	1.16	0.14	1.16	-0.01	1.03	1.12	2.92
–Ph	2.94	0.31	0.96	2.19	1.47	0.35	1.42	0.23	1.00	1.05	3.60
–CCH	3.09	0.29	0.95	2.13	1.32	0.25	1.29	0.16	1.00	1.05	3.16
–CF_3	3.25	0.27	0.96	2.05	1.11	0.10	1.11	0.06	1.00	1.04	2.85
–Me	3.39	0.30	0.95	2.05	1.12	0.11	1.11	0.05	1.00	1.05	2.81
–CHF_2	3.27	0.27	0.95	2.05	1.13	0.11	1.12	0.06	1.00	1.05	2.85
–CHO	2.89	0.26	0.96	2.13	1.33	0.26	1.28	0.20	1.00	1.04	3.08
–Cl	3.37	0.30	0.96	2.04	1.09	0.09	1.09	0.04	1.03	1.11	2.81
–CN	3.06	0.27	0.95	2.10	1.24	0.20	1.22	0.14	1.00	1.05	2.99
–COMe	2.94	0.25	0.96	2.12	1.30	0.24	1.25	0.18	1.00	1.04	3.06
–COOMe	2.99	0.25	0.95	2.10	1.25	0.21	1.23	0.14	1.00	1.05	3.01
–COOH	3.06	0.24	0.96	2.10	1.23	0.19	1.21	0.13	1.02	1.10	2.96
–F	3.58	0.32	0.95	2.01	1.05	0.04	1.05	0.01	1.00	1.05	2.71
–NMe_2	3.26	0.29	0.95	2.09	1.22	0.18	1.22	0.03	1.00	1.05	3.00
–NH_2	3.41	0.29	0.96	2.06	1.14	0.13	1.14	0.02	1.01	1.09	2.85
–NHMe	3.30	0.31	0.95	2.08	1.19	0.16	1.19	0.02	1.00	1.05	2.94
–NO_2	2.85	0.23	0.96	2.16	1.40	0.31	1.33	0.25	1.00	1.04	3.17
–OMe	3.48	0.27	0.95	2.04	1.10	0.09	1.10	0.03	1.00	1.05	2.79
–OH	3.52	0.30	0.95	2.03	1.08	0.07	1.08	0.02	1.00	1.05	2.77
–SO_2Me	3.12	0.25	0.96	2.06	1.14	0.13	1.14	0.05	1.02	1.11	2.94

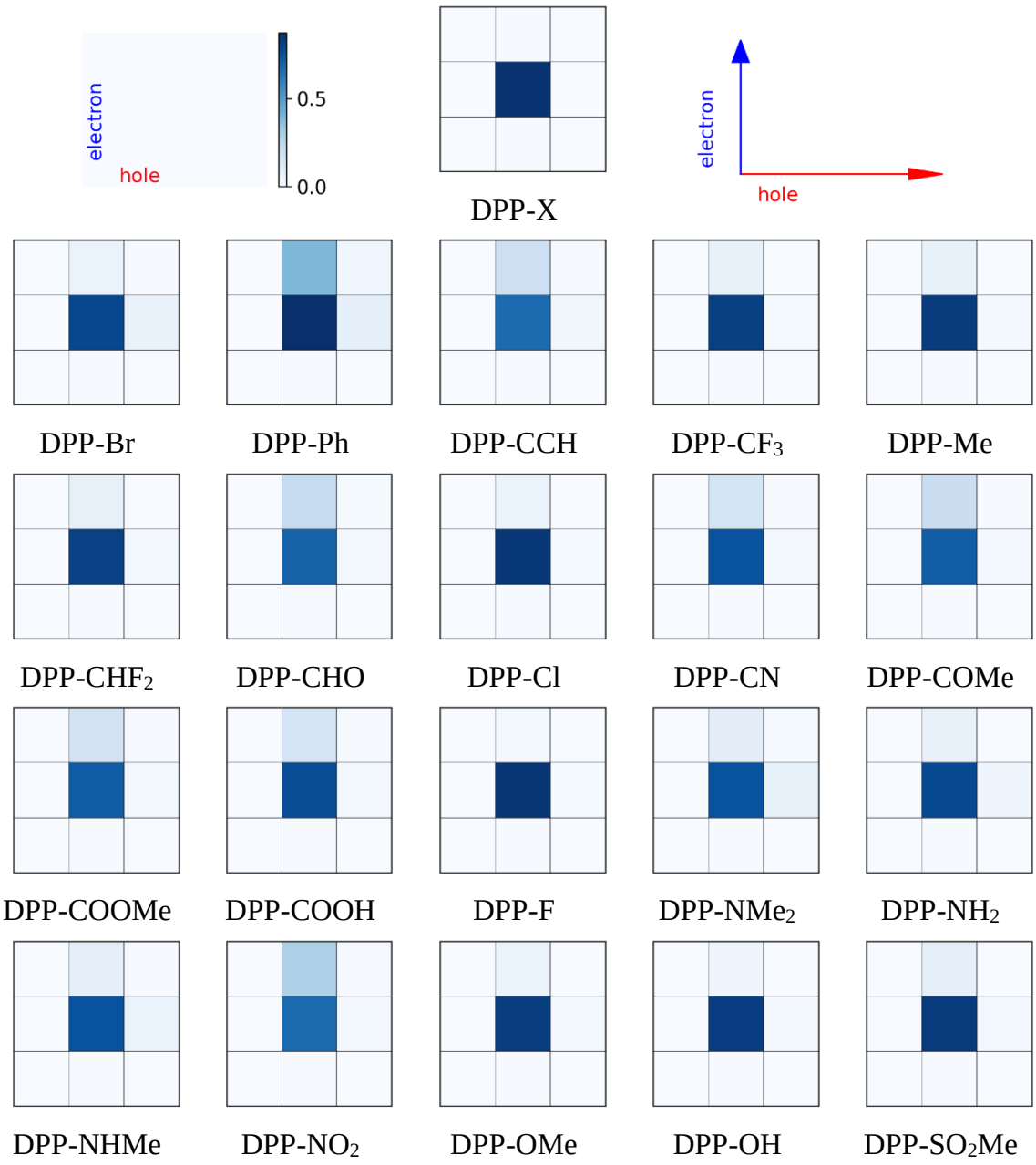


Figure S4. Transition density matrices (TDMs) of the ADC(2)-DPP-X_1 derivatives obtained from the TheoDORE software.

Table S6. Charge transfer calculations for the DPP-X_2 derivatives. Calculations at the ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	ΔE	f	Ω	POS	PR	CT	COH	CT_{nt}	PR_{NTO}	Z_{HE}	RMS_{eh}
–H	3.36	0.29	0.96	2.00	1.02	0.02	1.02	0.00	1.00	1.04	2.71
–Br	3.31	0.32	0.96	2.00	1.25	0.20	1.25	0.00	1.00	1.04	3.01
–Ph	2.65	0.51	0.95	2.00	1.96	0.51	1.81	0.00	1.00	1.05	4.24
–CCH	2.86	0.35	0.96	2.00	1.66	0.40	1.55	0.00	1.00	1.04	3.45
–CF_3	3.17	0.27	0.96	2.00	1.22	0.18	1.20	0.00	1.00	1.04	2.97
–Me	3.42	0.31	0.96	2.00	1.23	0.19	1.22	0.00	1.00	1.04	2.95
–CHF_2	3.22	0.27	0.96	2.00	1.24	0.19	1.22	0.00	1.00	1.04	2.99
–CHO	2.64	0.29	0.97	2.00	1.61	0.38	1.47	0.00	1.00	1.04	3.29
–Cl	3.38	0.32	0.96	2.00	1.19	0.16	1.19	0.00	1.00	1.05	2.87
–CN	2.88	0.30	0.95	2.00	1.49	0.33	1.41	0.00	1.00	1.05	3.21
–COMe	2.71	0.26	0.96	2.00	1.54	0.35	1.43	0.00	1.00	1.04	3.25
–COOMe	2.75	0.26	0.95	2.00	1.48	0.32	1.39	0.00	1.00	1.05	3.22
–COOH	2.89	0.24	0.96	2.00	1.41	0.29	1.34	0.00	1.00	1.04	3.14
–F	3.80	0.35	0.96	2.00	1.08	0.08	1.08	0.00	1.00	1.04	2.75
–NMe_2	3.17	0.39	0.95	2.00	1.49	0.33	1.49	0.00	1.00	1.05	3.18
–NH_2	3.52	0.37	0.95	2.00	1.31	0.24	1.31	0.00	1.00	1.05	2.85
–NHMe	3.32	0.43	0.95	2.00	1.47	0.32	1.46	0.00	1.00	1.05	3.17
–NO_2	2.72	0.25	0.96	2.00	1.64	0.40	1.47	0.00	1.00	1.04	3.33
–OMe	3.58	0.28	0.96	2.00	1.25	0.20	1.25	0.00	1.00	1.04	2.87
–OH	3.69	0.34	0.96	2.00	1.15	0.13	1.15	0.00	1.00	1.04	2.76
–SO_2Me	2.95	0.24	0.96	2.00	1.28	0.22	1.27	0.00	1.02	1.11	3.13

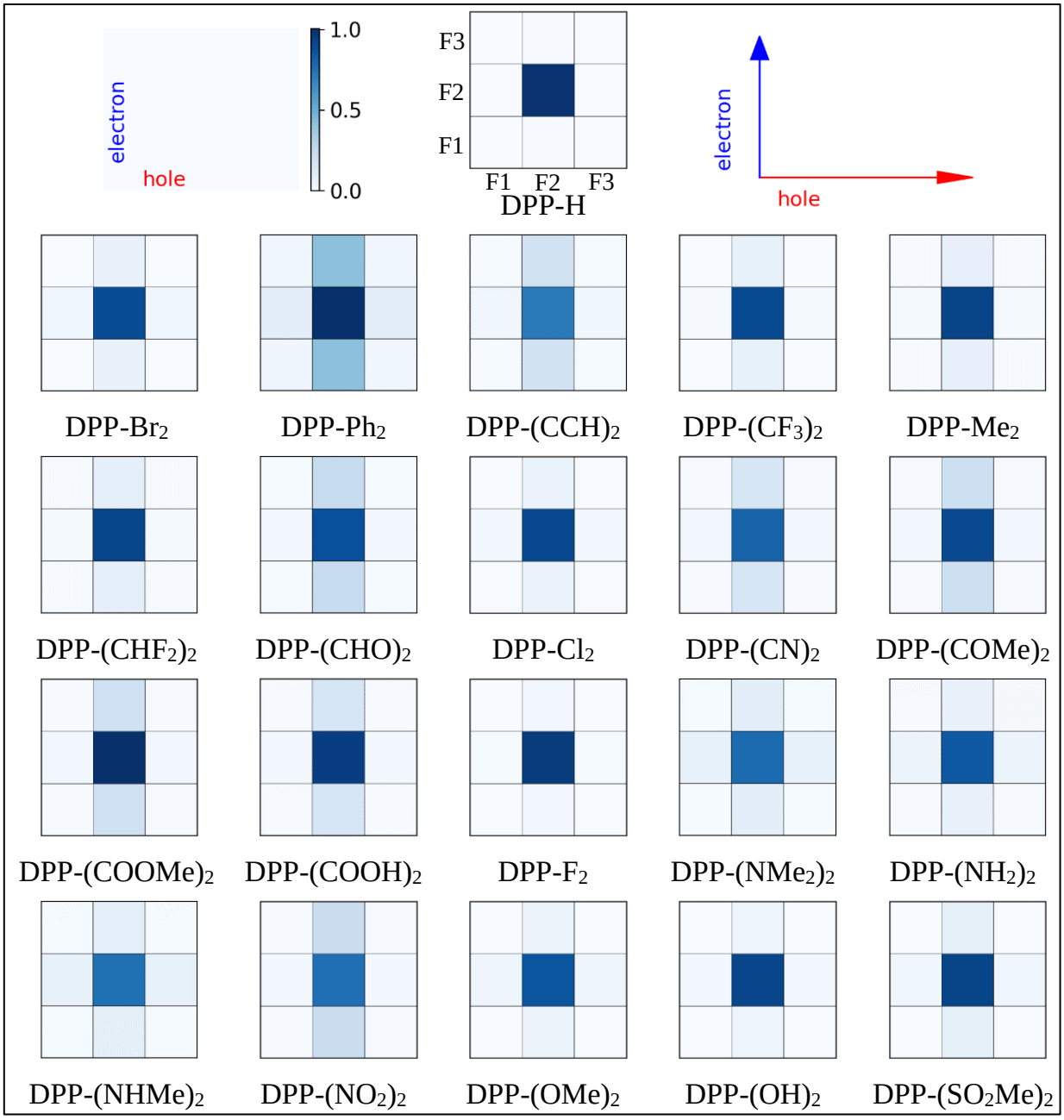
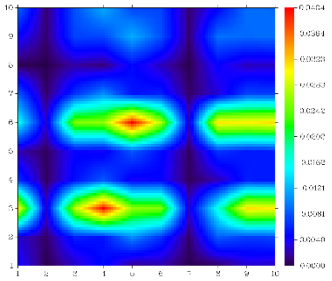
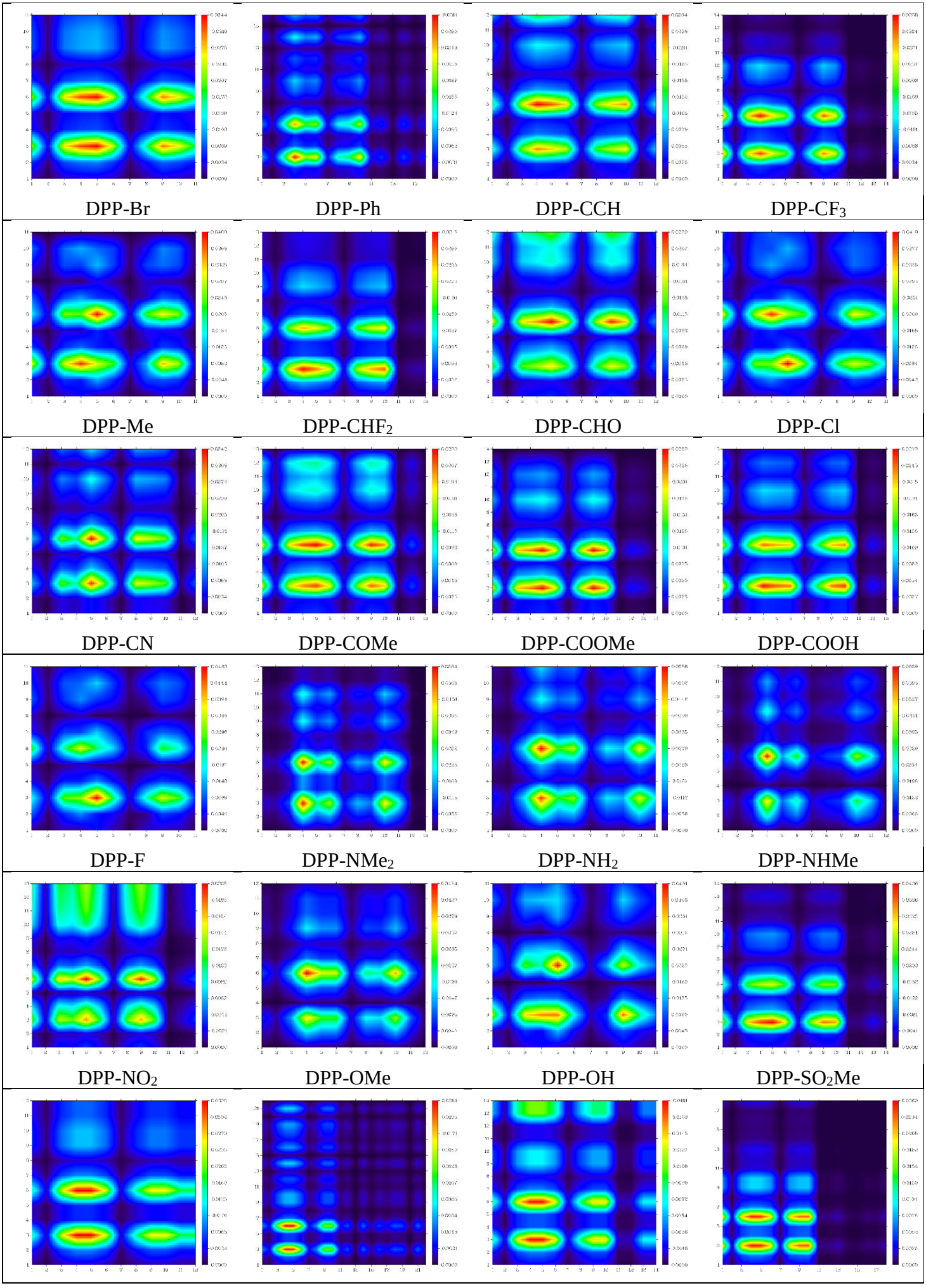


Figure S5. Transition density matrices (TDMs) of the ADC(2)-DPP-X_2 derivatives obtained from the TheoDORE software.

Transition Density Matrix (TDM) analysis



DPP-H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DPP-Ph
DPP-CCH
DPP-CF3
DPP-Me
DPP-CHF2
DPP-CHO
DPP-Cl
DPP-CN
DPP-COMe
DPP-COOMe
DPP-COOH
DPP-F
DPP-NMe2
DPP-NH2
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DPP-SO2Me

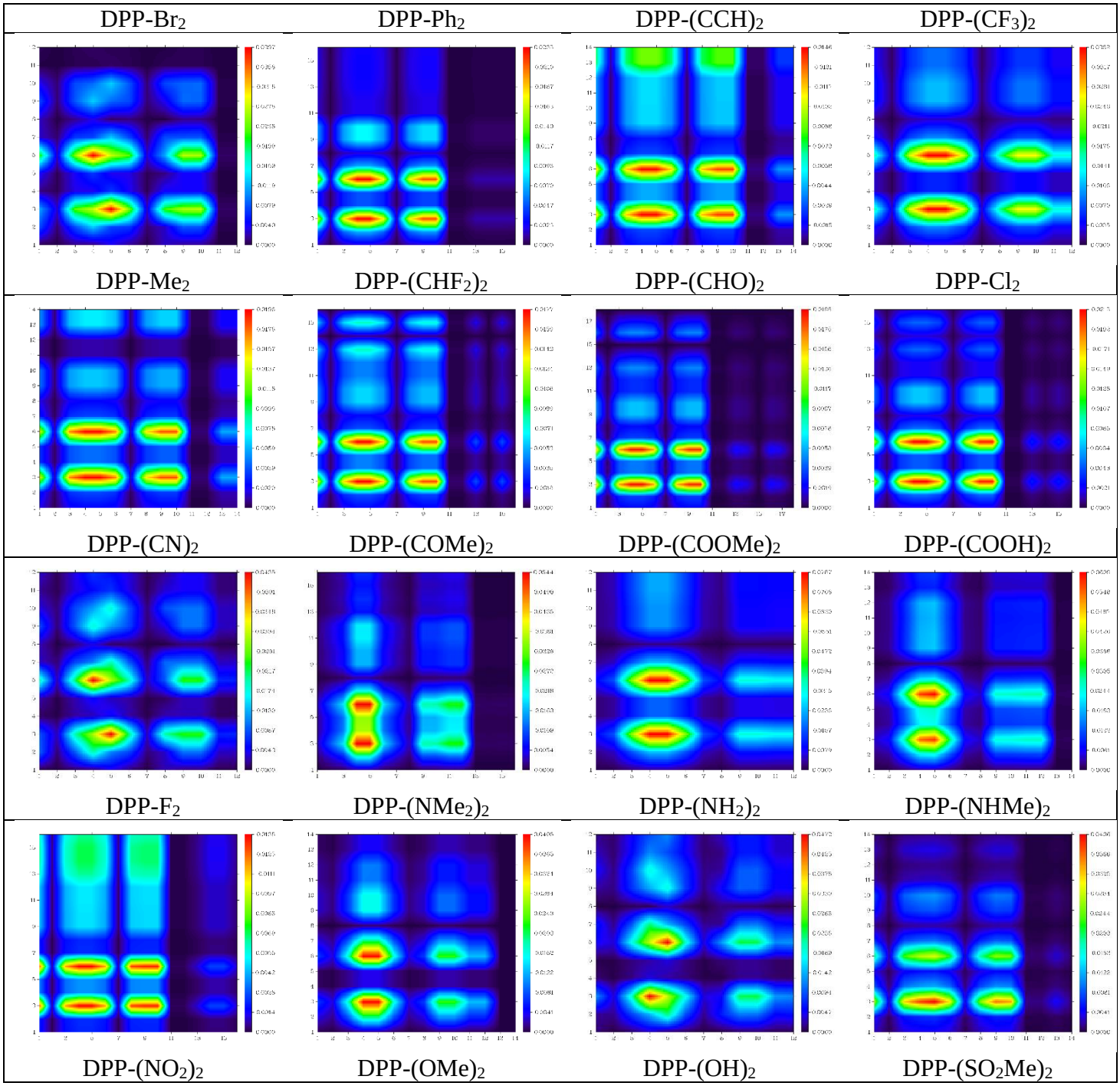
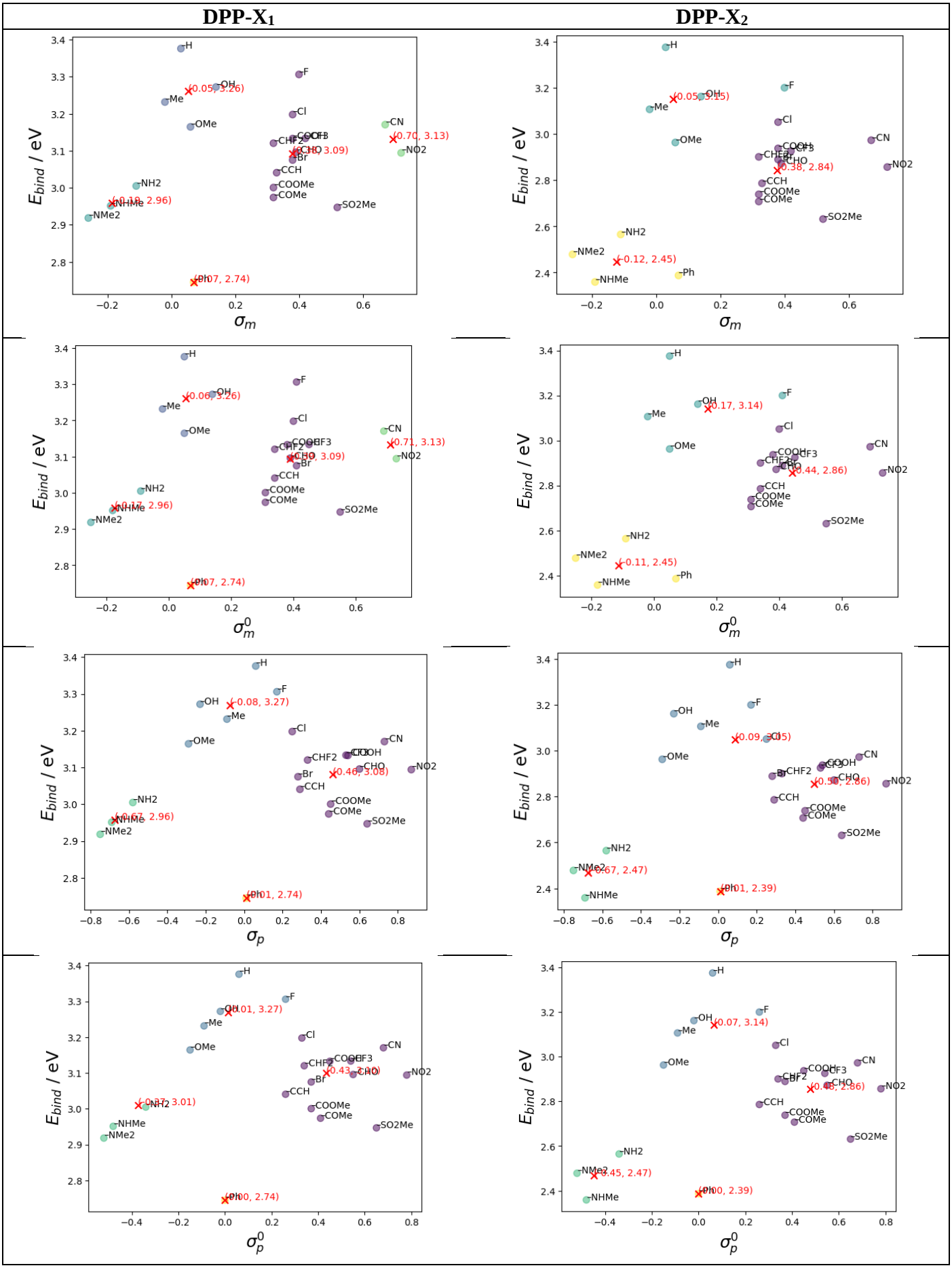


Figure S6. Transition density matrices (TDMs) of the DPP-X systems obtained from the Multiwfn software.

Exciton binding energy (E_{bind}) analysis



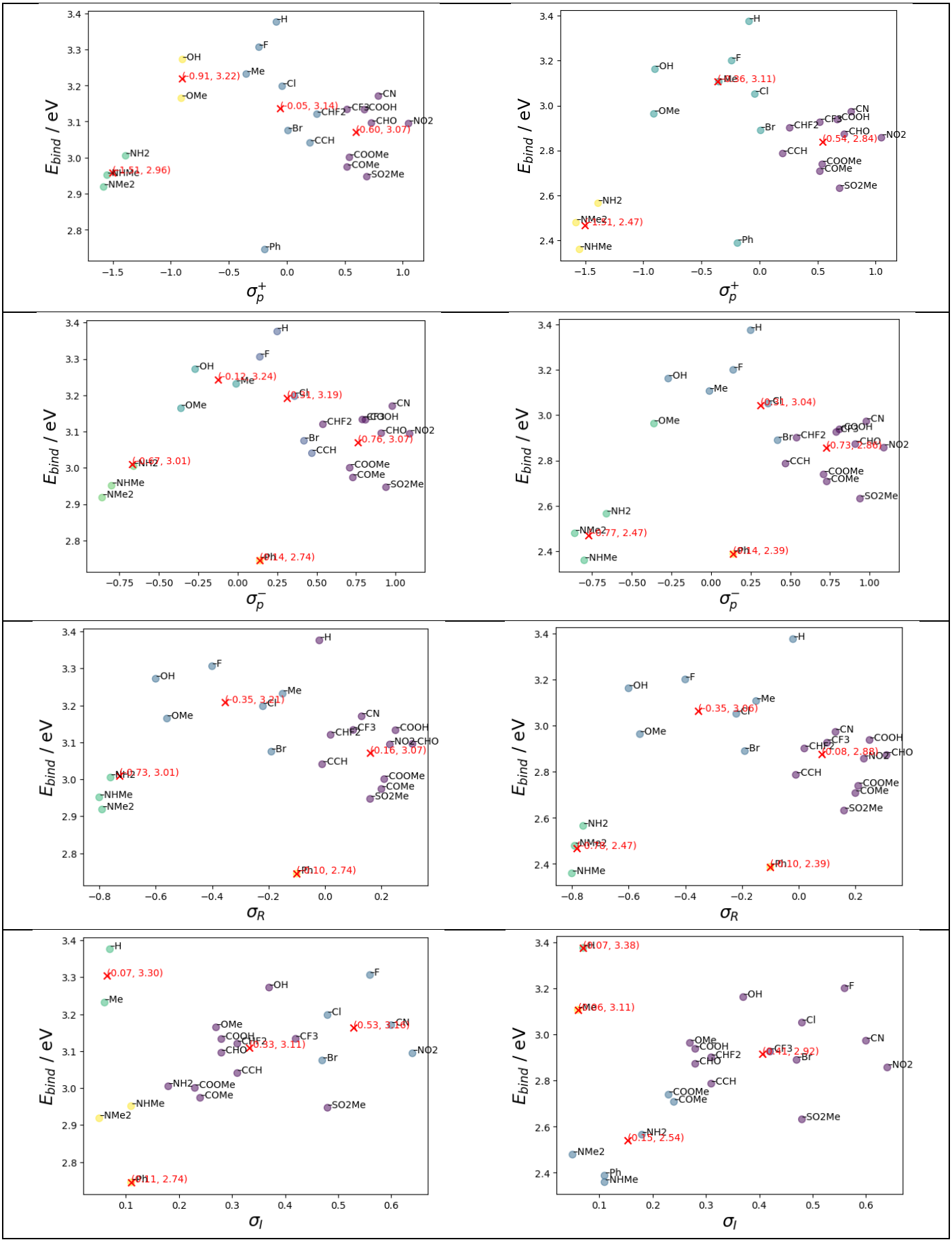
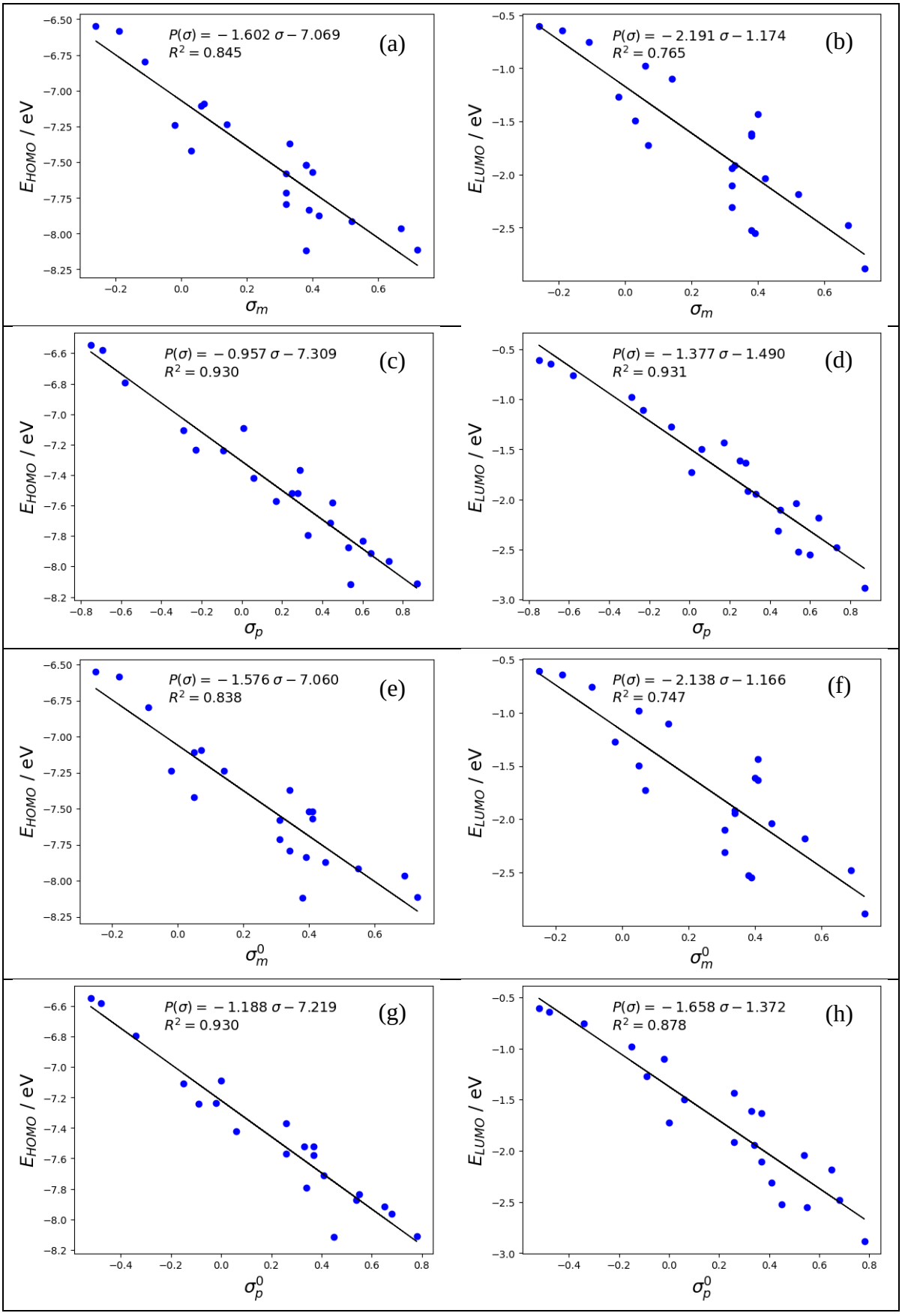


Figure S7. Binding energies (E_{bind}), in eV, by ML-based Hammett's constants for all DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level. ML analysis with the *MeanShift* algorithm.

Table S7. Exciton binding energy (E_{bind}), in eV, of all DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	E_{bind}**(DPP-X$_1$)**	E_{bind}**(DPP-X$_2$)**
–H	3.38	3.38
–Br	3.07	2.89
–Ph	2.74	2.39
–CCH	3.04	2.79
–CF_3	3.13	2.93
–Me	3.23	3.11
–CHF_2	3.12	2.90
–CHO	3.10	2.87
–Cl	3.20	3.05
–CN	3.17	2.97
–COMe	2.97	2.71
–COOMe	3.00	2.74
–COOH	3.13	2.94
–F	3.31	3.20
–NMe_2	2.92	2.48
–NH_2	3.00	2.56
–NHMe	2.95	2.36
–NO_2	3.09	2.86
–OMe	3.16	2.96
–OH	3.27	3.16
–SO_2Me	2.95	2.63

Photoelectronic properties analysis



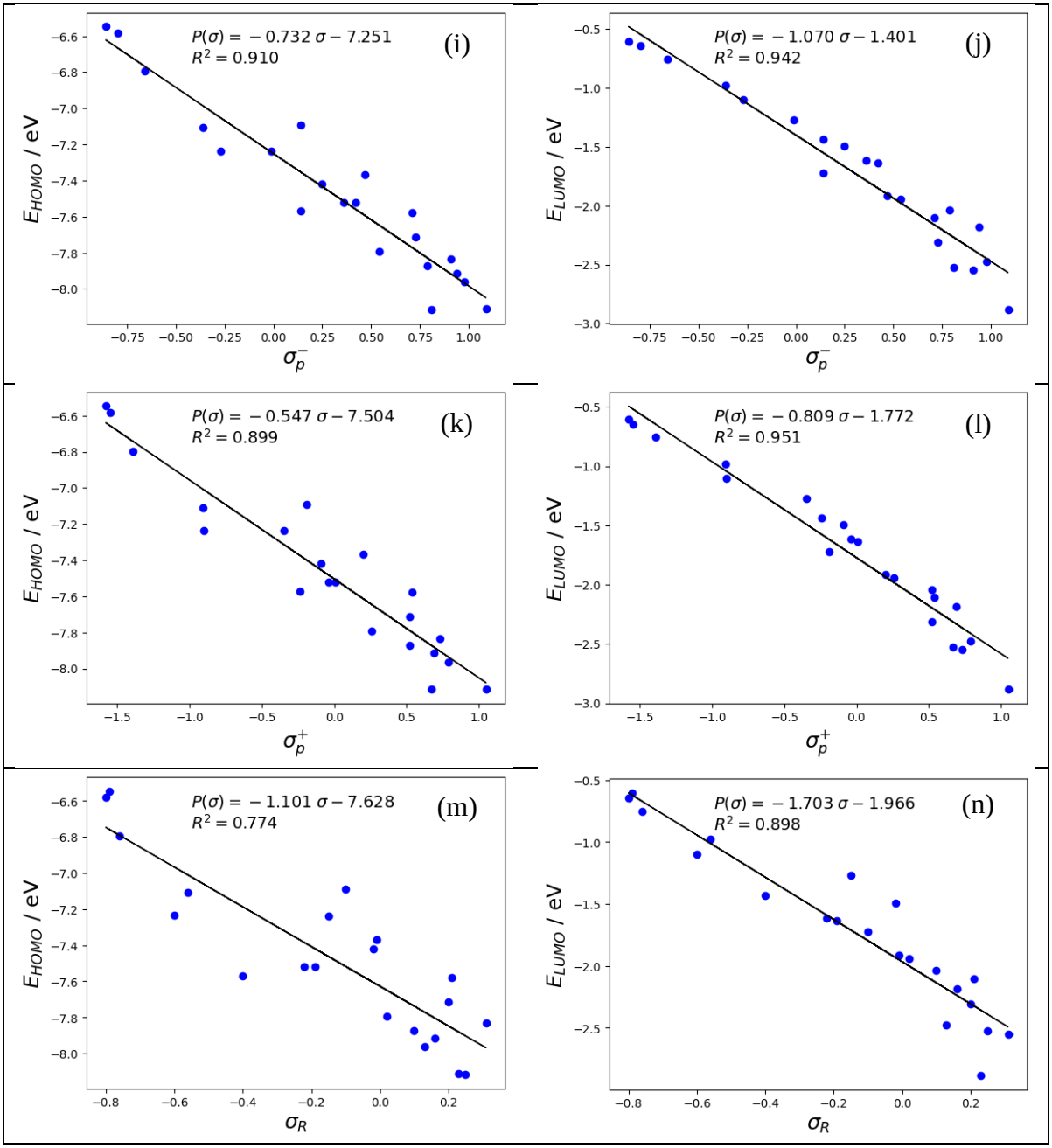
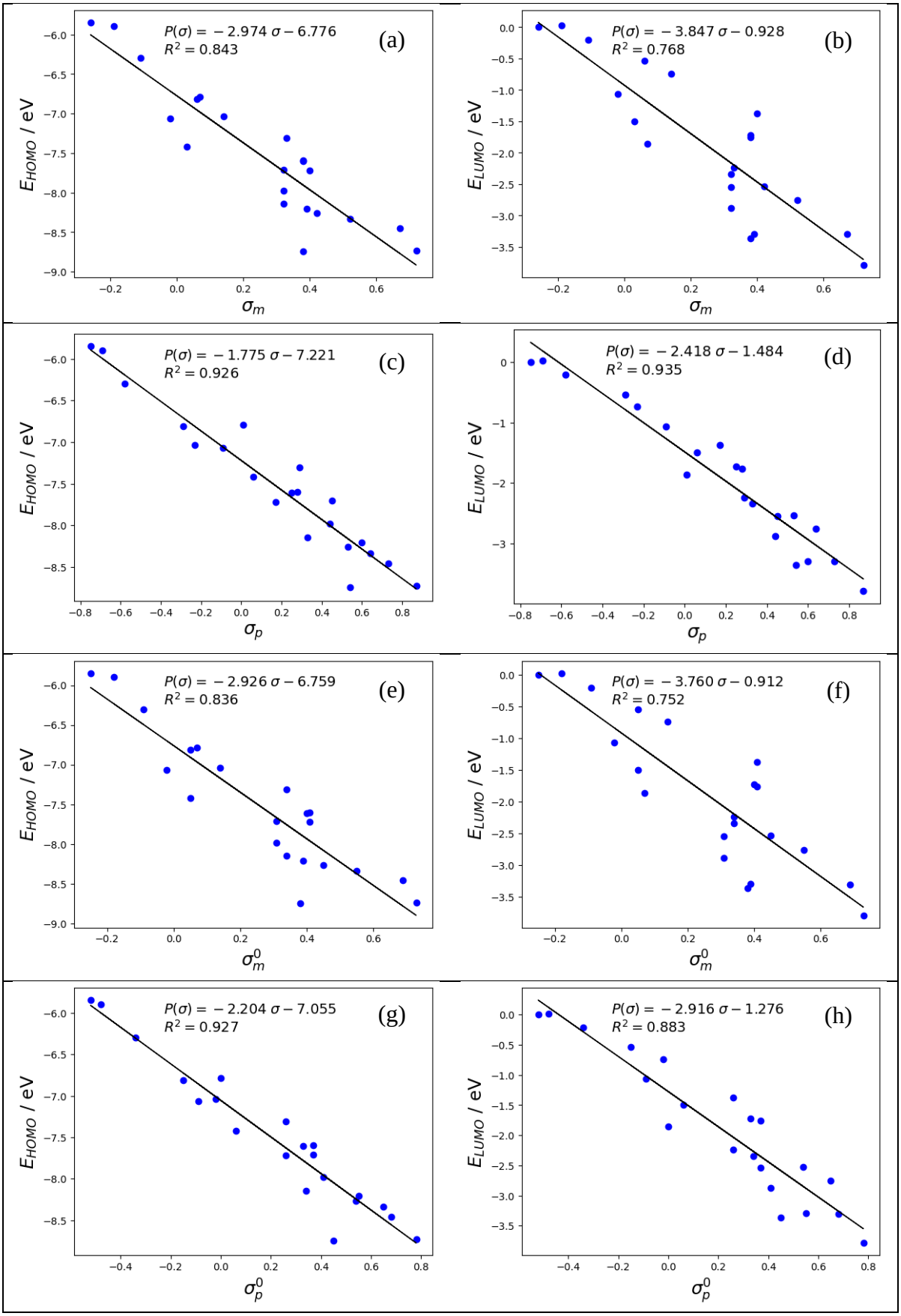


Figure S8. Correlation between ML-based Hammett's constants and DFT FMO energies (E_{HOMO} – right panels and E_{LUMO} – left panels) of the DPP-X_1 derivatives.


(a)
$P(\sigma) = -2.974\,\sigma - 6.776$
$R^2 = 0.843$
E_{HOMO} / eV
σ_m
(b)
$P(\sigma) = -3.847\,\sigma - 0.928$
$R^2 = 0.768$
E_{LUMO} / eV
σ_m
(c)
$P(\sigma) = -1.775\,\sigma - 7.221$
$R^2 = 0.926$
E_{HOMO} / eV
σ_p
(d)
$P(\sigma) = -2.418\,\sigma - 1.484$
$R^2 = 0.935$
E_{LUMO} / eV
σ_p
(e)
$P(\sigma) = -2.926\,\sigma - 6.759$
$R^2 = 0.836$
E_{HOMO} / eV
σ_m^0
(f)
$P(\sigma) = -3.760\,\sigma - 0.912$
$R^2 = 0.752$
E_{LUMO} / eV
σ_m^0
(g)
$P(\sigma) = -2.204\,\sigma - 7.055$
$R^2 = 0.927$
E_{HOMO} / eV
σ_p^0
(h)
$P(\sigma) = -2.916\,\sigma - 1.276$
$R^2 = 0.883$
E_{LUMO} / eV
σ_p^0

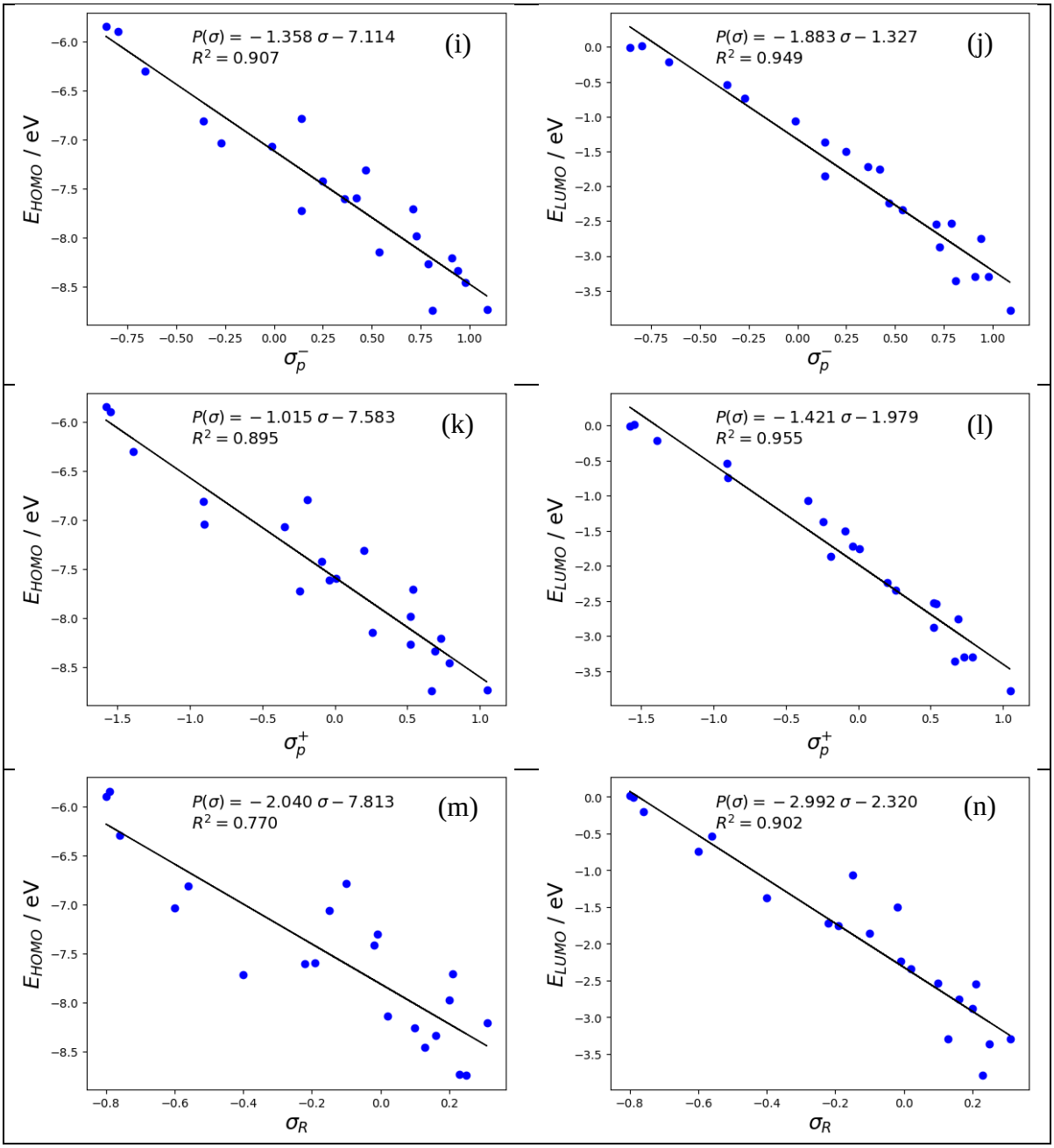


Figure S9. Correlation between ML-based Hammett's constants and DFT FMO energies (E_{HOMO} – right panels and E_{LUMO} – left panels) of the DPP-X_2 derivatives.

Table S8. HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) and HOMO-LUMO gap (E_g), in eV, of all DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	DPP-X₁			DPP-X₂		
	E_{HOMO}	E_{LUMO}	E_g	E_{HOMO}	E_{LUMO}	E_g
–H	-7.42	-1.50	5.92	-7.42	-1.50	5.92
–Br	-7.52	-1.63	5.89	-7.60	-1.76	5.84
–Ph	-7.09	-1.72	5.37	-6.79	-1.86	4.93
–CCH	-7.37	-1.92	5.45	-7.31	-2.24	5.07
–CF_3	-7.87	-2.04	5.83	-8.26	-2.53	5.73
–Me	-7.24	-1.27	5.97	-7.07	-1.06	6.00
–CHF_2	-7.79	-1.94	5.85	-8.14	-2.34	5.80
–CHO	-7.83	-2.55	5.28	-8.21	-3.30	4.91
–Cl	-7.52	-1.61	5.91	-7.61	-1.72	5.89
–CN	-7.96	-2.48	5.49	-8.46	-3.30	5.16
–COMe	-7.71	-2.31	5.40	-7.98	-2.88	5.10
–COOMe	-7.58	-2.10	5.48	-7.71	-2.54	5.17
–COOH	-8.12	-2.52	5.59	-8.74	-3.36	5.38
–F	-7.57	-1.43	6.14	-7.72	-1.37	6.35
–NMe_2	-6.55	-0.61	5.94	-5.85	0.00	5.84
–NH_2	-6.80	-0.76	6.04	-6.30	-0.21	6.09
–NHMe	-6.58	-0.64	5.94	-5.90	0.02	5.92
–NO_2	-8.11	-2.89	5.23	-8.73	-3.79	4.95
–OMe	-7.11	-0.98	6.13	-6.81	-0.54	6.27
–OH	-7.24	-1.10	6.13	-7.04	-0.74	6.30
–SO_2Me	-7.91	-2.18	5.73	-8.33	-2.75	5.58

Table S9. HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) and HOMO-LUMO gap (E_g), in eV, of all DPP-X systems. Calculations at the ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	DPP-X₁			DPP-X₂		
	E_{HOMO}	E_{LUMO}	E_g	E_{HOMO}	E_{LUMO}	E_g
–H	-8.22	1.05	9.27	-8.22	1.05	9.27
–Br	-8.34	0.88	9.22	-8.44	0.72	9.16
–Ph	-7.71	0.65	8.36	-7.24	0.45	7.69
–CF_3	-8.74	0.48	9.22	-9.19	-0.06	9.13
–Me	-8.03	1.31	9.34	-7.84	1.55	9.39
–CHF_2	-8.64	0.60	9.24	-9.04	0.20	9.24
–CHO	-8.62	-0.09	8.52	-8.98	-0.92	8.07
–Cl	-8.35	0.93	9.27	-8.46	0.81	9.26
–CN	-8.77	-0.07	8.70	-9.28	-1.01	8.26
–COMe	-8.51	0.15	8.65	-8.78	-0.49	8.28
–COOMe	-8.41	0.30	8.71	-8.57	-0.26	8.31
–COOH	-8.97	-0.13	8.84	-9.66	-1.08	8.58
–F	-8.44	1.18	9.62	-8.67	1.32	9.99
–NMe_2	-7.36	1.98	9.34	-6.63	2.60	9.23
–NH_2	-7.60	1.86	9.46	-7.12	2.46	9.58
–NHMe	-7.38	1.95	9.34	-6.67	2.66	9.33
–NO_2	-8.99	-0.52	8.47	-9.68	-1.58	8.10
–OMe	-7.96	1.65	9.61	-7.69	2.18	9.88
–OH	-8.08	1.53	9.61	-7.93	1.98	9.91
–SO_2Me	-8.79	0.27	9.05	-9.28	-0.39	8.88

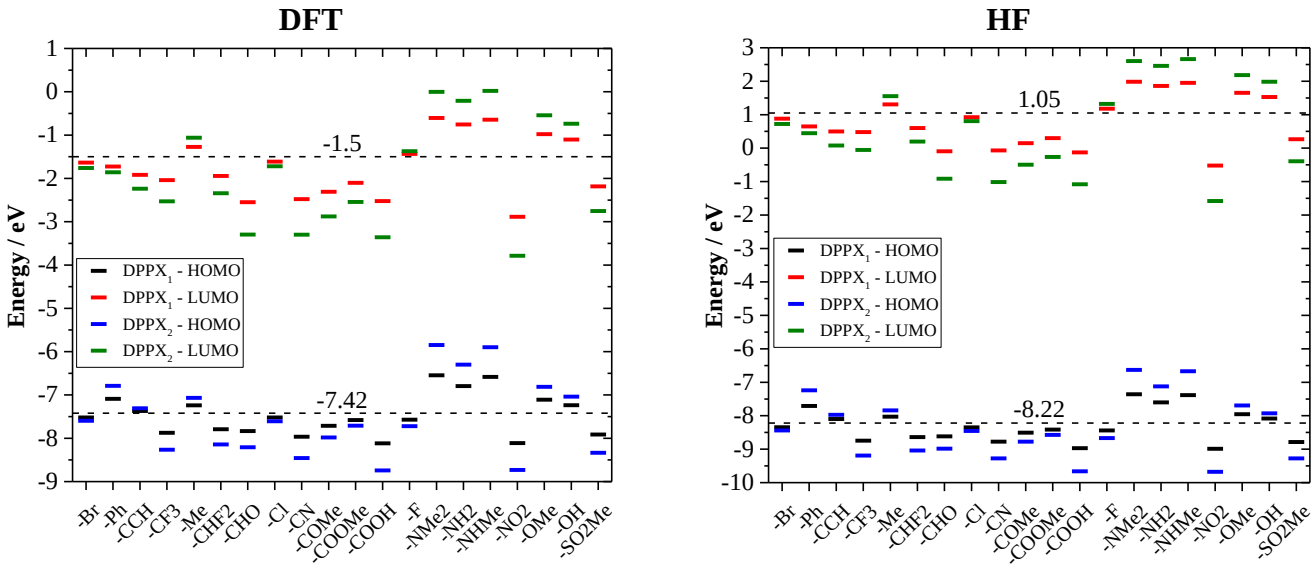


Figure S10. MO energies of all DPP-X systems. Calculations at the DFT and HF levels. The dashed lines with the values above show the FMO energies for the unsubstituted DPP-H system.

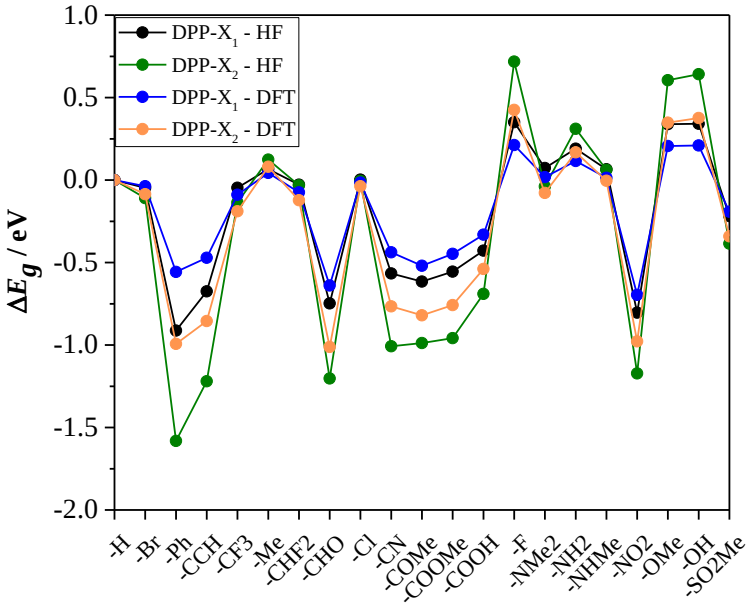


Figure S11. HOMO-LUMO gap (E_g), in eV, of all mono-substituted DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP and ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP levels.

Table S10. HOMO-LUMO gap variations in relation to the unsubstituted DPP-H (ΔE_g), in eV, of all DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP and ADC(2) levels.

–X	CAM-B3LYP		ADC(2)	
	ΔE_g(DPP-X$_1$)	ΔE_g(DPP-X$_2$)	ΔE_g(DPP-X$_1$)	ΔE_g(DPP-X$_2$)
–H	0.00	0.00	0.00	0.00
–Br	-0.04	-0.09	-0.05	-0.11
–Ph	-0.56	-0.99	-0.91	-1.58
–CCH	-0.47	-0.85	-0.68	-1.22
–CF_3	-0.09	-0.19	-0.05	-0.14
–Me	0.04	0.08	0.07	0.12
–CHF_2	-0.07	-0.12	-0.03	-0.03
–CHO	-0.64	-1.01	-0.75	-1.20
–Cl	-0.02	-0.04	-0.00	-0.01
–CN	-0.44	-0.77	-0.57	-1.01
–COMe	-0.52	-0.82	-0.62	-0.99
–COOMe	-0.45	-0.76	-0.56	-0.96
–COOH	-0.33	-0.54	-0.43	-0.69
–F	0.21	0.43	0.35	0.72
–NMe_2	0.02	-0.08	0.07	-0.04
–NH_2	0.12	0.17	0.19	0.31
–NHMe	0.01	0.00	0.07	0.06
–NO_2	-0.70	-0.98	-0.80	-1.17
–OMe	0.21	0.35	0.34	0.61
–OH	0.21	0.38	0.34	0.64
–SO_2Me	-0.19	-0.34	-0.22	-0.39

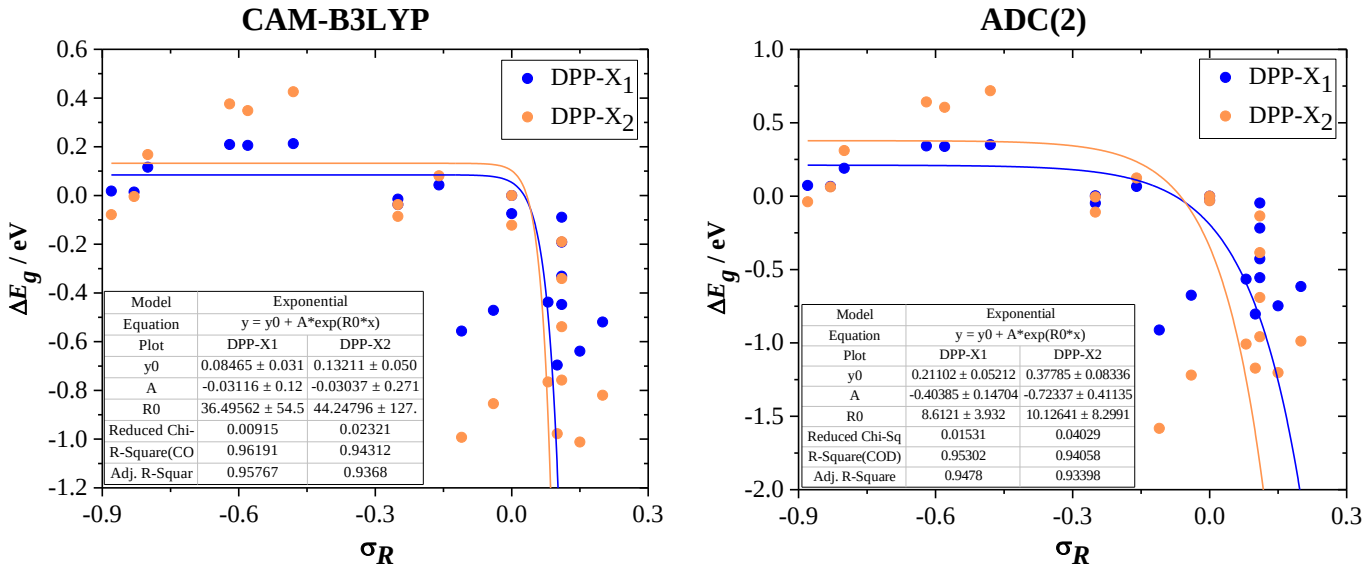
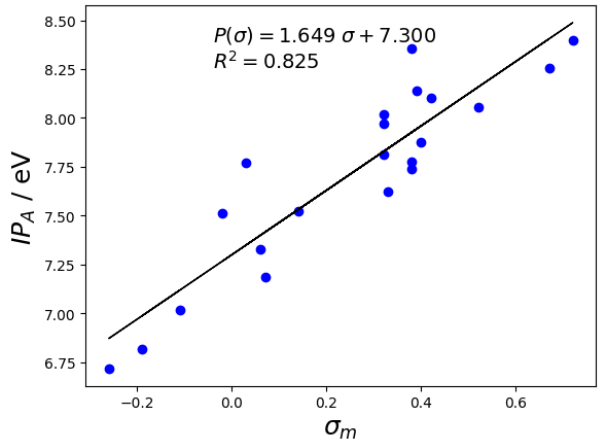
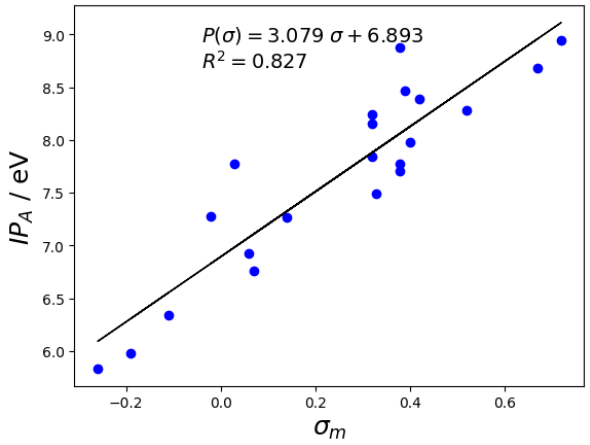
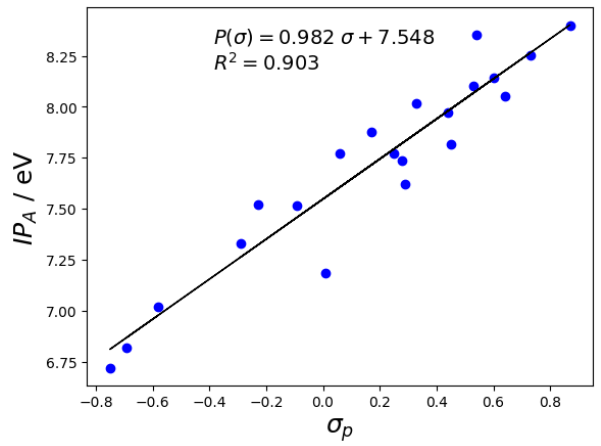
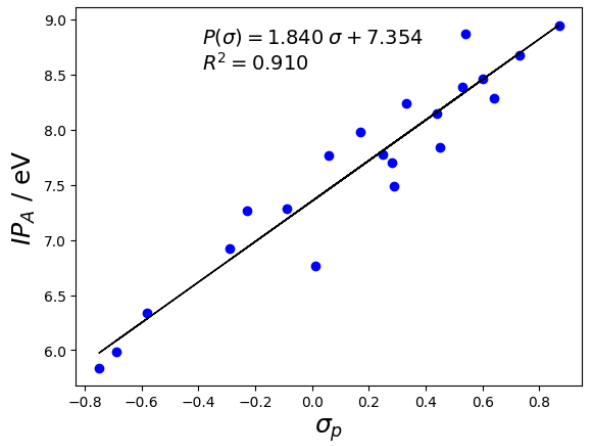
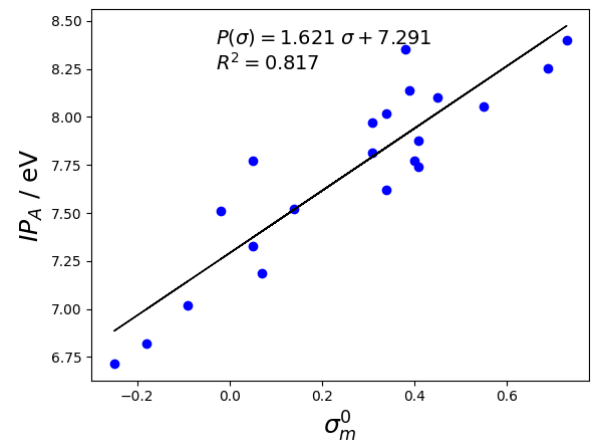
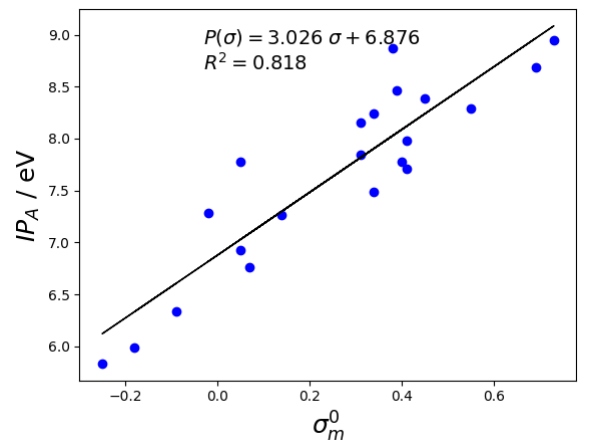
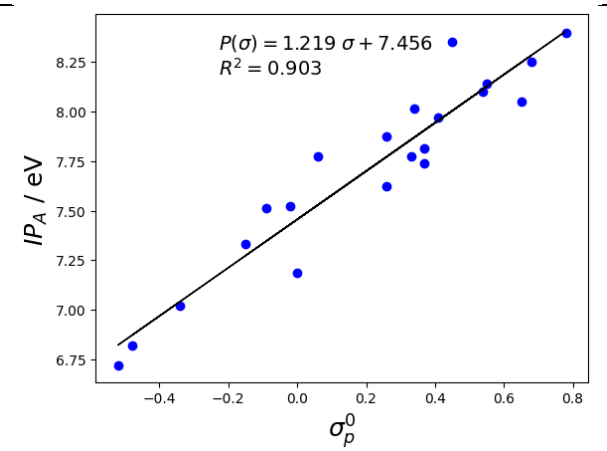
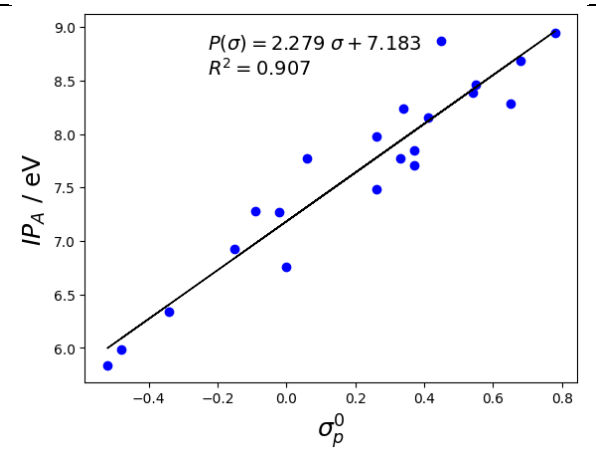


Figure S12. The best correspondences between the difference, in eV, between the HOMO-LUMO gaps of all DPP-X systems and the unsubstituted DPP-H system (ΔE_g) and our ML-based σ_R. Calculations at both CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP and ADC(2).

DPP-X1	DPP-X2
 $P(\sigma) = 1.649\ \sigma + 7.300$ $R^2 = 0.825$ IP_A / eV σ_m	 $P(\sigma) = 3.079\ \sigma + 6.893$ $R^2 = 0.827$ IP_A / eV σ_m
 $P(\sigma) = 0.982\ \sigma + 7.548$ $R^2 = 0.903$ IP_A / eV σ_p	 $P(\sigma) = 1.840\ \sigma + 7.354$ $R^2 = 0.910$ IP_A / eV σ_p
 $P(\sigma) = 1.621\ \sigma + 7.291$ $R^2 = 0.817$ IP_A / eV σ_m^0	 $P(\sigma) = 3.026\ \sigma + 6.876$ $R^2 = 0.818$ IP_A / eV σ_m^0
 $P(\sigma) = 1.219\ \sigma + 7.456$ $R^2 = 0.903$ IP_A / eV σ_p^0	 $P(\sigma) = 2.279\ \sigma + 7.183$ $R^2 = 0.907$ IP_A / eV σ_p^0

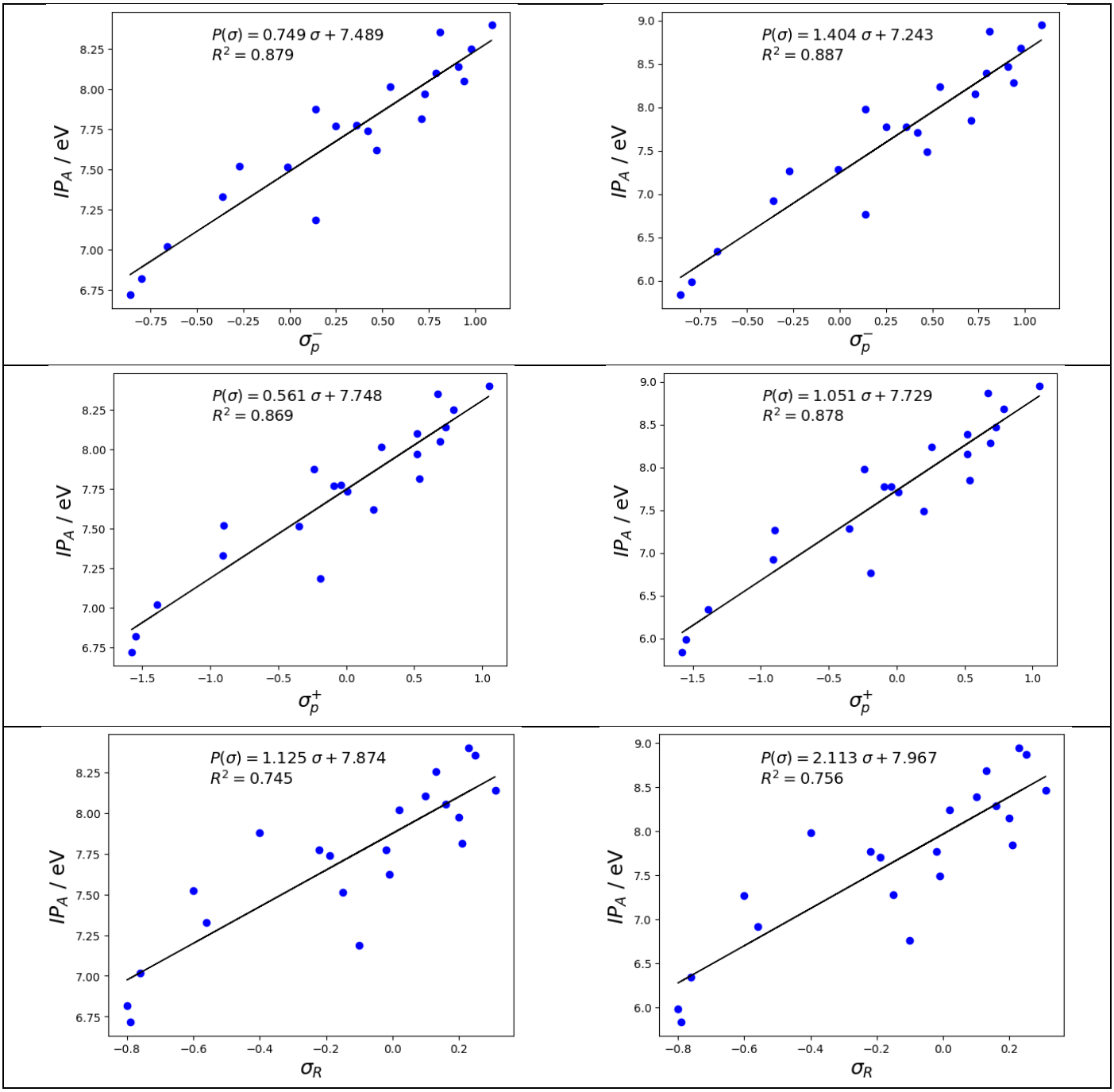
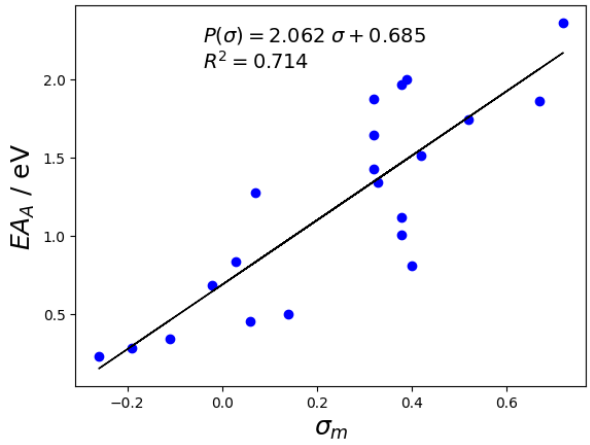
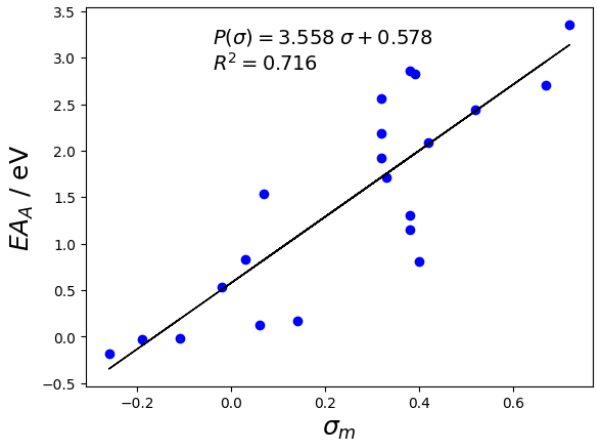
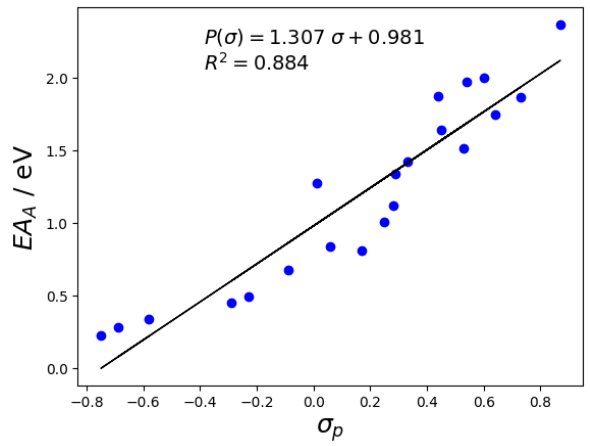
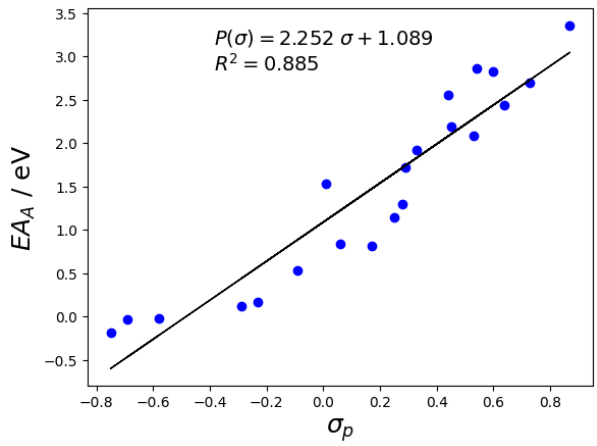
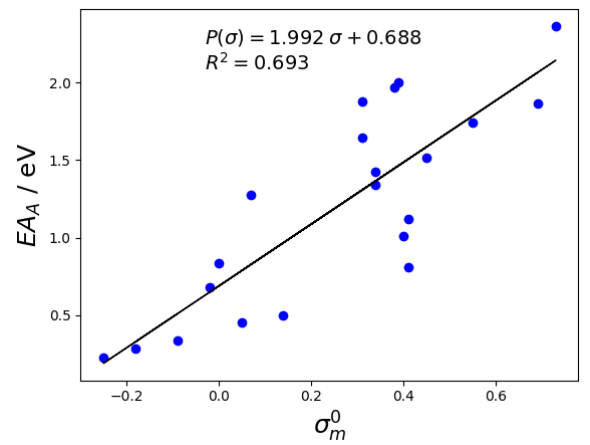
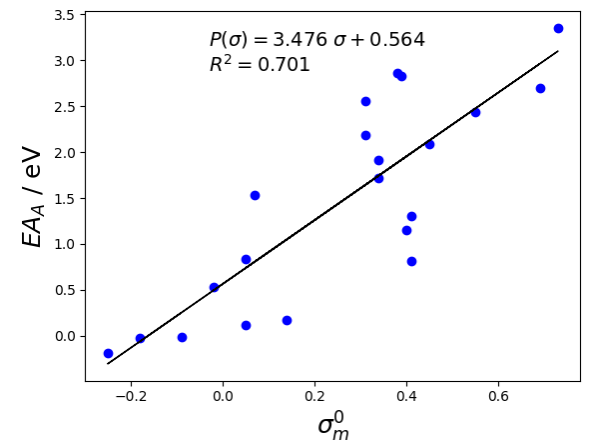
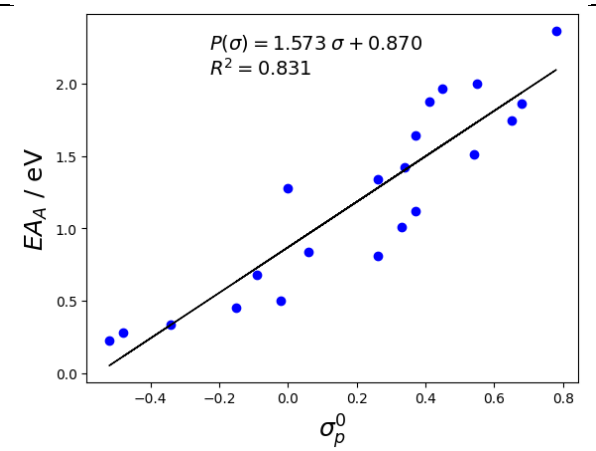
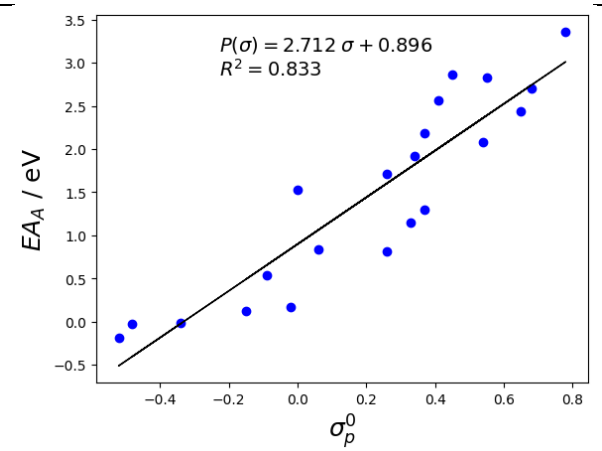


Figure S13. Correspondences between the adiabatic ionization potentials (IP_A) and our ML-based Hammett's constants. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

DPP-X1	DPP-X2
 $P(\sigma) = 2.062\ \sigma + 0.685$ $R^2 = 0.714$ EA_A / eV σ_m	 $P(\sigma) = 3.558\ \sigma + 0.578$ $R^2 = 0.716$ EA_A / eV σ_m
 $P(\sigma) = 1.307\ \sigma + 0.981$ $R^2 = 0.884$ EA_A / eV σ_p	 $P(\sigma) = 2.252\ \sigma + 1.089$ $R^2 = 0.885$ EA_A / eV σ_p
 $P(\sigma) = 1.992\ \sigma + 0.688$ $R^2 = 0.693$ EA_A / eV σ_m^0	 $P(\sigma) = 3.476\ \sigma + 0.564$ $R^2 = 0.701$ EA_A / eV σ_m^0
 $P(\sigma) = 1.573\ \sigma + 0.870$ $R^2 = 0.831$ EA_A / eV σ_p^0	 $P(\sigma) = 2.712\ \sigma + 0.896$ $R^2 = 0.833$ EA_A / eV σ_p^0

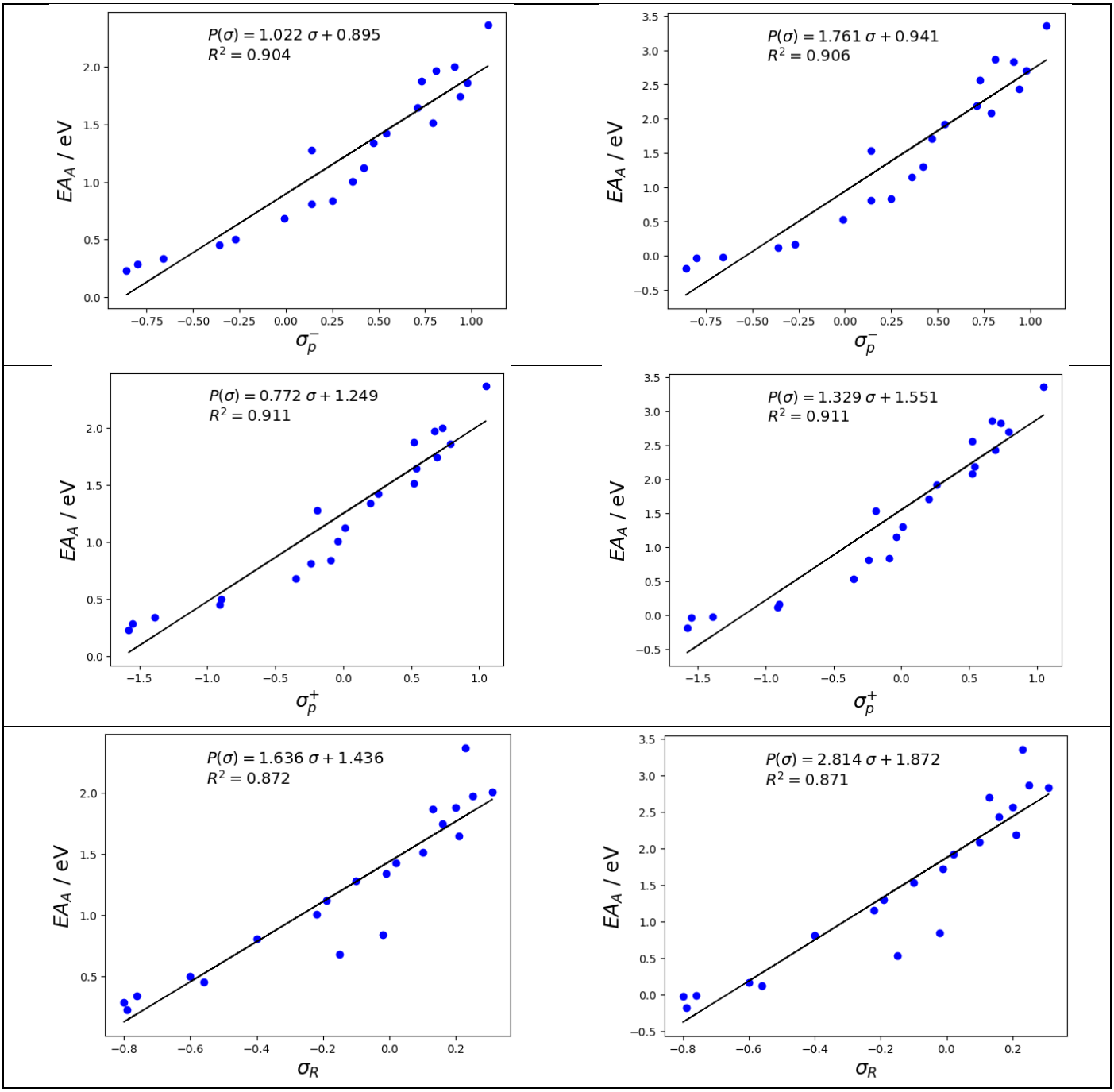


Figure S14. Correspondences between the adiabatic electron affinities (EA_A) and our ML-based Hammett's constants. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

Table S11. Adiabatic ionization potential (IP_A) and electron affinity (EA_A), in eV, of all DPP-X systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	DPP-X_1		DPP-X_2	
	IP_A [eV]	EA_A [eV]	IP_A [eV]	EA_A [eV]
–H	7.77	0.84	7.77	0.84
–Br	7.74	1.12	7.71	1.30
–Ph	7.19	1.28	6.76	1.53
–CCH	7.62	1.34	7.49	1.72
–CF_3	8.10	1.51	8.39	2.09
–Me	7.51	0.68	7.28	0.53
–CHF_2	8.02	1.42	8.24	1.92
–CHO	8.14	2.00	8.46	2.83
–Cl	7.77	1.01	7.77	1.15
–CN	8.25	1.86	8.68	2.70
–COMe	7.97	1.88	8.15	2.56
–COOMe	7.82	1.64	7.84	2.19
–COOH	8.35	1.97	8.87	2.86
–F	7.88	0.81	7.98	0.81
–NMe_2	6.72	0.23	5.84	-0.18
–NH_2	7.02	0.34	6.34	-0.02
–NHMe	6.82	0.28	5.98	-0.03
–NO_2	8.40	2.36	8.95	3.36
–OMe	7.33	0.45	6.92	0.12
–OH	7.52	0.50	7.27	0.17
–SO_2Me	8.05	1.74	8.28	2.44

Table S12. Maximum absorption wavelengths (λ_{max}) in nm, energies of the first singlet excited states (ΔE) in eV, the main transition orbitals assignment and its contribution, and oscillator strengths (f) for all DPP-X_1 systems and, in parenthesis, the same values regarding the DPP-X_2 systems. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	λ_{max} [nm]	ΔE [eV]	Assignment	Contribution [%]	f
–H	348.3	3.56	HOMO → LUMO	97.5.	0.26
–Br	350.0 (352.7)	3.54 (3.52)	HOMO → LUMO	97.5 (97.7)	0.27 (0.30)
–Ph	391.7 (436.2)	3.17 (2.84)	HOMO → LUMO	97.7 (97.9)	0.31 (0.55)
–CCH	382.6 (415.3)	3.24 (2.99)	HOMO → LUMO	97.7 (98.0)	0.28 (0.37)
–CF_3	358.7 (367.0)	3.46 (3.38)	HOMO → LUMO	96.5 (97.9)	0.24 (0.25)
–Me	344.3 (340.5)	3.60 (3.64)	HOMO → LUMO	97.5 (97.7)	0.27 (0.29)
–CHF_2	357.1 (362.6)	3.47 (3.42)	HOMO → LUMO	97.2 (97.8)	0.25 (0.26)
–CHO	407.5 (449.1)	3.04 (2.76)	HOMO → LUMO	97.8 (98.4)	0.24 (0.28)
–Cl	347.4 (347.1)	3.57 (3.57)	HOMO → LUMO	97.6 (97.7)	0.27 (0.29)
–CN	385.1 (412.5)	3.22 (3.01)	HOMO → LUMO	96.6 (98.1)	0.25 (0.29)
–COMe	397.0 (430.2)	3.12 (2.88)	HOMO → LUMO	98.0 (98.4)	0.23 (0.26)
–COOMe	391.0 (424.9)	3.17 (2.92)	HOMO → LUMO	97.9 (98.4)	0.24 (0.26)
–COOH	381.1 (403.9)	3.25 (3.07)	HOMO → LUMO	98.0 (98.1)	0.22 (0.23)
–F	329.5 (312.3)	3.76 (3.97)	HOMO → LUMO	97.4 (97.3)	0.27 (0.29)
–NMe_2	347.2 (350.3)	3.57 (3.54)	HOMO → LUMO	96.9 (98.2)	0.26 (0.38)
–NH_2	337.1 (327.0)	3.68 (3.79)	HOMO → LUMO	96.9 (97.9)	0.26 (0.32)
–NHMe	345.9 (339.3)	3.59 (3.65)	HOMO → LUMO	96.6 (98.1)	0.28 (0.41)
–NO_2	421.4 (453.5)	2.94 (2.73)	HOMO → LUMO	98.1 (98.8)	0.20 (0.24)
–OMe	333.8 (323.2)	3.71 (3.84)	HOMO → LUMO	97.4 (97.9)	0.24 (0.25)
–OH	330.5 (314.9)	3.75 (3.94)	HOMO → LUMO	97.0 (97.6)	0.26 (0.29)
–SO_2Me	368.7 (385.4)	3.36 (3.22)	HOMO → LUMO	97.5 (97.9)	0.23 (0.24)

Table S13. Maximum absorption wavelengths (λ_{max}) in nm, energies of the first singlet excited states (ΔE) in eV, the main transition orbitals assignment and its contribution, and oscillator strengths (f) for all DPP-X_1 systems and, in parenthesis, the same values regarding the DPP-X_2 systems. Calculations at the ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

X	λ_{max} [nm]	ΔE [eV]	Assignment	Contribution [%]	f
–H	368.57	3.36	HOMO → LUMO	92.1	0.29
–Br	371.77 (375.10)	3.33 (3.31)	HOMO → LUMO	91.9 (92.8)	0.30 (0.32)
–Ph	421.89 (467.46)	2.94 (2.65)	HOMO → LUMO	89.7 (90.3)	0.31 (0.51)
–CCH	401.70 (433.10)	3.09 (2.86)	HOMO → LUMO	89.9 (89.8)	0.29 (0.35)
–CF_3	381.47 (391.11)	3.25 (3.17)	HOMO → LUMO	91.0 (92.3)	0.27 (0.27)
–Me	366.26 (362.67)	3.39 (3.42)	HOMO → LUMO	92.1 (92.2)	0.30 (0.31)
–CHF_2	379.05 (385.43)	3.27 (3.22)	HOMO → LUMO	91.6 (91.9)	0.27 (0.27)
–CHO	428.92 (469.13)	2.89 (2.64)	HOMO → LUMO	91.6 (91.7)	0.26 (0.29)
–Cl	368.11 (367.15)	3.37 (3.38)	HOMO → LUMO	92.0 (93.0)	0.30 (0.32)
–CN	405.64 (430.16)	3.06 (2.88)	HOMO → LUMO	89.9 (90.5)	0.27 (0.30)
–COMe	421.15 (457.21)	2.94 (2.71)	HOMO → LUMO	92.0 (92.0)	0.25 (0.26)
–COOMe	414.57 (450.86)	2.99 (2.75)	HOMO → LUMO	91.9 (92.2)	0.25 (0.26)
–COOH	404.71 (428.68)	3.06 (2.89)	HOMO → LUMO	91.9 (91.4)	0.24 (0.24)
–F	346.67 (326.42)	3.58 (3.80)	HOMO → LUMO	92.8 (94.2)	0.32 (0.35)
–NMe_2	380.72 (390.98)	3.26 (3.17)	HOMO → LUMO	92.7 (93.1)	0.29 (0.39)
–NH_2	363.22 (351.78)	3.41 (3.52)	HOMO → LUMO	92.9 (93.7)	0.29 (0.37)
–NHMe	376.33 (373.85)	3.29 (3.32)	HOMO → LUMO	87.7 (94.7)	0.30 (0.43)
–NO_2	434.64 (455.34)	2.85 (2.72)	HOMO → LUMO	92.1 (93.2)	0.23 (0.25)
–OMe	356.60 (346.58)	3.48 (3.58)	HOMO → LUMO	92.9 (94.9)	0.27 (0.28)
–OH	351.82 (335.95)	3.52 (3.69)	HOMO → LUMO	92.9 (94.9)	0.30 (0.34)
–SO_2Me	396.92 (419.79)	3.12 (2.95)	HOMO → LUMO	91.8 (92.5)	0.25 (0.24)

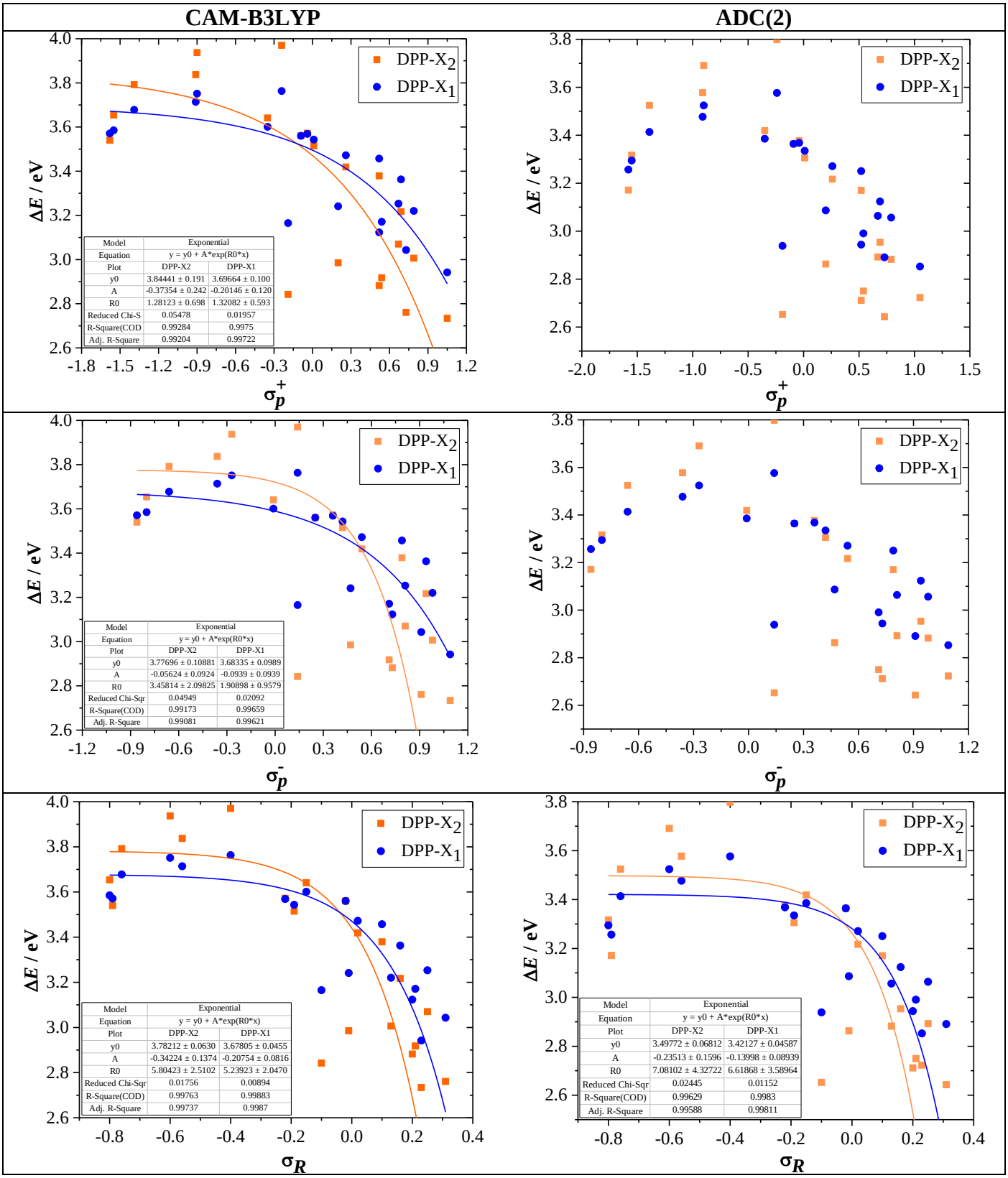
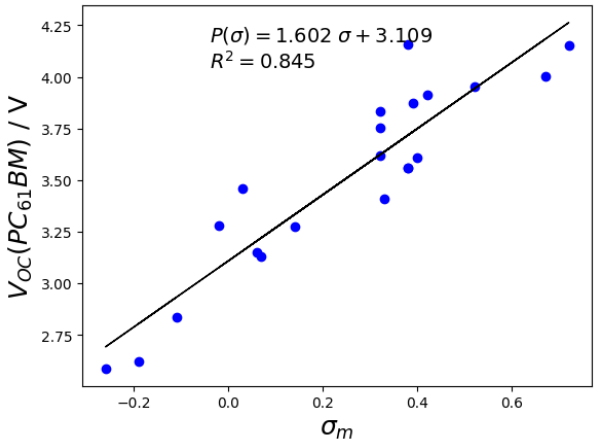
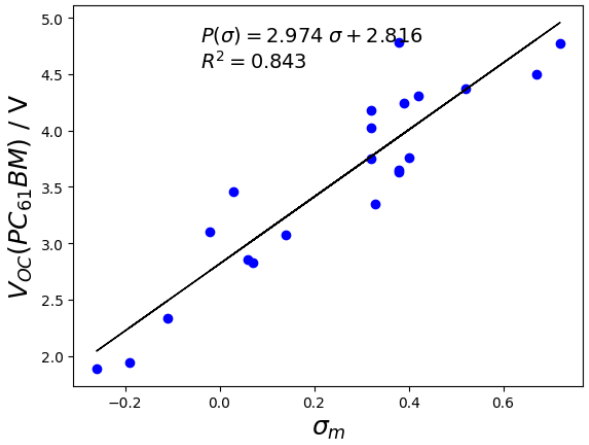
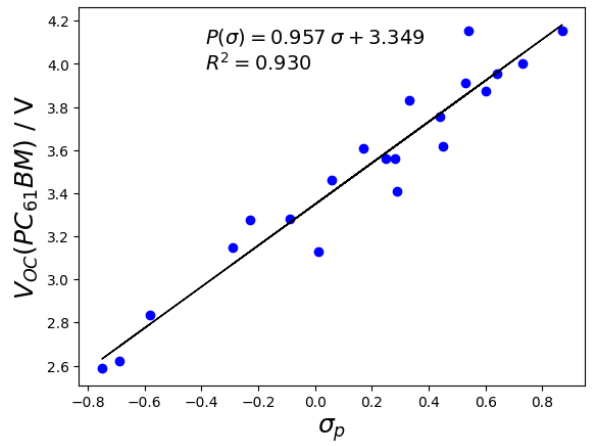
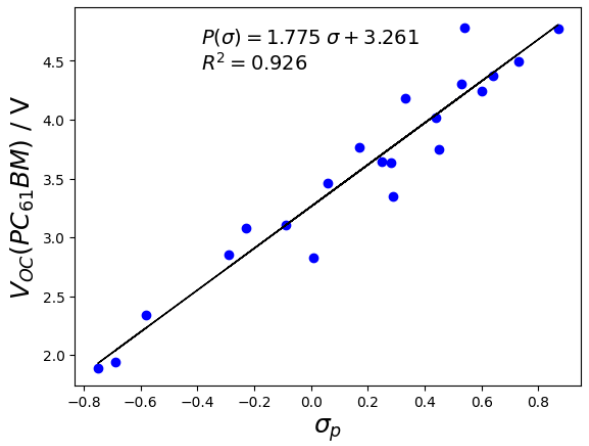
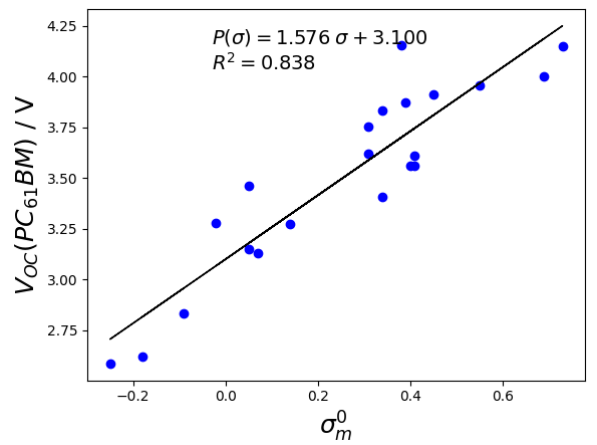
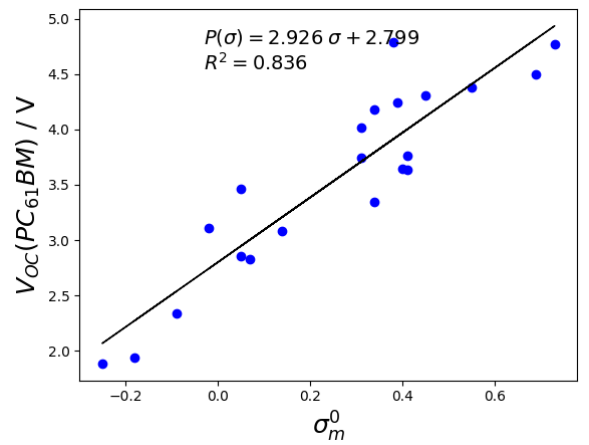
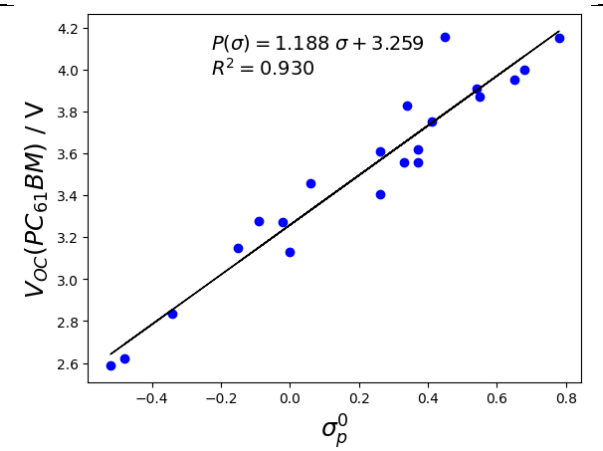
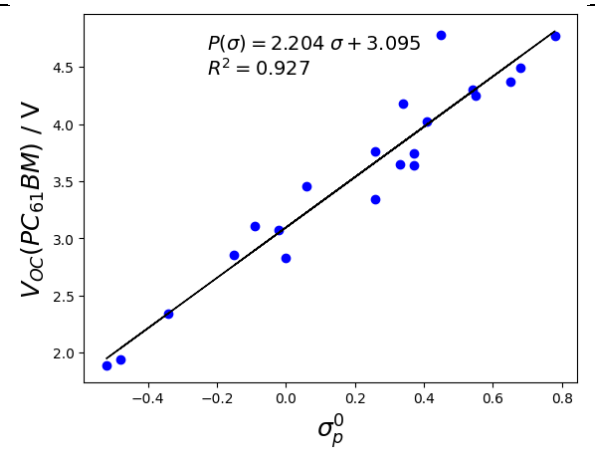


Figure S15. Correspondences between Hammett's parameters and the energy of the first singlet excited state (ΔE).

DPP-X$_1$	DPP-X$_2$
 $P(\sigma) = 1.602\ \sigma + 3.109$ $R^2 = 0.845$ $V_{OC}(PC_{61}BM)$ / V σ_m	 $P(\sigma) = 2.974\ \sigma + 2.816$ $R^2 = 0.843$ $V_{OC}(PC_{61}BM)$ / V σ_m
 $P(\sigma) = 0.957\ \sigma + 3.349$ $R^2 = 0.930$ $V_{OC}(PC_{61}BM)$ / V σ_p	 $P(\sigma) = 1.775\ \sigma + 3.261$ $R^2 = 0.926$ $V_{OC}(PC_{61}BM)$ / V σ_p
 $P(\sigma) = 1.576\ \sigma + 3.100$ $R^2 = 0.838$ $V_{OC}(PC_{61}BM)$ / V σ_m^0	 $P(\sigma) = 2.926\ \sigma + 2.799$ $R^2 = 0.836$ $V_{OC}(PC_{61}BM)$ / V σ_m^0
 $P(\sigma) = 1.188\ \sigma + 3.259$ $R^2 = 0.930$ $V_{OC}(PC_{61}BM)$ / V σ_p^0	 $P(\sigma) = 2.204\ \sigma + 3.095$ $R^2 = 0.927$ $V_{OC}(PC_{61}BM)$ / V σ_p^0

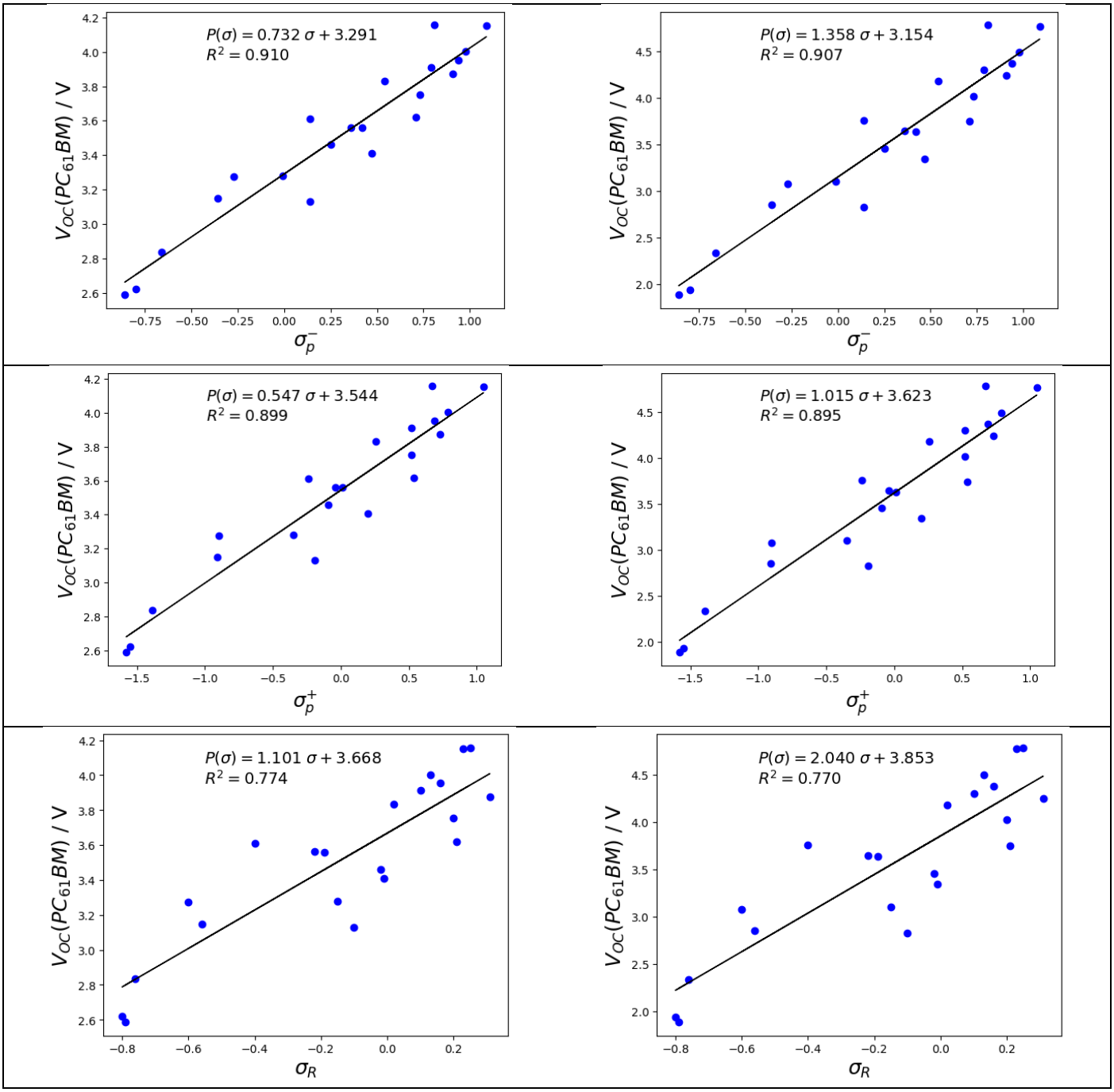
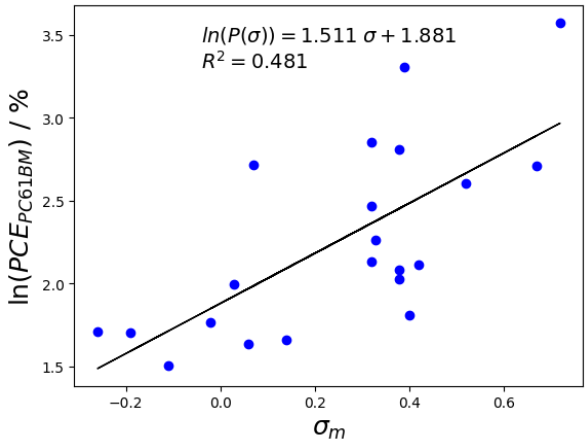
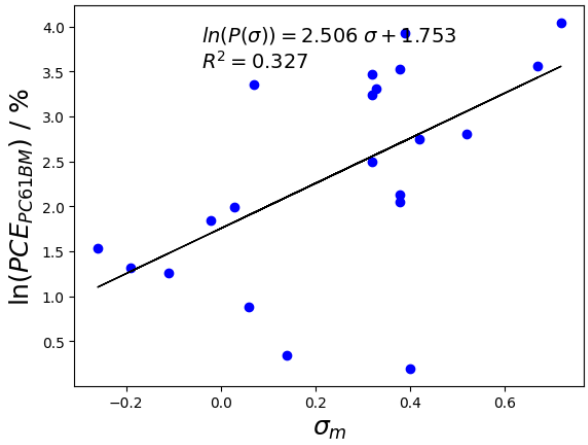
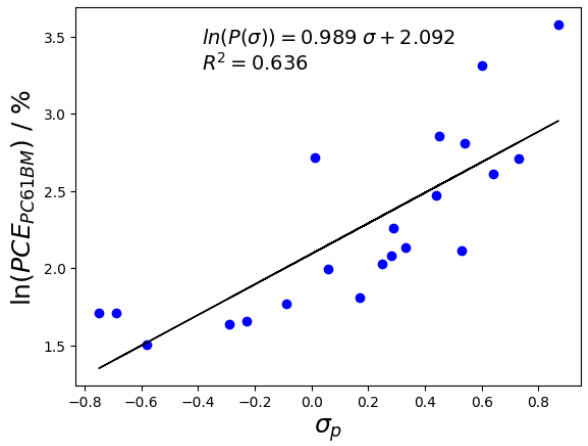
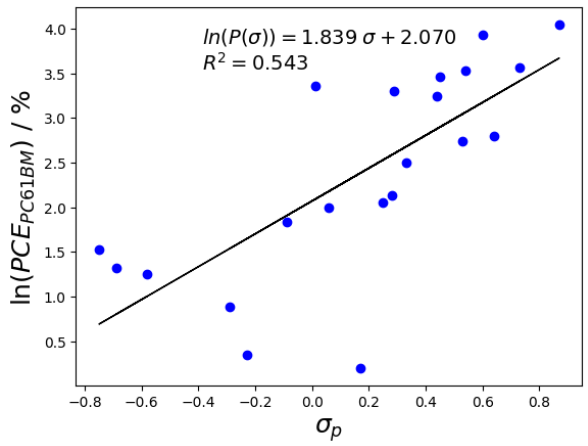
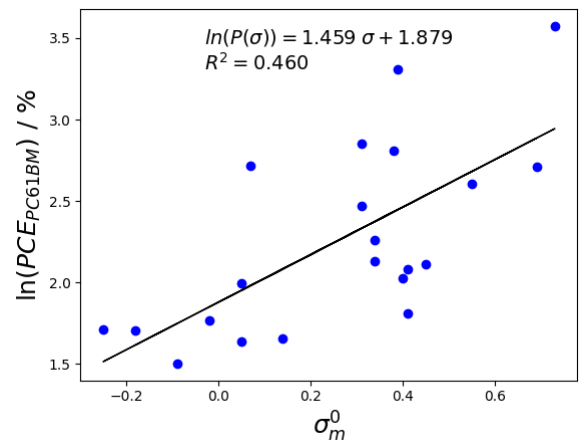
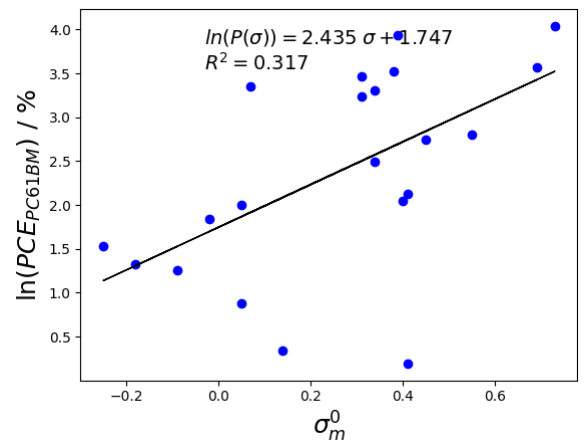
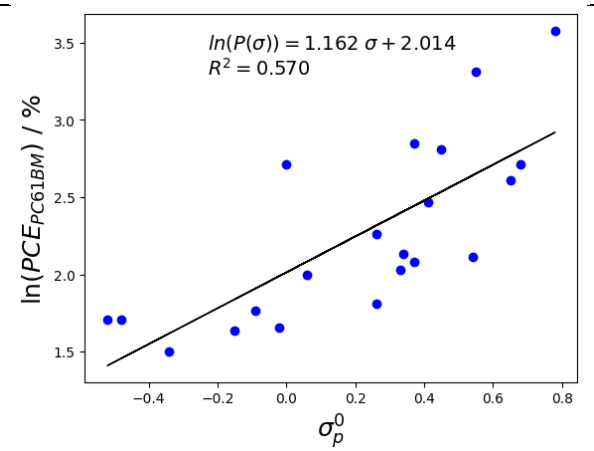
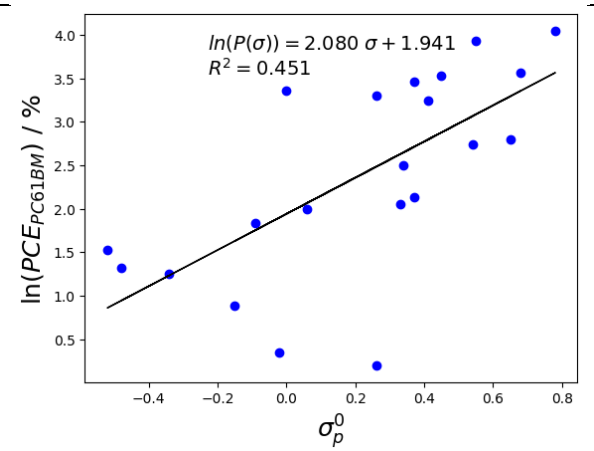


Figure S16. Correspondences between the open-circuit voltage (V_{OC}) and our ML-based Hammett's constants. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level and considering $PC_{61}BM$ as *A*-material.

DPP-X1	DPP-X2
 $ln(P(\sigma)) = 1.511\ \sigma + 1.881$ $R^2 = 0.481$ $\ln(PCE_{PC61BM})$ / % σ_m	 $ln(P(\sigma)) = 2.506\ \sigma + 1.753$ $R^2 = 0.327$ $\ln(PCE_{PC61BM})$ / % σ_m
 $ln(P(\sigma)) = 0.989\ \sigma + 2.092$ $R^2 = 0.636$ $\ln(PCE_{PC61BM})$ / % σ_p	 $ln(P(\sigma)) = 1.839\ \sigma + 2.070$ $R^2 = 0.543$ $\ln(PCE_{PC61BM})$ / % σ_p
 $ln(P(\sigma)) = 1.459\ \sigma + 1.879$ $R^2 = 0.460$ $\ln(PCE_{PC61BM})$ / % σ_m^0	 $ln(P(\sigma)) = 2.435\ \sigma + 1.747$ $R^2 = 0.317$ $\ln(PCE_{PC61BM})$ / % σ_m^0
 $ln(P(\sigma)) = 1.162\ \sigma + 2.014$ $R^2 = 0.570$ $\ln(PCE_{PC61BM})$ / % σ_p^0	 $ln(P(\sigma)) = 2.080\ \sigma + 1.941$ $R^2 = 0.451$ $\ln(PCE_{PC61BM})$ / % σ_p^0

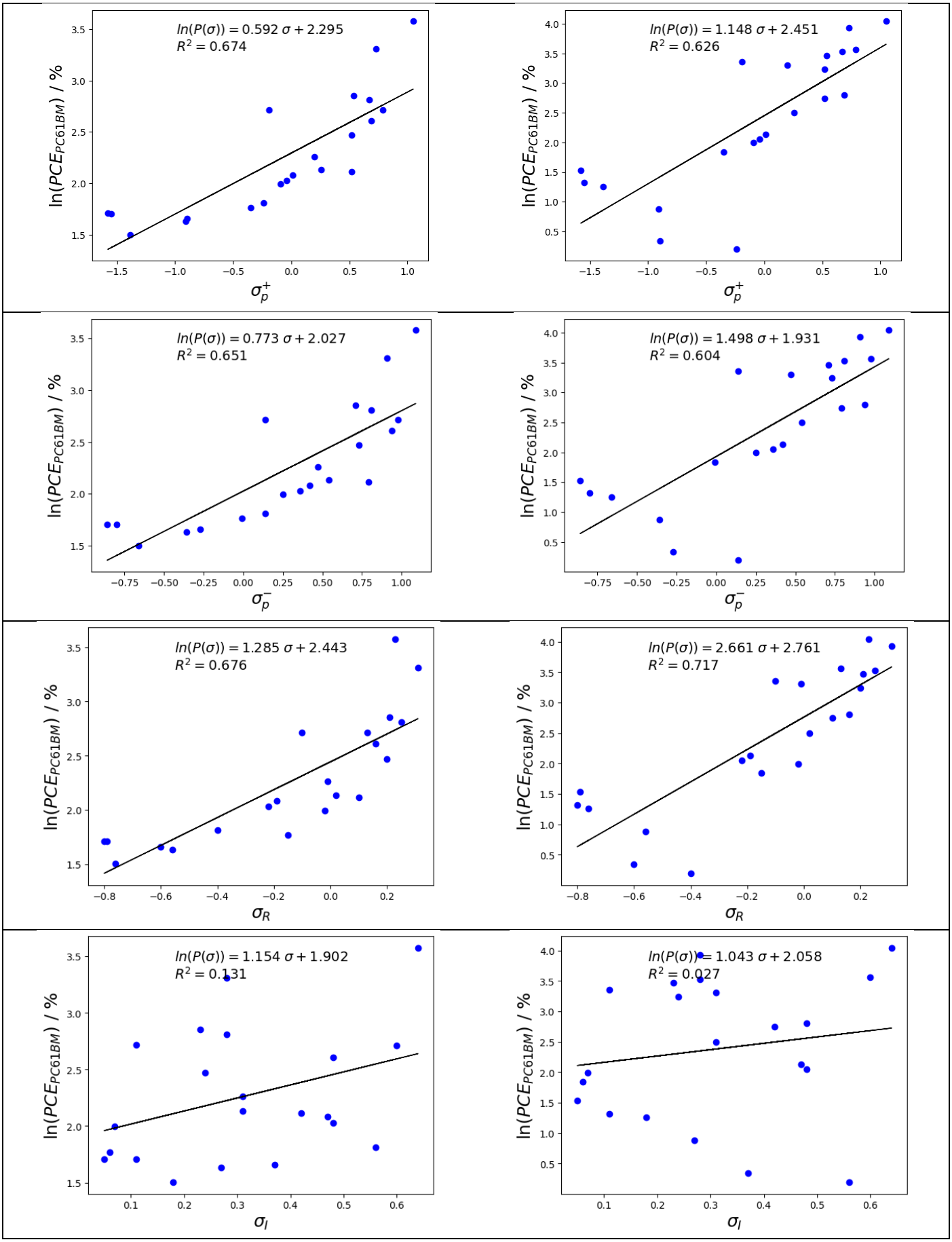


Figure S17. Correspondences between the power conversion efficiency (PCE) and our ML-based Hammett's constants. Calculations at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level. The calculations take into consideration the $PC_{61}BM$ as acceptor-material, the FF = 0.65 and J_{SC} calculated by eq. (12).

Table S14. Open-circuit voltage (V_{OC}) in V, fill factor (FF), short-circuit current (J_{SC}) in mA/cm^2, and power conversion efficiency (PCE) in % of all DPP-X systems calculated at the CAM-B3LYP/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	DPP-X$_1$				DPP-X$_2$			
	V_{OC}	FF	J_{SC}	PCE	V_{OC}	FF	J_{SC}	PCE
–H	3.46	0.98	3.27	11.06	3.46	0.98	3.27	11.06
–Br	3.56	0.98	3.47	12.06	3.64	0.98	3.56	12.67
–Ph	3.13	0.97	7.42	22.66	2.83	0.97	15.61	42.93
–CCH	3.41	0.98	4.33	14.41	3.35	0.98	12.53	40.94
–CF_3	3.91	0.98	3.26	12.49	4.30	0.98	5.56	23.49
–Me	3.28	0.98	2.74	8.78	3.11	0.97	3.12	9.44
–CHF_2	3.83	0.98	3.39	12.71	4.18	0.98	4.46	18.30
–CHO	3.87	0.98	10.87	41.24	4.25	0.98	18.47	76.92
–Cl	3.56	0.98	3.29	11.44	3.65	0.98	3.29	11.72
–CN	4.00	0.98	5.78	22.68	4.50	0.98	12.09	53.37
–COMe	3.75	0.98	4.85	17.80	4.02	0.98	9.76	38.46
–COOMe	3.62	0.98	7.36	26.04	3.75	0.98	13.13	48.16
–COOH	4.16	0.98	6.15	25.04	4.78	0.98	10.96	51.51
–F	3.61	0.98	2.61	9.20	3.76	0.98	0.50	1.83
–NMe_2	2.59	0.97	3.29	8.25	1.89	0.96	3.77	6.83
–NH_2	2.84	0.97	2.44	6.73	2.34	0.97	2.31	5.23
–NHMe	2.62	0.97	3.23	8.23	1.94	0.96	2.98	5.55
–NO_2	4.15	0.98	13.23	53.84	4.77	0.98	18.36	86.09
–OMe	3.15	0.97	2.51	7.70	2.85	0.97	1.30	3.61
–OH	3.28	0.98	2.47	7.88	3.08	0.97	0.70	2.11
–SO_2Me	3.95	0.98	5.28	20.45	4.37	0.98	5.78	24.83

Table S15. Open-circuit voltage (V_{OC}) in V, fill factor (FF), short-circuit current (J_{SC}) in mA/cm^2, and power conversion efficiency (PCE) in % of all DPP-X systems calculated at the ADC(2)/Def2-TZVP//B3LYP-D3/Def2-TZVP level.

–X	DPP-X$_1$				DPP-X$_2$			
	V_{OC}	FF	J_{SC}	PCE	V_{OC}	FF	J_{SC}	PCE
–H	4.26	0.96	5.28	15.85	4.26	0.96	5.28	15.85
–Br	4.38	0.96	5.28	16.31	4.48	0.96	4.72	14.93
–Ph	3.75	0.96	13.23	34.80	3.28	0.95	20.44	46.84
–CCH	4.14	0.96	10.92	31.80	4.01	0.96	13.38	37.74
–CF_3	4.78	0.97	6.15	20.79	5.23	0.97	7.63	28.27
–Me	4.07	0.96	5.39	15.42	3.88	0.96	4.46	12.17
–CHF_2	4.68	0.97	5.90	19.53	5.08	0.97	5.78	20.81
–CHO	4.66	0.97	12.59	41.42	5.02	0.97	20.76	73.86
–Cl	4.39	0.96	5.31	16.44	4.50	0.96	5.56	17.66
–CN	4.81	0.97	10.81	36.82	5.32	0.97	9.76	36.81
–COMe	4.55	0.97	13.23	42.47	4.82	0.97	19.74	67.25
–COOMe	4.45	0.96	12.09	38.02	4.61	0.97	19.18	62.51
–COOH	5.01	0.97	10.81	38.36	5.70	0.97	12.59	50.99
–F	4.48	0.96	3.24	10.24	4.71	0.97	2.25	7.49
–NMe_2	3.40	0.96	6.10	14.50	2.67	0.95	7.63	14.09
–NH_2	3.64	0.96	4.51	11.52	3.16	0.95	3.54	7.81
–NHMe	3.42	0.96	5.67	13.57	2.71	0.95	4.80	9.01
–NO_2	5.03	0.97	14.77	52.60	5.72	0.97	19.29	78.37
–OMe	4.00	0.96	3.88	10.89	3.73	0.96	3.24	8.48
–OH	4.12	0.96	3.54	10.28	3.97	0.96	2.69	7.50
–SO_2Me	4.83	0.97	5.19	17.73	5.32	0.97	12.52	47.20

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