Supplementary Information

First Theoretical Probe for Efficient Enhancement of Optical Nonlinearity *via* Structural Modifications into Phenylene Based D-π-A Configured Molecules

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Table S1: Cartesian coordinates of **PMD-1**

Atom	X-axis	Y-axis	Z-axis
C	0.704765	2.205986	-0.466073
C	-0.622649	1.805633	-0.472517
C	-1.021935	0.466021	-0.57113
C	-0.010276	-0.512449	-0.695143
C	1.316733	-0.11052	-0.705238
C	1.71697	1.226645	-0.580787
H	-1.398702	2.557407	-0.416298
H	2.090548	-0.856162	-0.830972
C	-8.753671	0.051678	0.209526

C	-8.174755	-1.063945	-0.412613
C	-6.799455	-0.955929	-0.525213
C	-6.294447	0.237451	0.004057
H	-8.791392	-1.887744	-0.745477
C	-5.678005	-1.810842	-1.086019
C	-4.487671	-0.918335	-0.790831
C	-3.102725	-0.989785	-0.994167
C	-2.436496	0.131794	-0.529579
C	-4.881799	0.251894	-0.164558
H	-2.578254	-1.805859	-1.466596
S	-3.555914	1.27554	0.192308
S	-7.509263	1.234807	0.643858
C	3.133349	1.554967	-0.558922
C	3.778085	2.74837	-0.837817
H	3.231888	3.636918	-1.114145
C	5.17184	2.64729	-0.729555
C	5.59467	1.381904	-0.360777
C	9.473936	1.505952	-0.154317
C	8.878094	2.712297	-0.543241
C	7.494344	2.647177	-0.587495
C	7.014813	1.376629	-0.264615
S	8.25396	0.2717	0.115134
H	9.478189	3.584942	-0.773417
C	6.34828	3.588691	-0.908004
S	4.286502	0.30172	-0.131309
C	6.28505	4.748996	0.094096
H	7.170687	5.383793	-0.000152
H	5.402395	5.366919	-0.094688
H	6.234938	4.377819	1.120096
C	6.433502	4.114303	-2.34609
H	7.323777	4.736755	-2.473958
H	6.481478	3.291282	-3.062863
H	5.557335	4.725536	-2.580763
C	-5.569753	-3.148398	-0.342666
H	-6.469028	-3.748524	-0.506522
H	-4.708954	-3.717215	-0.706111
H	-5.450499	-2.991383	0.731817
C	-5.848738	-2.039184	-2.593171
H	-4.993719	-2.591164	-2.994123
H	-6.752907	-2.621949	-2.789514
H	-5.927536	-1.089581	-3.127481
C	-10.071903	0.416103	0.544745
H	-10.116284	1.389219	1.022555

C	10.866172	1.288309	-0.135726
H	11.43298	2.074235	-0.638468
C	-13.004938	-1.762774	-0.10373
C	-13.616496	-0.658804	0.492155
C	-14.998062	-0.664708	0.681159
C	-15.701723	-1.779127	0.263228
C	-15.07218	-2.874402	-0.332189
C	-13.705651	-2.878244	-0.523907
C	-11.292623	-0.20938	0.390105
H	-15.551697	0.146268	1.134033
H	-13.20448	-3.721762	-0.984554
C	-11.548723	-1.539558	-0.199966
O	-10.763652	-2.334049	-0.679904
C	-12.576052	0.343622	0.809468
C	-12.840055	1.565193	1.388572
C	-11.855347	2.546273	1.685527
N	-11.085209	3.370252	1.941657
C	-14.148775	1.983993	1.752459
N	-15.197499	2.359205	2.062189
C	13.461388	-1.242337	-0.141697
C	12.526414	-1.906081	0.661595
C	12.728051	-3.242306	0.996555
C	13.860356	-3.864008	0.502036
C	14.791356	-3.18691	-0.289067
C	14.602738	-1.859804	-0.620084
C	11.664996	0.243128	0.249413
H	12.048062	-3.81743	1.611357
H	15.323018	-1.328187	-1.231369
C	11.47463	-0.943438	1.051431
C	10.6502	-1.073394	2.145735
C	9.965239	0.034712	2.710599
N	9.442987	0.932646	3.217523
C	10.532474	-2.285049	2.877556
N	10.411659	-3.272192	3.467077
C	13.010649	0.147996	-0.380664
O	13.591755	1.00412	-1.006754
O	1.101219	3.493558	-0.351382
O	-0.406512	-1.801405	-0.793659
C	0.553355	-2.867051	-0.768633
H	1.351807	-2.599258	-0.065515
C	0.150072	4.531612	-0.076968
H	-0.607686	4.13578	0.610583
C	0.923396	5.626142	0.628597

H	1.392624	5.241861	1.53628
H	1.704436	6.024855	-0.025062
H	0.253868	6.445855	0.900815
C	-0.498256	5.013916	-1.363111
H	-1.006447	4.206881	-1.89514
H	-1.232578	5.794527	-1.146593
H	0.261555	5.43287	-2.028749
C	-0.183841	-4.075961	-0.231162
H	-0.596587	-3.866578	0.757537
H	-1.004344	-4.351813	-0.899668
H	0.495539	-4.928406	-0.15328
C	1.123393	-3.10328	-2.156597
H	1.604582	-2.210159	-2.560888
H	1.864454	-3.906739	-2.128998
H	0.323929	-3.397426	-2.842346
F	-17.019547	-1.82601	0.425622
F	-15.816885	-3.908289	-0.707744
F	14.086093	-5.143445	0.779211
F	15.859066	-3.850685	-0.718669

Table S2: Cartesian coordinates of **PMDC2**

Atom	**X-axis**	**Y-axis**	**Z-axis**
C	-0.553625	2.002185	-0.168306
C	-1.859414	1.540761	-0.254467
C	-2.189212	0.215883	-0.565766
C	-1.125232	-0.676259	-0.829796
C	0.178179	-0.211823	-0.761377
C	0.508813	1.108663	-0.423323
H	-2.674408	2.233091	-0.090178
H	0.990234	-0.888335	-0.993308
C	-9.892356	-0.714482	0.069459
C	-9.288594	-1.670476	-0.706942
C	-7.895814	-1.47595	-0.800169
C	-7.46218	-0.37377	-0.091493
H	-9.856291	-2.46583	-1.174314
C	-6.733289	-2.173753	-1.48251
C	-5.585421	-1.284355	-1.040606
C	-4.194151	-1.253859	-1.23819
C	-3.58503	-0.193821	-0.594566
C	-6.03858	-0.25627	-0.241961

H	-3.629073	-1.957671	-1.830093
S	-4.76976	0.760952	0.287164
S	-8.736891	0.450227	0.699328
C	1.90542	1.501106	-0.333372
C	2.488243	2.75544	-0.412244
H	1.896661	3.646855	-0.552148
C	3.884409	2.709949	-0.303818
C	4.373018	1.425398	-0.134449
C	8.240334	1.715206	0.122962
C	7.580536	2.936537	-0.074694
C	6.203692	2.808432	-0.140755
C	5.789765	1.478505	-0.02714
S	7.084695	0.392502	0.18402
H	8.134482	3.864299	-0.159043
C	5.009634	3.727631	-0.319567
S	3.121242	0.256741	-0.093784
C	4.882728	4.709712	0.852481
H	5.733022	5.397516	0.8686
H	3.968026	5.301674	0.755078
H	4.851166	4.178452	1.806279
C	5.068578	4.478019	-1.655531
H	5.924296	5.159114	-1.674747
H	5.161777	3.782274	-2.492599
H	4.160882	5.0711	-1.799527
C	-6.558659	-3.606459	-0.963459
H	-7.426302	-4.218939	-1.226478
H	-5.671109	-4.067862	-1.4066
H	-6.445246	-3.616116	0.123036
C	-6.892834	-2.165365	-3.007895
H	-6.012168	-2.603403	-3.486915
H	-7.767286	-2.75149	-3.306046
H	-7.0164	-1.146141	-3.381287
C	9.639672	1.57048	0.114665
H	10.163504	2.458532	-0.243966
C	12.363379	-0.788395	-0.303631
C	11.469276	-1.62308	0.377057
C	11.743549	-2.983162	0.490166
C	12.904905	-3.454673	-0.09528
C	13.794117	-2.609167	-0.76178
C	13.533319	-1.257616	-0.872219
C	10.494382	0.516151	0.32077
H	11.098359	-3.68628	1.000549
H	14.221029	-0.595523	-1.385827

C	10.369394	-0.793377	0.91433
C	9.5558	-1.146719	1.967751
C	8.820562	-0.184173	2.708409
N	8.258902	0.589678	3.357961
C	9.501786	-2.467965	2.485635
N	9.433456	-3.544691	2.901422
C	11.837393	0.596594	-0.313416
O	12.370075	1.572684	-0.790249
O	-0.227411	3.275855	0.153491
O	-1.454641	-1.953303	-1.136717
C	-0.441777	-2.957941	-1.263293
H	0.337748	-2.764224	-0.515649
C	-1.233261	4.203167	0.580647
H	-1.971154	3.662582	1.186219
C	-0.522196	5.209085	1.462194
H	-0.035883	4.708507	2.301671
H	0.238876	5.747788	0.890385
H	-1.2354	5.938362	1.854582
C	-1.903277	4.852745	-0.61804
H	-2.366083	4.116098	-1.278061
H	-2.678853	5.548826	-0.286955
H	-1.164831	5.412435	-1.199032
C	-1.117626	-4.27256	-0.93209
H	-1.5477	-4.240981	0.070797
H	-1.918782	-4.480589	-1.647026
H	-0.395368	-5.091533	-0.978339
C	0.150261	-2.946487	-2.662543
H	0.585677	-1.977552	-2.915975
H	0.932818	-3.705316	-2.749086
H	-0.628212	-3.170503	-3.397262
F	13.199692	-4.748876	-0.029628
F	14.893944	-3.135879	-1.290647
N	-11.245913	-0.592286	0.370524
C	-12.185689	0.105962	-0.383747
C	-13.436501	0.032637	0.262266
C	-14.539193	0.658217	-0.317678
C	-14.374587	1.338816	-1.514113
C	-13.122617	1.400529	-2.136636
C	-12.00946	0.785358	-1.582445
H	-15.512092	0.613921	0.161031
H	-15.22418	1.830483	-1.975319
H	-13.0187	1.940265	-3.072048
H	-11.037539	0.829775	-2.061298

C	-12.196131	-2.254508	3.550713
C	-13.551549	-1.906007	3.5372
C	-14.079821	-1.151723	2.501035
C	-13.240036	-0.740583	1.466951
C	-11.878483	-1.104315	1.500723
C	-11.338938	-1.860433	2.533597
H	-11.805968	-2.845205	4.372849
H	-14.193739	-2.231255	4.348399
H	-15.131588	-0.884504	2.495353
H	-10.288451	-2.129304	2.539381

Table S3: Cartesian coordinates of **PMDC3**

Atom	X-axis	Y-axis	Z-axis
C	-0.124395	1.898772	-0.140979
C	-1.441059	1.470326	-0.231122
C	-1.803414	0.160462	-0.568884
C	-0.761978	-0.750516	-0.8562
C	0.552449	-0.318452	-0.783962
C	0.915677	0.98624	-0.41963
H	-2.238754	2.17808	-0.048544
H	1.34742	-1.008768	-1.033679
C	-9.524547	-0.600833	0.078251
C	-8.946283	-1.554413	-0.720216
C	-7.549591	-1.391086	-0.814749
C	-7.087384	-0.31461	-0.084958
H	-9.534243	-2.326134	-1.201959
C	-6.406284	-2.101574	-1.516205
C	-5.236111	-1.249041	-1.060343
C	-3.845192	-1.247115	-1.263346
C	-3.20877	-0.215526	-0.600353
C	-5.661882	-0.227645	-0.23852
H	-3.299127	-1.951407	-1.872285
S	-4.367242	0.748016	0.306392
S	-8.339504	0.522628	0.727818
C	2.321755	1.34382	-0.328219
C	2.933805	2.585098	-0.384522
H	2.363026	3.492996	-0.503441
C	4.329244	2.504454	-0.283946
C	4.787946	1.205855	-0.143106
C	8.662586	1.398367	0.099397

C	8.03119	2.63869	-0.069551
C	6.651094	2.544474	-0.130751
C	6.206711	1.222832	-0.042329
S	7.476238	0.102829	0.140483
H	8.606853	3.554375	-0.138913
C	5.478419	3.495215	-0.284542
S	3.509046	0.066609	-0.11993
C	5.380353	4.455604	0.908035
H	6.247047	5.122347	0.934199
H	4.479691	5.071218	0.827496
H	5.34027	3.905448	1.850743
C	5.549222	4.271513	-1.604997
H	6.421001	4.932167	-1.614568
H	5.622001	3.591106	-2.456574
H	4.65535	4.888968	-1.732321
C	-6.263848	-3.548664	-1.028203
H	-7.14668	-4.134777	-1.300645
H	-5.388992	-4.02141	-1.484446
H	-6.146923	-3.583946	0.057388
C	-6.570867	-2.057125	-3.040433
H	-5.702355	-2.505367	-3.532046
H	-7.459888	-2.616125	-3.347509
H	-6.671684	-1.027576	-3.391681
C	10.058893	1.222264	0.07482
H	10.598374	2.106331	-0.270823
C	12.740578	-1.15573	-0.425367
C	11.821357	-1.99588	0.268215
C	10.895274	0.148032	0.248373
C	10.741579	-1.172294	0.819739
C	9.922148	-1.563704	1.855912
C	9.178038	-0.646164	2.639498
N	8.607456	0.093447	3.320843
C	9.907663	-2.914369	2.292085
N	9.898634	-4.023676	2.618645
C	12.241299	0.234152	-0.406649
O	12.762201	1.226661	-0.860086
O	0.233217	3.157459	0.206161
O	-1.122544	-2.012918	-1.188466
C	-0.134094	-3.038014	-1.340131
H	0.652529	-2.878436	-0.591872
C	-0.748556	4.098483	0.657913
H	-1.496309	3.562508	1.255492
C	-0.010158	5.06843	1.557185

H	0.468201	4.538603	2.38317
H	0.760772	5.601316	0.993193
H	-0.704226	5.80556	1.968793
C	-1.408623	4.789139	-0.523249
H	-1.891884	4.077797	-1.196246
H	-2.165853	5.496213	-0.173495
H	-0.659762	5.343329	-1.096128
C	-0.839477	-4.343139	-1.033732
H	-1.265082	-4.322506	-0.028652
H	-1.647918	-4.517218	-1.749552
H	-0.136862	-5.177683	-1.100059
C	0.453029	-3.01119	-2.741263
H	0.910202	-2.047626	-2.976118
H	1.217246	-3.786142	-2.846811
H	-0.333173	-3.201409	-3.477297
N	-10.873876	-0.452793	0.386889
C	-11.798994	0.283708	-0.348808
C	-13.049209	0.226468	0.300014
C	-14.138397	0.890536	-0.262392
C	-13.961277	1.592525	-1.444595
C	-12.710117	1.637651	-2.070191
C	-11.610302	0.984314	-1.533337
H	-15.110569	0.859257	0.218823
H	-14.800275	2.114157	-1.892085
H	-12.596193	2.194732	-2.994202
H	-10.639072	1.015768	-2.014609
C	-11.853757	-2.159807	3.534157
C	-13.200464	-1.778751	3.533095
C	-13.713727	-0.98996	2.515244
C	-12.867572	-0.576932	1.487123
C	-11.515014	-0.973754	1.508086
C	-10.990555	-1.764599	2.522589
H	-11.475286	-2.777193	4.34203
H	-13.847713	-2.105876	4.33951
H	-14.758786	-0.697558	2.519129
H	-9.946801	-2.058547	2.518756
C	13.817459	-1.817653	-0.924505
C	12.213686	-3.30462	0.291588
S	13.703561	-3.493157	-0.55053
H	14.661027	-1.42866	-1.47561
H	11.734001	-4.162777	0.737966

Table S4: Cartesian coordinates of **PMDC4**

Atom	X-axis	Y-axis	Z-axis
C	-0.361115	1.918524	-0.137551
C	-1.675216	1.482677	-0.230149
C	-2.029393	0.167283	-0.554624
C	-0.98196	-0.742235	-0.82537
C	0.329851	-0.303213	-0.750386
C	0.684787	1.00756	-0.399371
H	-2.477284	2.188694	-0.060558
H	1.129415	-0.992719	-0.987368
C	-9.74992	-0.623705	0.058532
C	-9.162793	-1.58336	-0.726074
C	-7.76641	-1.414321	-0.814903
C	-7.313407	-0.327459	-0.094774
H	-9.744466	-2.363259	-1.20223
C	-6.615981	-2.127172	-1.502156
C	-5.452376	-1.263982	-1.049567
C	-4.060418	-1.257833	-1.244534
C	-3.432624	-0.215721	-0.58967
C	-5.887575	-0.235308	-0.241744
H	-3.507611	-1.966425	-1.842296
S	-4.600779	0.752655	0.299313
S	-8.573872	0.512687	0.701886
C	2.088359	1.37272	-0.303878
C	2.69466	2.616709	-0.369728
H	2.120052	3.520367	-0.501534
C	4.089492	2.544051	-0.2603
C	4.553873	1.248886	-0.103056
C	8.425295	1.462886	0.159753
C	7.788134	2.699129	-0.025906
C	6.409913	2.597639	-0.094129
C	5.971097	1.273933	0.005786
S	7.244254	0.161933	0.208388
H	8.360011	3.616648	-0.101907
C	5.23345	3.540714	-0.264922
S	3.280353	0.103523	-0.075265
C	5.123489	4.513345	0.916669
H	5.986532	5.184846	0.940504
H	4.220183	5.12333	0.824149
H	5.080706	3.973351	1.865117
C	5.307955	4.303069	-1.593303
H	6.176247	4.968217	-1.604853

H	5.389315	3.614058	-2.437141
H	4.41162	4.914346	-1.732361
C	-6.469418	-3.568015	-0.997178
H	-7.348023	-4.161288	-1.26774
H	-5.589954	-4.041716	-1.443457
H	-6.358191	-3.590641	0.08935
C	-6.77249	-2.100568	-3.02766
H	-5.899295	-2.550255	-3.509555
H	-7.657238	-2.667137	-3.333161
H	-6.876191	-1.075521	-3.391023
C	9.820986	1.294846	0.142238
H	10.357056	2.180163	-0.205339
C	12.516375	-1.066064	-0.335399
C	11.604125	-1.912845	0.367971
C	10.663869	0.224733	0.323144
C	10.517316	-1.088514	0.906249
C	9.693936	-1.476423	1.941956
C	8.942655	-0.555544	2.713817
N	8.365976	0.188651	3.385127
C	9.683401	-2.822934	2.389238
N	9.678905	-3.93003	2.723722
C	12.008758	0.31927	-0.333117
O	12.518074	1.312906	-0.7943
O	-0.011552	3.182695	0.196822
O	-1.33489	-2.009885	-1.144979
C	-0.341	-3.032284	-1.279179
H	0.440493	-2.860529	-0.528231
C	-1.000522	4.124855	0.63083
H	-1.749494	3.592757	1.230302
C	-0.272154	5.10912	1.522639
H	0.203327	4.591786	2.358153
H	0.499825	5.638681	0.956952
H	-0.972183	5.848016	1.920726
C	-1.65616	4.797783	-0.562913
H	-2.131982	4.076037	-1.23011
H	-2.418767	5.505601	-0.226637
H	-0.90626	5.348382	-1.137885
C	-1.04238	-4.336919	-0.961812
H	-1.473986	-4.306628	0.040458
H	-1.845773	-4.522942	-1.680297
H	-0.335675	-5.168979	-1.014366
C	0.254108	-3.018858	-2.677113
H	0.708453	-2.05606	-2.920479

H	1.022269	-3.791599	-2.769351
H	-0.526938	-3.22101	-3.415439
N	-11.101481	-0.479073	0.358654
C	-12.026289	0.245733	-0.389025
C	-13.279536	0.18878	0.253921
C	-14.368973	0.842004	-0.320561
C	-14.189115	1.533204	-1.508693
C	-12.93499	1.578235	-2.128307
C	-11.834834	0.935539	-1.579419
H	-15.343459	0.810722	0.155942
H	-15.028281	2.04634	-1.965581
H	-12.818984	2.126726	-3.057182
H	-10.861324	0.966963	-2.056068
C	-12.089514	-2.160001	3.517414
C	-13.438007	-1.785538	3.505634
C	-13.949743	-1.0092	2.477488
C	-13.100228	-0.602097	1.449777
C	-11.745931	-0.992139	1.481639
C	-11.22295	-1.770472	2.506507
H	-11.712311	-2.767627	4.333238
H	-14.087885	-2.107942	4.311832
H	-14.996204	-0.721878	2.473113
H	-10.177788	-2.059378	2.51097
C	13.575938	-1.759702	-0.813798
C	11.986198	-3.220246	0.411297
S	13.481686	-3.447466	-0.427607
H	11.501206	-4.069158	0.868887
F	14.609791	-1.319174	-1.494582

Table S5: Cartesian coordinates of **PMDC5**

Atom	**X-axis**	**Y-axis**	**Z-axis**
C	-0.598674	1.930673	-0.128422
C	-1.910954	1.490291	-0.22538
C	-2.259391	0.171704	-0.543002
C	-1.207804	-0.736499	-0.80187
C	0.102267	-0.2931	-0.722457
C	0.451329	1.021061	-0.378251
H	-2.716063	2.195002	-0.065021
H	0.905188	-0.981768	-0.950362
C	-9.980468	-0.639753	0.034868
C	-9.386352	-1.602039	-0.741204
C	-7.990067	-1.429111	-0.8239

C	-7.544159	-0.336682	-0.107773
H	-9.963167	-2.386481	-1.215802
C	-6.833915	-2.142302	-1.501125
C	-5.675337	-1.272884	-1.047563
C	-4.282398	-1.263605	-1.235242
C	-3.661247	-0.215779	-0.583179
C	-6.117889	-0.240884	-0.248006
H	-3.724286	-1.973974	-1.825932
S	-4.836975	0.75417	0.293996
S	-8.811284	0.504015	0.677648
C	1.853235	1.391044	-0.277283
C	2.456255	2.636336	-0.348759
H	1.879774	3.537288	-0.490539
C	3.850606	2.568614	-0.230742
C	4.317848	1.275988	-0.06125
C	8.186916	1.503438	0.222509
C	7.547318	2.73639	0.023733
C	6.169844	2.630315	-0.051588
C	5.734268	1.306056	0.055689
S	7.009476	0.199344	0.273756
H	8.116943	3.655016	-0.055742
C	4.991644	3.56861	-0.236178
S	3.047534	0.127084	-0.032426
C	4.872037	4.54965	0.937496
H	5.732977	5.223841	0.961297
H	3.967523	5.156274	0.835225
H	4.825331	4.016598	1.889679
C	5.071596	4.321288	-1.569753
H	5.938005	4.988886	-1.581265
H	5.159808	3.626279	-2.407964
H	4.174309	4.928875	-1.718483
C	-6.685468	-3.579749	-0.987099
H	-7.560817	-4.17733	-1.258728
H	-5.802253	-4.053237	-1.426138
H	-6.579751	-3.595786	0.100096
C	-6.982667	-2.124969	-3.027539
H	-6.105621	-2.574681	-3.502365
H	-7.864071	-2.696061	-3.334277
H	-7.087694	-1.102361	-3.397337
C	9.583067	1.338953	0.215511
H	10.11919	2.222477	-0.136494
C	12.28879	-1.023114	-0.221534
C	11.374116	-1.860654	0.483814

C	10.426905	0.27236	0.411876
C	10.280301	-1.035586	1.006926
C	9.452351	-1.417118	2.040895
C	8.691508	-0.492488	2.799065
N	8.106867	0.255015	3.459652
C	9.44487	-2.759607	2.500718
N	9.443151	-3.863495	2.845541
C	11.775585	0.361707	-0.235059
O	12.288746	1.350101	-0.703911
O	-0.254678	3.198079	0.199353
O	-1.555266	-2.007241	-1.115035
C	-0.557715	-3.027685	-1.236504
H	0.218949	-2.848519	-0.482284
C	-1.248803	4.140212	0.621523
H	-1.999558	3.609931	1.22037
C	-0.528303	5.132575	1.510737
H	-0.056093	4.622292	2.352419
H	0.245354	5.660523	0.945836
H	-1.232689	5.872117	1.899829
C	-1.899707	4.803188	-0.580352
H	-2.369606	4.075583	-1.245378
H	-2.666309	5.510926	-0.253107
H	-1.14823	5.352213	-1.154771
C	-1.257208	-4.332121	-0.914209
H	-1.694666	-4.296199	0.085334
H	-2.055918	-4.525365	-1.635998
H	-0.547858	-5.162489	-0.956987
C	0.045391	-3.022126	-2.631058
H	0.498435	-2.059733	-2.878425
H	0.816233	-3.793293	-2.713582
H	-0.730815	-3.231554	-3.372452
N	-11.333967	-0.497778	0.327432
C	-12.25725	0.220261	-0.428613
C	-13.51355	0.162616	0.208284
C	-14.602117	0.809423	-0.37504
C	-14.418424	1.495091	-1.565788
C	-13.161328	1.540922	-2.179294
C	-12.061944	0.904547	-1.621564
H	-15.578902	0.777481	0.096689
H	-15.256879	2.003207	-2.02954
H	-13.042355	2.084998	-3.110388
H	-11.086139	0.936604	-2.093455
C	-12.332681	-2.165691	3.489726

C	-13.682274	-1.795593	3.469208
C	-14.191241	-1.026138	2.434533
C	-13.337815	-0.621578	1.409062
C	-11.982477	-1.007148	1.449765
C	-11.462236	-1.778568	2.48123
H	-11.957704	-2.767937	4.31055
H	-14.33521	-2.115951	4.273749
H	-15.238569	-0.742177	2.423404
H	-10.416198	-2.064109	2.492448
C	13.367544	-1.701973	-0.69322
C	11.766837	-3.166011	0.541578
S	13.265053	-3.383496	-0.283485
H	11.284736	-4.013719	1.00533
Cl	14.698095	-1.101871	-1.56921

Table S6: Cartesian coordinates of **PMDC6**

Atom	**X-axis**	**Y-axis**	**Z-axis**
C	1.153915	-1.785623	-0.098628
C	2.482909	-1.396859	-0.189463
C	2.885144	-0.118657	-0.596092
C	1.873398	0.800605	-0.955219
C	0.546949	0.408305	-0.879002
C	0.143568	-0.863293	-0.445854
H	3.258731	-2.112654	0.047678
H	-0.22563	1.102771	-1.181782
C	10.60927	0.489813	0.161426
C	10.071732	1.404147	-0.708201
C	8.672881	1.272201	-0.81865
C	8.168594	0.257565	-0.030448
H	10.689419	2.126186	-1.228231
C	7.562743	1.962611	-1.589956
C	6.362193	1.16983	-1.106125
C	4.975879	1.189666	-1.337166
C	4.300138	0.219269	-0.622688
C	6.745111	0.193556	-0.211434
H	4.460242	1.866598	-2.001204
S	5.415241	-0.712236	0.3679
S	9.382164	-0.555448	0.861458
C	-1.272895	-1.177214	-0.356279
C	-1.91771	-2.40361	-0.359841
H	-1.370559	-3.331203	-0.426413
C	-3.311124	-2.280304	-0.284113

C	-3.736957	-0.963988	-0.214614
C	-7.614238	-1.02272	-0.021692
C	-7.007785	-2.294836	-0.09915
C	-5.631861	-2.248292	-0.163102
C	-5.156654	-0.930888	-0.138394
S	-6.38461	0.247316	-0.037794
H	-7.612074	-3.194872	-0.107936
C	-4.486725	-3.239073	-0.260075
S	-2.426268	0.140212	-0.230671
C	-4.430537	-4.157088	0.967401
H	-5.317662	-4.795572	1.008199
H	-3.549154	-4.803253	0.919724
H	-4.38124	-3.574766	1.890347
C	-4.56334	-4.062875	-1.551574
H	-5.453892	-4.697815	-1.547917
H	-4.60673	-3.413303	-2.42877
H	-3.685922	-4.709508	-1.643948
C	7.446775	3.441337	-1.199302
H	8.349681	3.987264	-1.48885
H	6.593996	3.904297	-1.70473
H	7.307954	3.549757	-0.121147
C	7.75773	1.815615	-3.104097
H	6.911294	2.251786	-3.642792
H	8.666783	2.332167	-3.426416
H	7.839782	0.76342	-3.386286
C	-9.012929	-0.926302	0.050411
H	-9.469106	-1.907184	0.014372
C	-11.833036	1.407707	0.5603
C	-10.727169	2.299223	0.504201
C	-9.910853	0.119672	0.148817
C	-9.501504	1.535573	0.243813
C	-11.360896	0.029328	0.288379
O	0.756783	-3.012255	0.313377
O	2.273706	2.030674	-1.355416
C	1.315421	3.067143	-1.59757
H	0.510019	2.97832	-0.857524
C	1.708178	-3.959058	0.815759
H	2.465039	-3.418043	1.397138
C	0.934674	-4.867451	1.749042
H	0.463453	-4.288475	2.545653
H	0.154689	-5.403792	1.201054
H	1.60414	-5.604083	2.200305
C	2.359545	-4.719031	-0.326976

H	2.868132	-4.051584	-1.025764
H	3.094115	-5.429827	0.061377
H	1.601118	-5.277953	-0.882364
C	2.048651	4.37202	-1.364368
H	2.453534	4.409065	-0.35121
H	2.875478	4.476948	-2.072586
H	1.369686	5.217324	-1.502115
C	0.755955	2.959812	-3.006065
H	0.27872	1.994112	-3.185583
H	0.014156	3.744132	-3.179937
H	1.561287	3.080607	-3.736039
N	11.946893	0.334228	0.513831
C	12.858201	-0.516696	-0.106615
C	14.097711	-0.422521	0.558278
C	15.17251	-1.185858	0.104706
C	14.991934	-2.019923	-0.987752
C	13.751778	-2.098545	-1.631636
C	12.66643	-1.348565	-1.202418
H	16.136309	-1.128622	0.600148
H	15.8197	-2.619804	-1.349959
H	13.635093	-2.759	-2.484441
H	11.704087	-1.405062	-1.699016
C	12.929579	2.377864	3.452661
C	14.261997	1.956047	3.52702
C	14.765363	1.032843	2.623702
C	13.923751	0.525564	1.634723
C	12.585976	0.966336	1.577687
C	12.071287	1.890883	2.477562
H	12.558538	3.100593	4.171732
H	14.905912	2.357694	4.301805
H	15.799244	0.709034	2.68606
H	11.038468	2.215405	2.415512
C	-13.014209	2.046103	0.81368
C	-11.069298	3.597818	0.709289
S	-12.772932	3.74212	0.982711
C	-12.262171	-0.992079	0.202501
O	-8.373026	1.973421	0.144412
N	-12.1266	-2.360263	-0.170606
N	-13.681732	-0.70917	0.500465
O	-11.077335	-2.745627	-0.663563
O	-13.101638	-3.067492	0.009575
O	-14.401304	-0.480927	-0.444744
O	-14.002902	-0.685067	1.666812

Cl	-10.06456500	4.971026	0.721606
H	-14.016854	1.661968	0.926665

Table S7: Cartesian coordinates of **PMDC7**

Atom	X-axis	Y-axis	Z-axis
C	0.019352	1.964269	-0.103772
C	-1.293169	1.524519	-0.194446
C	-1.643846	0.214267	-0.544407
C	-0.595003	-0.681924	-0.844538
C	0.716249	-0.237143	-0.772326
C	1.067873	1.066005	-0.394513
H	-2.097637	2.222083	-0.002053
H	1.517588	-0.916073	-1.0327
C	-9.35525	-0.637332	0.130661
C	-8.771187	-1.571809	-0.685924
C	-7.376556	-1.393519	-0.783826
C	-6.921169	-0.324802	-0.038581
H	-9.35373	-2.341033	-1.178208
C	-6.229273	-2.080136	-1.502495
C	-5.065626	-1.222958	-1.038573
C	-3.675577	-1.202705	-1.250414
C	-3.046111	-0.175874	-0.574527
C	-5.497289	-0.220279	-0.197703
H	-3.125615	-1.890918	-1.874141
S	-4.20882	0.759598	0.355929
S	-8.177729	0.486186	0.793948
C	2.471866	1.43751	-0.303201
C	3.075178	2.680408	-0.36138
H	2.497994	3.584518	-0.480889
C	4.47416	2.610097	-0.263322
C	4.941617	1.318078	-0.12327
C	8.828264	1.54965	0.114831
C	8.189187	2.776837	-0.029755
C	6.800131	2.663675	-0.111105
C	6.367008	1.349068	-0.028499
S	7.657455	0.240688	0.149283
H	8.747172	3.705205	-0.071864
C	5.620123	3.606022	-0.270225
S	3.672365	0.170004	-0.09827

C	5.517522	4.578282	0.911438
H	6.383165	5.247114	0.935345
H	4.616504	5.192335	0.822496
H	5.472472	4.03688	1.859159
C	5.689098	4.369801	-1.598213
H	6.558476	5.033973	-1.615076
H	5.764984	3.679775	-2.441688
H	4.79239	4.981643	-1.733334
C	-6.068845	-3.533376	-1.039024
H	-6.946513	-4.12474	-1.316945
H	-5.190909	-3.988864	-1.506771
H	-5.946294	-3.584894	0.045303
C	-6.401865	-2.012679	-3.02494
H	-5.530772	-2.443005	-3.527888
H	-7.286187	-2.576377	-3.33713
H	-6.515595	-0.978633	-3.358618
C	10.237535	1.376917	0.220715
H	10.786458	2.314429	0.188454
C	11.954378	-2.061028	0.54398
C	12.067119	-3.441016	0.629251
C	14.336076	-1.336049	0.64087
C	10.992068	0.260763	0.349823
H	14.830673	-0.911092	-0.236558
O	0.367015	3.224496	0.254722
O	-0.943191	-1.945052	-1.189619
C	0.056103	-2.956146	-1.360067
H	0.845096	-2.797762	-0.614117
C	-0.623019	4.151437	0.712354
H	-1.365522	3.605299	1.307588
C	0.105965	5.123991	1.616855
H	0.589817	4.593824	2.439462
H	0.872053	5.666422	1.055327
H	-0.594724	5.852549	2.032669
C	-1.29193	4.843424	-0.463407
H	-1.767322	4.131043	-1.14084
H	-2.056924	5.539685	-0.108662
H	-0.549369	5.409446	-1.032996
C	-0.632466	-4.273488	-1.067678
H	-1.052953	-4.271231	-0.060202
H	-1.442881	-4.44706	-1.781429
H	0.079321	-5.098893	-1.149087
C	0.635741	-2.904188	-2.763627
H	1.079983	-1.932064	-2.987593

H	1.408896	-3.668186	-2.883074
H	-0.151959	-3.094255	-3.498172
N	-10.704623	-0.508573	0.449101
C	-11.639012	0.24006	-0.261737
C	-12.886055	0.15424	0.390221
C	-13.983144	0.824448	-0.149127
C	-13.81693	1.56046	-1.31206
C	-12.568826	1.633408	-1.941252
C	-11.461346	0.974774	-1.427222
H	-14.953004	0.771518	0.334896
H	-14.662159	2.087197	-1.741526
H	-12.463519	2.216729	-2.849985
H	-10.492424	1.027435	-1.911272
C	-11.656142	-2.311302	3.551078
C	-13.006127	-1.942128	3.566355
C	-13.530601	-1.129574	2.573214
C	-12.692574	-0.680548	1.553519
C	-11.336517	-1.066094	1.557593
C	-10.800865	-1.880413	2.547432
H	-11.268808	-2.947788	4.339724
H	-13.647008	-2.297434	4.36593
H	-14.578114	-0.846466	2.589675
H	-9.754586	-2.16477	2.530747
S	10.35173	-1.375464	0.412983
C	10.874026	-4.207451	0.597025
N	9.894447	-4.822197	0.569342
C	13.269083	-4.176255	0.748133
N	14.230672	-4.813277	0.84606
N	12.907275	-1.102496	0.545047
H	14.55521	-2.396432	0.688647
H	14.724153	-0.852544	1.541514
C	12.450391	0.226905	0.451755
C	13.281303	1.281376	0.460881
H	12.887224	2.285104	0.391663
H	14.353313	1.177525	0.537621

Table S8: Cartesian coordinates of **PMDC8**

Atom	X-axis	Y-axis	Z-axis
C	0.464568	1.774976	-0.14048
C	-0.86167	1.376212	-0.223161
C	-1.254362	0.069918	-0.541357
C	-0.235082	-0.867743	-0.816514

C	1.089885	-0.465102	-0.751153
C	1.483082	0.835201	-0.405519
H	-1.643109	2.104413	-0.050496
H	1.869212	-1.176029	-0.992246
C	-8.989747	-0.513575	0.138725
C	-8.43599	-1.483936	-0.656852
C	-7.036173	-1.353513	-0.756329
C	-6.546747	-0.284544	-0.03337
H	-9.043067	-2.243968	-1.133497
C	-5.91158	-2.09256	-1.458623
C	-4.720764	-1.264498	-1.01106
C	-3.330615	-1.29465	-1.220351
C	-2.668572	-0.274668	-0.565455
C	-5.120086	-0.230195	-0.192653
H	-2.802992	-2.013889	-1.828181
S	-3.800905	0.718551	0.342116
S	-7.776688	0.584724	0.779775
C	2.898054	1.163145	-0.319952
C	3.540768	2.383919	-0.416718
H	2.993122	3.301361	-0.568964
C	4.935986	2.272472	-0.310066
C	5.361694	0.971164	-0.124349
C	9.247511	1.086489	0.123879
C	8.650005	2.329845	-0.066881
C	7.260779	2.258416	-0.150385
C	6.785821	0.958642	-0.024306
S	8.036864	-0.184167	0.198087
H	9.241425	3.235287	-0.13816
C	6.112038	3.231382	-0.346336
S	4.055705	-0.134646	-0.067091
C	6.036271	4.246229	0.801218
H	6.922341	4.887911	0.805467
H	5.155234	4.884641	0.687411
H	5.971742	3.739623	1.766879
C	6.208616	3.946951	-1.699361
H	7.09852	4.582308	-1.734965
H	6.265333	3.226959	-2.518956
H	5.332091	4.581837	-1.85831
C	-5.799634	-3.54026	-0.964614
H	-6.696192	-4.107947	-1.231329
H	-4.936987	-4.034308	-1.421573
H	-5.679668	-3.573108	0.120733
C	-6.080729	-2.051304	-2.982417

H	-5.224024	-2.520625	-3.475101
H	-6.982998	-2.591862	-3.283946
H	-6.160038	-1.021288	-3.337789
C	10.640917	0.858961	0.242996
H	11.266975	1.747516	0.177752
C	12.387341	-2.564722	0.764068
C	14.720584	-1.790448	0.824224
C	11.340345	-0.287351	0.425706
H	15.210654	-0.821277	0.741658
O	0.853035	3.031242	0.186516
O	-0.624789	-2.126633	-1.131551
C	0.340331	-3.173725	-1.277531
H	1.133347	-3.025092	-0.53373
C	-0.106604	4.002574	0.617598
H	-0.867605	3.496772	1.224954
C	0.653087	4.973455	1.498168
H	1.117502	4.449334	2.335707
H	1.437778	5.475186	0.924671
H	-0.023563	5.73562	1.892956
C	-0.75016	4.685177	-0.577537
H	-1.248307	3.971635	-1.237194
H	-1.491868	5.415683	-0.242854
H	0.01162	5.211058	-1.160043
C	-0.392297	-4.460479	-0.957191
H	-0.813633	-4.42167	0.049183
H	-1.207354	-4.622542	-1.668316
H	0.291335	-5.311021	-1.019084
C	0.923083	-3.172467	-2.680821
H	1.400253	-2.221154	-2.925472
H	1.669958	-3.964746	-2.782082
H	0.130261	-3.351964	-3.412473
N	-10.334321	-0.33398	0.452335
C	-11.242974	0.430257	-0.275248
C	-12.492524	0.399345	0.376753
C	-13.566503	1.094107	-0.177805
C	-13.375336	1.799818	-1.355587
C	-12.12516	1.81827	-1.984583
C	-11.040386	1.134193	-1.455543
H	-14.537846	1.08343	0.306003
H	-14.202392	2.345204	-1.796971
H	-12.000063	2.378719	-2.905116
H	-10.070023	1.14471	-1.93946
C	-11.347162	-2.039102	3.589978

C	-12.684151	-1.625155	3.595674
C	-13.180708	-0.816573	2.585082
C	-12.327544	-0.416961	1.557435
C	-10.985049	-0.847059	1.571432
C	-10.477358	-1.657837	2.578743
H	-10.981707	-2.671429	4.392288
H	-13.337011	-1.942219	4.401603
H	-14.21826	-0.498626	2.594198
H	-9.44107	-1.97701	2.56951
S	10.755476	-1.929745	0.582966
N	13.297017	-1.553067	0.703416
H	15.056291	-2.460054	0.03033
H	14.941699	-2.252399	1.788084
C	12.804812	-0.252585	0.517043
S	12.705299	-4.159495	0.973371
O	13.514594	0.724161	0.447209

Table S9: Calculated energies (*E*) and energy gap (Δ*E*) of HOMO-1, LUMO+1, HOMO-2 and LUMO+2 for **PMD-1** and **PMDC2-PMDC8**

Compounds	**HOMO-1**	**LUMO+1**	**Δ*E***	**HOMO-2**	**LUMO+2**	**Δ*E***
PMD-1	-6.153	-3.269	2.884	-6.503	-2.745	3.758
PMDC2	-6.068	-2.647	3.421	-6.208	-1.991	4.217
PMDC3	-6.048	-2.282	3.766	-6.205	-1.944	4.261
PMDC4	-6.065	-2.295	3.770	-6.208	-1.938	4.270
PMDC5	-6.608	-2.342	4.266	-6.208	-2.000	4.208
PMDC6	-6.101	-2.659	3.442	-6.209	-2.493	3.716
PMDC7	-5.781	-1.861	3.920	-6.190	-1.346	4.844
PMDC8	-5.919	-1.921	3.998	-6.198	-1.351	4.847

E=energy, $\Delta E(eV)=E_{LUMO}-E_{HOMO}$; HOMO=highest occupied molecular orbital; LUMO=lowest unoccupied molecular orbital, MO=molecular orbital, Units in e*V*

Table S10: Wave length, excitation energy and oscillator strength of **PMD-1** and **PMDC2-PMDC8** in gaseous phase

Compounds	λ **(*nm*)**	***E* (*eV*)**	f_{os}	**MO contributions**
PMD-1	671.128	1.847	2.508	H→L (96%), H-1→L+1 (3%)
	578.284	2.144	0.105	H→L+1 (97%)
	507.529	2.443	0.111	H-1→L (88%), H→L+3 (6%)
	486.594	2.548	0.239	H→L+2 (86%), H-1→L+2 (3%), H-1→L+3 (6%)
	470.225	2.637	0.397	H-1→L+1 (82%), H-2→L (2%), H→L (3%), H→L+3 (9%), H→L+4 (2%)
	464.273	2.671	0.018	H→L+3 (71%), H-1→L (9%), H-1→L+1 (7%), H-

				1→L+2 (4%), H→L+2 (2%)
PMDC2	669.968	1.851	1.222	H→L (98%)
	509.468	2.434	0.187	H-2→L (39%), H-1→L (51%), H→L+1 (3%), H→L+2 (3%)
	499.533	2.482	0.590	H→L+1 (88%), H-2→L+1 (2%), H-1→L+1 (3%)
	473.891	2.616	0.002	H-2→L (55%), H-1→L (44%)
	438.153	2.830	0.023	H-4→L (96%)
	433.648	2.859	0.000	H-3→L (99%)
PMDC3	659.561	1.880	1.334	H→L (98%)
	503.878	2.461	0.338	H-1→L (87%), H-2→L (6%), H→L+1 (3%)
	463.666	2.674	0.004	H-2→L (92%), H-1→L (7%)
	445.458	2.783	0.650	H→L+1 (89%), H-1→L (2%), H-1→L+1 (2%), H-1→L+2 (2%)
	433.012	2.863	0.006	H-4→L (96%)
	424.793	2.919	0.000	H-3→L (100%)
PMDC4	670.765	1.848	1.304	H→L (99%)
	511.106	2.426	0.353	H-2→L (15%), H-1→L (78%), H→L+1 (3%)
	474.762	2.612	0.003	H-2→L (82%), H-1→L (17%)
	445.874	2.781	0.658	H→L+1 (85%), H-4→L (4%), H-1→L (2%)
	439.629	2.820	0.017	H-4→L (93%), H→L+1 (4%)
	434.301	2.855	0.000	H-3→L (100%)
PMDC5	672.840	1.843	1.335	H→L (99%)
	512.056	2.421	0.363	H-2→L (17%), H-1→L (76%), H→L+1 (2%)
	475.965	2.605	0.003	H-2→L (80%), H-1→L (19%)
	447.807	2.769	0.605	H→L+1 (86%), H-5→L (2%), H-4→L (3%), H-1→L+1 (2%)
	440.457	2.815	0.010	H-4→L (94%), H→L+1 (3%)
	435.338	2.848	0.000	H-3→L (100%)
PMDC6	663.905	1.868	1.491	H→L (99%)
	503.591	2.462	0.767	H-2→L (72%), H-1→L (14%), H→L+1 (8%), H→L+3 (4%)
	483.558	2.564	0.157	H→L+1 (85%), H-2→L (6%), H-2→L+1 (3%), H-1→L (3%)
	478.925	2.589	0.000	H-2→L (18%), H-1→L (82%)
	439.193	2.823	0.063	H-4→L (94%), H-3→L (3%)
	437.921	2.831	0.002	H-3→L (97%), H-4→L (2%)
PMDC7	553.205	2.241	1.891	H→L (97%)
	438.200	2.829	0.470	H-1→L (61%), H→L+1 (36%)
	416.082	2.980	0.228	H-1→L (37%), H→L+1 (60%)
	386.256	3.210	0.001	H-2→L (94%), H-2→L+1 (4%)
	375.926	3.298	0.023	H-4→L (92%), H-4→L+1 (3%)
	361.365	3.431	0.016	H→L+2 (90%), H-6→L (2%), H-1→L+1 (3%)
PMDC8	560.457	2.212	1.840	H→L (98%)
	443.355	2.797	0.493	H-1→L (75%), H→L+1 (23%)
	427.487	2.900	0.000	H-5→L (85%), H-5→L+1 (6%), H-5→L+2 (5%), H-5→L+4 (2%)

	410.966	3.017	0.303	H-1→L (24%), H→L+1 (73%)
	398.304	3.113	0.001	H-2→L (96%), H-2→L+1 (3%)
	384.352	3.226	0.021	H-4→L (94%), H-4→L+1 (2%)

Table S11: Wave length λ (*nm*), excitation energy (*E*) and oscillator strength (*f*) of **PMD-1**and **PMDC2-PMDC8** in dichloromethane (DCM) at PBE1PBE functional

Compounds	λ (*nm*)	*E*(*eV*)	*f*	MO contributions
PMD-1	734.243	1.689	2.644	H→L (95%), H-1→L+1 (4%)
	628.373	1.973	0.152	H→L+1 (97%)
	533.679	2.323	0.104	H-1→L (89%), H-2→L+1 (3%), H→L+3 (3%)
	519.110	2.388	0.285	H→L+2 (86%), H-1→L+3 (6%)
	495.323	2.503	0.105	H→L+3 (81%), H-1→L (3%), H-1→L+1 (4%), H-1→L+2 (5%)
	493.136	2.514	0.373	H-2→L (13%), H-1→L+1 (71%), H-1→L (2%), H→L (3%), H→L+2 (3%), H→L+3 (3%)
PMDC2	731.298	1.695	1.314	H→L (96%), H-1→L (2%)
	536.868	2.309	0.093	H-1→L (72%), H→L+1 (18%), H-3→L (3%), H-1→L+1 (2%)
	530.368	2.338	0.693	H-1→L (18%), H→L+1 (73%), H-1→L+1 (4%)
	465.336	2.664	0.021	H-3→L (66%), H-2→L (28%), H-1→L (4%)
	459.899	2.696	0.005	H-3→L (28%), H-2→L (71%)
	425.361	2.915	0.655	H→L+2 (94%)
PMDC3	721.174	1.719	1.451	H→L (97%), H-1→L (2%)
	529.372	2.342	0.285	H-1→L (92%), H-3→L (3%), H→L (2%)
	467.900	2.650	0.682	H→L+1 (89%), H-1→L+1 (4%), H→L+2 (2%)
	460.942	2.690	0.032	H-3→L (75%), H-2→L (19%), H-1→L (4%)
	454.771	2.726	0.006	H-3→L (20%), H-2→L (79%)
	417.920	2.967	0.360	H→L+2 (88%), H-5→L (2%), H-1→L+1 (3%)
PMDC4	733.461	1.690	1.436	H→L (97%)
	536.496	2.311	0.299	H-1→L (92%), H-3→L (3%), H→L (2%)
	468.554	2.646	0.014	H-3→L (71%), H-2→L (25%), H-1→L (3%)
	466.861	2.656	0.713	H→L+1 (89%), H-1→L+1 (3%), H→L+2 (2%)
	463.042	2.678	0.018	H-3→L (25%), H-2→L (74%)
	420.870	2.946	0.000	H-4→L (100%)
PMDC5	736.292	1.684	1.464	H→L (97%)
	537.752	2.306	0.308	H-1→L (92%), H-3→L (3%), H→L (2%)
	472.465	2.624	0.600	H→L+1 (89%), H-1→L+1 (5%), H→L+2 (2%)
	469.797	2.639	0.027	H-3→L (69%), H-2→L (26%), H-1→L (4%)
	464.569	2.669	0.009	H-3→L (26%), H-2→L (73%)
	422.117	2.937	0.000	H-4→L (100%)
PMDC6	739.542	1.677	1.568	H→L (98%)
	538.243	2.304	0.695	H-1→L (84%), H-3→L (2%), H→L+1 (9%)
	523.162	2.370	0.198	H-1→L (10%), H→L+1 (84%), H-1→L+1 (4%)
	487.034	2.546	0.000	H-1→L+2 (11%), H→L+2 (84%), H-5→L+2 (2%)
	475.984	2.605	0.003	H-2→L (96%), H-3→L (3%)

	473.168	2.620	0.067	H-3→L (92%), H-2→L (3%), H-1→L (2%)
PMDC7	567.200	2.186	2.153	H→L (96%)
	436.949	2.838	0.412	H-1→L (32%), H→L+1 (63%), H→L (2%)
	432.498	2.867	0.160	H-1→L (64%), H→L+1 (32%)
	374.597	3.310	0.040	H-3→L (88%), H-3→L+1 (5%), H-2→L (4%)
	370.777	3.344	0.026	H-1→L+1 (14%), H→L+2 (82%)
	362.697	3.418	0.001	H-2→L (88%), H-3→L (4%), H-2→L+1 (6%)
PMDC8	600.902	2.063	1.930	H→L (96%)
	457.743	2.709	0.400	H-1→L (90%), H→L+1 (6%)
	428.537	2.893	0.550	H→L+1 (90%), H-1→L (7%)
	400.673	3.094	0.039	H-3→L (91%), H-3→L+1 (2%), H-2→L (4%)
	400.104	3.099	0.000	H-5→L (85%), H-5→L+1 (6%), H-5→L+2 (6%)
	390.920	3.172	0.001	H-2→L (94%), H-3→L (4%)

Table S12: Natural bond orbitals analysis for the reference compound (**PMD-1**) with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C9-C10	π	C51-C61	π*	30.03	0.31	0.086
C85-N86	π	C83-N84	π*	0.64	0.48	0.016
C53-H54	σ	C78-C81	σ*	9.24	1.03	0.087
C51-C61	σ	C9-C10	σ*	0.50	1.31	0.023
O89	LP(2)	C1-C2	π*	32.44	0.36	0.102
O88	LP(2)	C78-C87	σ*	22.00	0.72	0.114
C9-C10	π	C11-C12	π*	18.94	0.29	0.068
C29-C30	π	C25-C26	π*	15.22	0.31	0.062
C16-C17	π	C3-C4	π*	12.73	0.31	0.060
C81-C82	π	C73-C74	π*	9.83	0.33	0.052
C66-C67	π	C51-C61	π*	8.10	0.33	0.047
C64-O65	π	C55-C60	π*	4.56	0.43	0.043
C64-O65	π	C51-C61	π*	3.94	0.43	0.040
C68-N69	π	C70-N71	π*	0.85	0.47	0.018
C83-N84	π	C85-N86	π*	0.66	0.47	0.016
C53-H54	σ	C27-S31	σ*	8.86	0.73	0.072
C15-C18	σ	C12-S21	σ*	8.39	0.96	0.080
C51-H52	σ	C9-C10	σ*	7.35	1.10	0.080
C27-C28	σ	C29-C33	σ*	7.17	1.16	0.082
C53-C78	σ	C78-C81	σ*	6.38	1.26	0.080
C67-C68	σ	C66-C67	σ*	6.14	1.35	0.081
C27-S31	σ	C26-C30	σ*	5.98	1.21	0.076
C10-H13	σ	C9-S21	σ*	5.78	0.74	0.058
C28-H32	σ	C27-S31	σ*	5.58	0.75	0.058
C78-C87	σ	C27-C53	σ*	5.33	1.21	0.072
C9-C51	σ	C9-C10	σ*	4.93	1.32	0.072

C27-C28	σ	C27-C53	σ*	4.72	1.29	0.070
C55-C56	σ	C66-C67	σ*	3.79	1.31	0.063
C15-C16	σ	C12-C18	σ*	3.41	1.24	0.058
C72-C87	σ	C72-C73	σ*	2.69	1.24	0.051
C11-C12	σ	C11-C14	σ*	2.42	1.14	0.047
C28-C29	σ	C28-H32	σ*	1.83	1.18	0.042
C59-C60	σ	C60-H63	σ*	1.14	1.2	0.033
C55-C60	σ	C61-C64	σ*	0.94	1.2	0.03
C93-C95	σ	C93-H94	σ*	0.63	1.07	0.023
O90	LP(2)	C3-C4	π*	29.25	0.36	0.099
S34	LP(2)	C25-C26	π*	24.75	0.29	0.076
S21	LP(2)	C9-C10	π*	19.41	0.28	0.066
O65	LP(2)	C55-C64	σ*	20.74	0.75	0.113
N69	LP(1)	C67-C68	σ*	12.83	1.04	0.103
O90	LP(1)	C4-C5	σ*	7.42	1.14	0.082
O89	LP(2)	C93-C95	σ*	0.82	0.74	0.023
O89	LP(1)	C95-H98	σ*	0.61	0.98	0.022

Table S13: Natural bond orbitals analysis for **PMDC2** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C59	π*	29.56	0.31	0.086
C64-N65	π	C66-N67	π*	0.66	0.47	0.016
C51-H52	σ	C59-C62	σ*	9.14	1.03	0.087
C74-H75	σ	O70-C74	σ*	0.50	0.82	0.018
N94	LP(1)	C108-C109	π*	35.62	0.31	0.097
O69	LP(2)	C59-C68	σ*	21.87	0.73	0.114
C1-C2	π	C5-C6	π*	18.74	0.30	0.070
C25-C26	π	C22-C23	π*	16.85	0.31	0.066
C15-C18	π	C11-C12	π*	15.39	0.31	0.064
C22-C23	π	C5-C6	π*	13.69	0.31	0.062
C51-C59	π	C27-C28	π*	11.96	0.29	0.055
C62-C63	π	C54-C55	π*	9.83	0.33	0.052
C62-C63	π	C51-C59	π*	8.82	0.34	0.050
C68-O69	π	C53-C58	π*	4.38	0.42	0.042
C68-O69	π	C51-C59	π*	2.78	0.43	0.033
C51-H52	σ	C27-S31	σ*	8.99	0.73	0.072
C66-N67	σ	C63-C66	σ*	8.22	1.60	0.103
C27-C28	σ	C29-C33	σ*	7.21	1.16	0.082
C16-C17	σ	C14-C15	σ*	6.63	1.17	0.079
C59-C62	σ	C51-C59	σ*	6.24	1.31	0.081
C27-S31	σ	C26-C30	σ*	5.96	1.22	0.076
C4-C5	σ	C3-C4	σ*	5.72	1.29	0.077

C23-C25	σ	C6-C22	σ*	5.07	1.22	0.070
C2-H7	σ	C1-C6	σ*	4.79	1.09	0.065
C59-C62	σ	C54-C55	σ*	4.24	1.27	0.066
C23-C25	σ	C25-C26	σ*	3.95	1.28	0.064
C80-H81	σ	C74-C76	σ*	3.35	0.92	0.050
C5-C6	σ	C22-C23	σ*	3.16	1.29	0.057
C59-C62	σ	C68-O69	σ*	2.94	1.32	0.056
C63-C66	σ	C63-C64	σ*	2.70	1.27	0.052
C59-C62	σ	C54-C62	σ*	2.21	1.16	0.045
C4-O71	σ	C4-C5	σ*	1.55	1.52	0.043
C51-C59	σ	C54-C62	σ*	1.29	1.21	0.035
C11-C14	σ	C9-C10	σ*	0.95	1.22	0.031
C22-S34	σ	C25-C33	σ*	0.50	1.11	0.021
N94	LP(1)	C95-C96	π*	35.61	0.31	0.097
O70	LP(2)	C1-C2	π*	32.08	0.36	0.102
S21	LP(2)	C9-C10	π*	22.76	0.28	0.072
O69	LP(2)	C53-C68	σ*	21.49	0.74	0.114
N67	LP(1)	C63-C66	σ*	12.69	1.05	0.103
O71	LP(2)	C72-C88	σ*	5.89	0.73	0.061
O70	LP(2)	C80-H82	σ*	0.71	0.76	0.022

Table S14: Natural bond orbitals analysis for **PMDC3** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C55	π*	29.15	0.31	0.086
C56-C57	π	C60-N61	π*	0.50	0.41	0.013
C51-H52	σ	C55-C56	σ*	9.16	1.03	0.087
C58-N59	σ	C56-C57	σ*	0.50	1.66	0.026
N86	LP(1)	C87-C88	π*	35.63	0.31	0.097
O63	LP(2)	C55-C62	σ*	22.28	0.71	0.114
C25-C26	π	C22-C23	π*	16.88	0.31	0.066
C29-C30	π	C25-C26	π*	15.21	0.31	0.062
C3-C4	π	C16-C17	π*	13.91	0.29	0.058
C51-C55	π	C27-C28	π*	12.1	0.29	0.055
C56-C57	π	C54-C108	π*	11.6	0.32	0.056
C56-C57	π	C51-C55	π*	8.66	0.34	0.049
C62-O63	π	C53-C107	π*	5.12	0.42	0.045
C62-O63	π	C51-C55	π*	2.64	0.43	0.032
C58-N59	π	C60-N61	π*	0.58	0.47	0.015
C51-H52	σ	C27-S31	σ*	9.01	0.72	0.072
C25-C26	σ	C30-S31	σ*	8.52	0.96	0.081
C60-N61	σ	C57-C60	σ*	8.13	1.6	0.103
C22-C23	σ	C25-C33	σ*	6.72	1.17	0.079

C9-S21	σ	C12-C18	σ*	6.17	1.2	0.077
C27-S31	σ	C26-C30	σ*	5.97	1.21	0.076
C55-C62	σ	C27-C51	σ*	5.43	1.21	0.073
C87-C88	σ	C87-C92	σ*	5.09	1.28	0.072
C102-H106	σ	C100-C101	σ*	4.94	1.09	0.066
C9-C10	σ	C10-C11	σ*	4.55	1.32	0.069
C12-S21	σ	C11-C14	σ*	3.65	1.15	0.058
C12-C18	σ	C15-C16	σ*	3.33	1.3	0.059
C55-C56	σ	C54-C56	σ*	2.48	1.18	0.048
C22-C23	σ	C5-C6	σ*	2.31	1.31	0.049
C55-C62	σ	C55-C56	σ*	1.79	1.15	0.041
C4-C5	σ	C5-H8	σ*	1.7	1.19	0.04
C51-C55	σ	C54-C56	σ*	1.29	1.23	0.036
C51-H52	σ	C27-C51	σ*	0.9	1.08	0.028
C70-H72	σ	O64-C68	σ*	0.63	0.81	0.02
O64	LP(2)	C1-C2	π*	32.03	0.36	0.102
S34	LP(2)	C25-C26	π*	24.42	0.29	0.075
S31	LP(2)	C27-C28	π*	21.16	0.27	0.068
O63	LP(2)	C53-C62	σ*	21.84	0.74	0.115
N86	LP(1)	C9-S21	σ*	14.65	0.48	0.081
O64	LP(2)	C68-C74	σ*	5.83	0.73	0.06
O65	LP(1)	C66-H67	σ*	1.86	0.98	0.038

Table S15: Natural bond orbitals analysis for **PMDC4** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C55	π*	29.86	0.31	0.087
C60-N61	π	C58-N59	π*	0.55	0.48	0.014
C51-H52	σ	C55-C56	σ*	9.09	1.03	0.087
C22-S34	σ	C25-C33	σ*	0.50	1.11	0.021
N86	LP(1)	C100-C101	π*	35.62	0.31	0.097
O63	LP(2)	C55-C62	σ*	22.02	0.71	0.113
C15-C18	π	C16-C17	π*	18.14	0.31	0.069
C25-C26	π	C22-C23	π*	16.84	0.31	0.066
C29-C30	π	C25-C26	π*	15.25	0.31	0.062
C3-C4	π	C16-C17	π*	13.88	0.29	0.058
C51-C55	π	C27-C28	π*	12.19	0.29	0.055
C56-C57	π	C51-C55	π*	8.78	0.33	0.049
C62-O63	π	C53-C107	π*	5.07	0.41	0.044
C62-O63	π	C51-C55	π*	2.60	0.43	0.032
C58-N59	π	C60-N61	π*	0.58	0.47	0.015
C51-H52	σ	C27-S31	σ*	9.08	0.72	0.072
C57-C60	σ	C60-N61	σ*	8.46	1.67	0.107

C60-N61	σ	C57-C60	σ*	8.15	1.60	0.103
C27-C28	σ	C29-C33	σ*	7.24	1.16	0.082
C9-C10	σ	C11-C14	σ*	6.64	1.19	0.079
C9-S21	σ	C12-C18	σ*	6.17	1.20	0.077
C56-C57	σ	C57-C60	σ*	5.66	1.28	0.076
C51-C55	σ	C27-C51	σ*	5.36	1.32	0.075
C15-C16	σ	C3-C17	σ*	5.24	1.21	0.071
C55-C56	σ	C56-C57	σ*	4.59	1.28	0.068
C2-C3	σ	C3-C17	σ*	4.35	1.23	0.065
C10-C11	σ	C11-C14	σ*	3.91	1.14	0.060
C1-C2	σ	C6-C22	σ*	3.87	1.24	0.062
C28-C29	σ	C27-C28	σ*	3.46	1.28	0.059
C10-H13	σ	C11-C12	σ*	2.78	1.13	0.050
C3-C17	σ	C15-C16	σ*	1.85	1.29	0.044
C2-C3	σ	C2-H7	σ*	1.63	1.17	0.039
C18-S20	σ	C11-C12	σ*	0.94	1.30	0.031
C68-H69	σ	O64-C68	σ*	0.50	0.82	0.018
N86	LP(1)	C87-C88	π*	35.61	0.31	0.097
O64	LP(2)	C1-C2	π*	32.1	0.36	0.102
S31	LP(2)	C27-C28	π*	21.03	0.27	0.068
O63	LP(2)	C53-C62	σ*	23.04	0.73	0.118
N61	LP(1)	C57-C60	σ*	12.61	1.05	0.103
N86	LP(1)	C9-C10	σ*	6.62	0.87	0.074
O65	LP(1)	C78-H81	σ*	0.62	0.98	0.022

Table S16: Natural bond orbitals analysis for **PMDC5** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C55	π*	29.88	0.31	0.087
C60-N61	π	C58-N59	π*	0.55	0.48	0.014
C51-H52	σ	C55-C56	σ*	9.09	1.03	0.087
C68-H69	σ	O64-C68	σ*	0.50	0.82	0.018
N86	LP(1)	C100-C101	π*	35.62	0.31	0.097
O63	LP(2)	C53-C62	σ*	22.84	0.73	0.117
C27-C28	π	C29-C30	π*	18.55	0.30	0.068
C25-C26	π	C22-C23	π*	16.83	0.31	0.066
C9-C10	π	C11-C12	π*	15.49	0.33	0.068
C54-C108	π	C56-C57	π*	14.35	0.32	0.063
C51-C55	π	C27-C28	π*	12.18	0.29	0.055
C56-C57	π	C51-C55	π*	8.76	0.33	0.049
C62-O63	π	C53-C107	π*	5.46	0.40	0.046
C62-O63	π	C51-C55	π*	2.62	0.43	0.032
C56-C57	π	C60-N61	π*	0.55	0.40	0.014

C51-H52	σ	C27-S31	σ*	9.07	0.72	0.072
C29-C30	σ	C26-S34	σ*	8.53	0.95	0.081
C11-C12	σ	C18-S20	σ*	8.25	0.96	0.080
C27-C28	σ	C29-C33	σ*	7.24	1.16	0.082
C22-C23	σ	C25-C33	σ*	6.72	1.17	0.079
C51-C55	σ	C55-C56	σ*	6.11	1.26	0.079
C27-S31	σ	C26-C30	σ*	5.98	1.22	0.076
C57-C60	σ	C56-C57	σ*	5.59	1.34	0.077
C1-C6	σ	C6-C22	σ*	5.08	1.22	0.070
C3-C4	σ	C3-C17	σ*	4.92	1.22	0.069
C22-C23	σ	C23-C25	σ*	4.54	1.32	0.069
C3-C4	σ	C2-C3	σ*	4.08	1.29	0.065
C1-C2	σ	C6-C22	σ*	3.87	1.24	0.062
C12-C18	σ	C15-C16	σ*	3.33	1.30	0.059
C53-C62	σ	C51-C55	σ*	2.69	1.29	0.053
C55-C56	σ	C54-C56	σ*	2.48	1.18	0.048
C33-C39	σ	C29-C33	σ*	1.82	1.05	0.039
C12-S21	σ	C11-C12	σ*	1.24	1.30	0.036
C5-H8	σ	C4-C5	σ*	1.18	1.13	0.033
C62-O63	σ	C53-C54	σ*	0.50	1.64	0.026
N86	LP(1)	C87-C88	π*	35.61	0.31	0.097
S34	LP(2)	C22-C23	π*	23.82	0.28	0.073
S31	LP(2)	C27-C28	π*	21.03	0.27	0.068
N61	LP(1)	C57-C60	σ*	12.62	1.05	0.103
O64	LP(1)	C1-C2	σ*	7.35	1.14	0.082
Cl111	LP(1)	C53-C107	σ*	3.62	1.55	0.067
O64	LP(1)	C68-H69	σ*	1.83	0.98	0.038

Table S17: Natural bond orbitals analysis for **PMDC6** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C55	π*	34.98	0.31	0.093
C56-O105	π	C51-C55	π*	3.58	0.43	0.038
C51-H52	σ	C27-S31	σ*	11.12	0.72	0.080
C22-S34	σ	C25-C33	σ*	0.50	1.11	0.021
N80	LP(1)	C81-C86	π*	40.4	0.31	0.102
O105	LP(2)	C54-C56	σ*	22.61	0.75	0.118
C5-C6	π	C1-C2	π*	20.27	0.30	0.070
C91-C92	π	C95-C96	π*	19.91	0.29	0.069
C16-C17	π	C15-C18	π*	18.22	0.31	0.071
C25-C26	π	C22-C23	π*	16.76	0.31	0.065
C29-C30	π	C25-C26	π*	15.43	0.30	0.062
C22-C23	π	C5-C6	π*	13.57	0.31	0.061

C51-C55	π	C27-C28	π*	12.05	0.29	0.054
C56-O105	π	C54-C102	π*	5.66	0.40	0.047
N106-O109	π	C57-C104	π*	4.98	0.49	0.048
C51-H52	σ	C55-C56	σ*	6.97	0.98	0.074
C10-C11	σ	C9-N80	σ*	6.38	1.15	0.077
C22-S34	σ	C26-C30	σ*	5.92	1.21	0.076
C95-C96	σ	C94-C95	σ*	5.53	1.29	0.075
C29-C33	σ	C23-C25	σ*	5.27	1.21	0.072
C6-C22	σ	C5-C6	σ*	4.71	1.29	0.070
C29-C33	σ	C28-C29	σ*	4.57	1.24	0.067
C3-C17	σ	C16-C17	σ*	4.49	1.30	0.068
C23-C25	σ	C25-C26	σ*	3.93	1.28	0.063
C3-C4	σ	O59-C60	σ*	3.63	1.01	0.054
C14-C15	σ	C15-C18	σ*	3.43	1.21	0.058
C26-C30	σ	C23-C25	σ*	3.14	1.32	0.057
C81-C82	σ	C82-C94	σ*	2.93	1.22	0.054
C81-C82	σ	C83-H87	σ*	2.64	1.15	0.049
C81-C86	σ	N80-C95	σ*	2.26	1.18	0.046
C27-C51	σ	C28-C29	σ*	1.77	1.36	0.044
C82-C94	σ	C83-C84	σ*	1.47	1.27	0.039
C33-C35	σ	C29-C30	σ*	1.03	1.17	0.031
C18-S20	σ	C11-C12	σ*	0.94	1.30	0.031
C86-H90	σ	N80-C81	σ*	0.51	0.98	0.020
N80	LP(1)	C95-C96	π*	40.37	0.31	0.102
O58	LP(2)	C1-C2	π*	32.22	0.36	0.102
Cl112	LP(3)	C54-C102	π*	17.16	0.35	0.075
O105	LP(2)	C55-C56	σ*	18.11	0.75	0.105
O108	LP(2)	C104-N106	σ*	12.93	0.64	0.081
N80	LP(1)	C9-C10	σ*	6.63	0.87	0.074
O59	LP(2)	C60-H61	σ*	2.95	0.76	0.043

Table S18: Natural bond orbitals analysis for **PMDC7** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C56	π*	24.95	0.31	0.079
C102-N103	π	C53-C54	π*	1.42	0.34	0.022
C51-H52	σ	C56-S101	σ*	10.3	0.73	0.078
C86-H90	σ	N80-C81	σ*	0.51	0.98	0.020
N106	LP(1)	C53-C54	π*	70.27	0.27	0.125
N80	LP(1)	C9-S21	σ*	14.62	0.48	0.081
C15-C18	π	C16-C17	π*	17.76	0.31	0.069
C25-C26	π	C29-C30	π*	16.50	0.31	0.066
C29-C30	π	C25-C26	π*	15.17	0.31	0.064

C16-C17	π	C2-C3	π*	14.01	0.31	0.063
C22-C23	π	C1-C6	π*	12.72	0.31	0.060
C109-C110	π	C51-C56	π*	10.73	0.33	0.056
C53-C54	π	C102-N103	π*	5.00	0.42	0.043
C110-H111	σ	N106-C109	σ*	9.75	0.94	0.086
C25-C26	σ	C30-S31	σ*	8.65	0.95	0.081
C102-N103	σ	C54-C102	σ*	8.12	1.60	0.103
C110-H112	σ	C56-C109	σ*	7.96	1.01	0.081
C27-C28	σ	C29-C33	σ*	6.94	1.17	0.081
C16-C17	σ	C14-C15	σ*	6.63	1.17	0.079
C51-C56	σ	C27-C51	σ*	6.29	1.33	0.082
C23-H24	σ	C22-S34	σ*	5.96	0.75	0.06
C25-C26	σ	C26-C30	σ*	5.65	1.24	0.075
C25-C33	σ	C28-C29	σ*	5.24	1.21	0.071
C6-C22	σ	C5-C6	σ*	4.71	1.28	0.070
C94-C95	σ	C93-C94	σ*	4.16	1.28	0.065
C6-C22	σ	C1-C6	σ*	3.97	1.26	0.063
N80-C95	σ	C9-N80	σ*	3.73	1.25	0.061
C92-C93	σ	C91-C92	σ*	3.07	1.30	0.057
C82-C94	σ	C81-C82	σ*	2.85	1.23	0.053
N80-C95	σ	N80-C81	σ*	2.45	1.25	0.050
C33-C39	σ	C25-C33	σ*	1.83	1.05	0.039
C27-C51	σ	C51-H52	σ*	1.02	1.17	0.031
C76-H79	σ	O59-C60	σ*	0.51	0.81	0.018
N80	LP(1)	C81-C82	π*	35.73	0.31	0.097
O59	LP(2)	C4-C5	π*	31.56	0.36	0.101
O58	LP(2)	C1-C6	π*	28.33	0.36	0.098
S101	LP(2)	C51-C56	π*	21.40	0.30	0.072
N105	LP(1)	C54-C104	σ*	12.93	1.05	0.104
O58	LP(1)	C1-C2	σ*	7.29	1.14	0.082
N106	LP(1)	C55-H57	σ*	4.31	0.69	0.055

Table S19: Natural bond orbitals analysis **PMDC8** with its representative values

Donor(i)	**Type**	**Acceptor(j)**	**Type**	***E*(2)[a]**	***E*(J)*E*(i)[b]**	**F(i,j)[c]**
C27-C28	π	C51-C55	π*	28.5	0.31	0.084
C104-O106	π	C51-C55	π*	3.14	0.43	0.035
C51-H52	σ	C55-S100	σ*	10.86	0.73	0.080
C95-H99	σ	N79-C94	σ*	0.51	0.98	0.020
N101	LP(1)	C53-S105	π*	84.27	0.20	0.118
O106	LP(2)	N101-C104	σ*	29.74	0.69	0.130
C2-C3	π	C4-C5	π*	19.53	0.30	0.069
C16-C17	π	C15-C18	π*	18.32	0.31	0.071

C25-C26	π	C29-C30	π*	17.37	0.30	0.067
C15-C18	π	C11-C12	π*	15.45	0.31	0.064
C29-C30	π	C25-C26	π*	14.96	0.31	0.063
C2-C3	π	C16-C17	π*	14.71	0.3	0.060
C22-C23	π	C1-C6	π*	12.47	0.31	0.059
C51-C55	π	C27-C28	π*	11.48	0.32	0.057
C25-C26	σ	C30-S31	σ*	8.58	0.95	0.081
C15-C18	σ	C12-S21	σ*	8.19	0.95	0.079
C27-C28	σ	C29-C33	σ*	7.01	1.17	0.081
C9-C10	σ	C11-C14	σ*	6.64	1.19	0.079
C9-S21	σ	C12-C18	σ*	6.16	1.20	0.077
C51-C55	σ	C27-C51	σ*	5.82	1.33	0.079
C94-C95	σ	C93-C94	σ*	5.52	1.29	0.075
C29-C33	σ	C23-C25	σ*	5.16	1.21	0.071
C3-C4	σ	C3-C17	σ*	4.96	1.22	0.070
C26-C30	σ	C25-C26	σ*	4.68	1.31	0.070
C1-C6	σ	C5-C6	σ*	4.22	1.29	0.066
C6-C22	σ	C1-C6	σ*	3.97	1.26	0.063
C5-C6	σ	C1-O57	σ*	3.88	1.10	0.058
C80-C85	σ	C84-C85	σ*	3.52	1.33	0.061
C93-C94	σ	C81-C93	σ*	2.94	1.22	0.054
C6-C22	σ	C1-C2	σ*	2.16	1.30	0.047
C14-C43	σ	C14-C15	σ*	1.84	1.05	0.039
C5-C6	σ	C5-H8	σ*	1.59	1.17	0.039
C29-C33	σ	C33-C39	σ*	1.49	1.02	0.035
C61-C63	σ	C63-H65	σ*	0.53	1.06	0.021
N101	LP(1)	C104-O106	π*	51.3	0.30	0.113
O57	LP(2)	C1-C6	π*	28.63	0.36	0.098
S20	LP(2)	C16-C17	π*	22.43	0.29	0.072
O106	LP(2)	C55-C104	σ*	20.08	0.73	0.110
S105	LP(2)	C53-S100	σ*	15.46	0.41	0.072
O58	LP(2)	C59-C75	σ*	5.93	0.73	0.061
N101	LP(1)	C54-H103	σ*	4.43	0.7	0.056

Table S20: Dipole moment and major contributing tensors (*D*) of the studied Compounds **PMD-1** and **PMDC2-PMDC8**

Compounds	μ_{xx}	μ_{yy}	μ_{zz}	μ_{total}
PMD-1	4.589	-0.311	-10.504	11.467
PMDC2	-7.747	3.903	-7.488	11.459
PMDC3	-5.667	2.371	-7.894	10.002
PMDC4	-7.582	1.976	-7.199	10.640
PMDC5	-7.691	2.083	-7.255	10.776

PMDC6	-12.081	1.166	1.769	12.265
PMDC7	-0.660	11.401	2.757	11.748
PMDC8	5.255	4.799	3.050	7.742

Table S21: Linear polarizability and its major contributing tensors (*esu* $\times 10^{-22}$) of **PMD-1** and **MDC2-MDC8**.

Compounds	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
PMD-1	5.723	1.838	1.020	2.860
PMDC2	4.076	1.634	1.165	2.292
PMDC3	4.053	1.653	1.145	2.284
PMDC4	4.117	1.651	1.148	2.306
PMDC5	4.223	1.655	1.173	2.350
PMDC6	4.638	1.691	1.024	2.451
PMDC7	3.449	1.612	1.005	2.022
PMDC8	3.481	1.569	9.876	2.012

Table S22: The calculated first hyperpolarizability (β) along its major contributing tensors (*esu*) of **PMD-1** and **PMDC2-PMDC8**.

Systems	PMD-1	PMDC2	PMDC3	PMDC4	PMDC5	PMDC6	PMDC7	PMDC8
β_{xxx}	6.622×10^{-28}	-3.122×10^{-27}	-3.120×10^{-27}	-3.370×10^{-27}	-3.519×10^{-27}	-4.452×10^{-27}	7.720×10^{-28}	1.450×10^{-27}
β_{xxy}	2.021×10^{-28}	6.935×10^{-29}	1.895×10^{-28}	1.641×10^{-28}	1.608×10^{-28}	4.292×10^{-29}	8.557×10^{-29}	1.420×10^{-28}
β_{xyy}	-5.306×10^{-29}	-4.662×10^{-29}	-6.916×10^{-29}	-6.547×10^{-29}	-6.654×10^{-29}	-1.260×10^{-29}	-8.374×10^{-31}	1.725×10^{-29}
β_{yyy}	1.277×10^{-29}	1.300×10^{-29}	3.010×10^{-29}	2.885×10^{-29}	2.881×10^{-29}	1.583×10^{-29}	-3.417×10^{-29}	-1.694×10^{-29}
β_{xxz}	-4.783×10^{-28}	-2.643×10^{-28}	-2.336×10^{-28}	-2.732×10^{-28}	-2.874×10^{-28}	1.869×10^{-28}	5.380×10^{-29}	1.022×10^{-28}
β_{yyz}	-1.979×10^{-29}	-1.893×10^{-29}	-2.035×10^{-29}	-2.103×10^{-29}	-2.054×10^{-29}	-3.242×10^{-30}	-1.956×10^{-30}	-1.231×10^{-30}
β_{xzz}	-8.978×10^{-30}	-2.249×10^{-29}	-1.631×10^{-29}	-2.097×10^{-29}	-2.346×10^{-29}	1.198×10^{-31}	-2.475×10^{-30}	1.176×10^{-31}
β_{yzz}	1.268×10^{-29}	7.243×10^{-30}	6.276×10^{-30}	7.221×10^{-30}	7.292×10^{-30}	-5.812×10^{-31}	7.720×10^{-31}	1.415×10^{-30}
β_{zzz}	-6.810×10^{-30}	-4.189×10^{-30}	-2.865×10^{-30}	-3.857×10^{-30}	-4.593×10^{-30}	2.680×10^{-30}	2.957×10^{-30}	3.140×10^{-30}
β_{tot}	0.817×10^{-27}	3.205×10^{-27}	3.224×10^{-27}	3.475×10^{-27}	3.628×10^{-27}	4.469×10^{-27}	0.772×10^{-27}	1.476×10^{-27}

Table S23: The average second hyperpolarizability (γ in *esu*) and its major contributing tensor components noticed for all nominated molecules.

Compounds	$\gamma_x\times10^{-32}$	$\gamma_y\times10^{-34}$	$\gamma_z\times10^{-34}$	$\gamma_{tot}\times10^{-32}$
PMD-1	7.221	4.150	3.332	7.295
PMDC2	3.758	3.373	2.721	3.819
PMDC3	3.764	3.166	2.257	3.818
PMDC4	4.062	3.018	2.651	4.119
PMDC5	4.266	3.226	2.925	4.328
PMDC6	5.555	3.483	1.042	5.600
PMDC7	1.428	2.522	0.680	1.460
PMDC8	1.865	2.622	0.899	1.900

Table S24: The IUPAC names and abbreviations of investigated compounds.

Compound	IUPAC name
PMD-1	2,2'-((2*Z*,2'*Z*)-((6,6'-(2,5-diisobutoxy-1,4-phenylene)bis(4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-b']dithiophene-6,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile
PMDC2	(*Z*)-2-(2-((6-(4-(6-(9*H*-carbazol-9-yl)-4-methyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4-methyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile
PMDC3	(*E*)-2-(5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-4-ylidene)malononitrile
PMDC4	(*E*)-2-(5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-1-fluoro-6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-4-ylidene)malononitrile
PMDC5	(*E*)-2-(5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-1-chloro-6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-4-ylidene)malononitrile
PMDC6	(*E*)-5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-3-chloro-6-(dinitromethylene)- 5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-4-one
PMDC7	(*Z*)-2-(5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-3-methyl-4-methylenethiazolidin-2-ylidene)malononitrile

PMDC8	(*Z*)-5-((6-(4-(6-(9*H*-carbazol-9-yl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)-2,5-diisobutoxyphenyl)-4,4-dimethyl-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophen-2-yl)methylene)-3-methyl-2-thioxothiazolidin-4-one

Table S25: The GRPs of **PMD-1** and **PMDC2-PMDC8**

Compounds	*IP*	*EA*	*X*	η	σ	μ	ω
PMD-1	0.2049	0.1266	0.1657	0.0392	12.7693	-0.1657	0.3507
PMDC2	0.1987	0.1223	0.1605	0.0382	13.0887	-0.1605	0.3373
PMDC3	0.1983	0.1210	0.1597	0.0386	12.9393	-0.1597	0.3298
PMDC4	0.1988	0.1229	0.1609	0.0379	13.1774	-0.1609	0.3410
PMDC5	0.1989	0.1233	0.1611	0.0378	13.2158	-0.1611	0.3430
PMDC6	0.1995	0.1259	0.1627	0.0368	13.5785	-0.1627	0.3596
PMDC7	0.1908	0.0932	0.1420	0.0488	10.2453	-0.1420	0.2066
PMDC8	0.1950	0.1037	0.1494	0.0457	10.9502	-0.1494	0.2443

Units in *Hartree* (E_h)

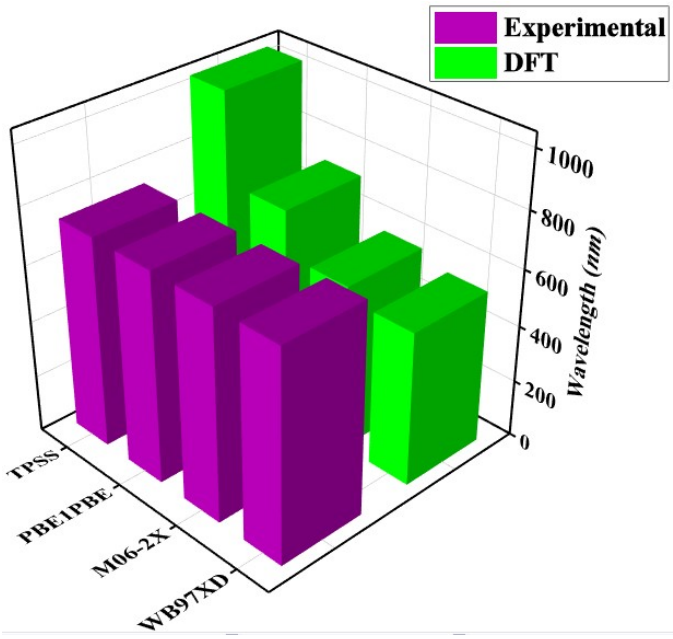
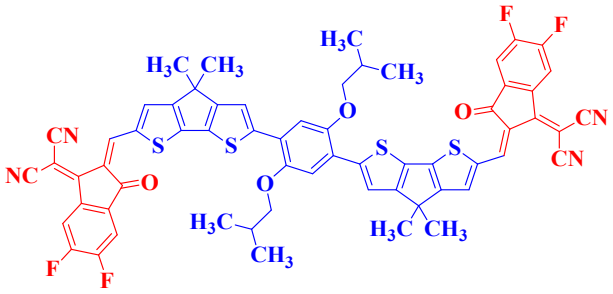
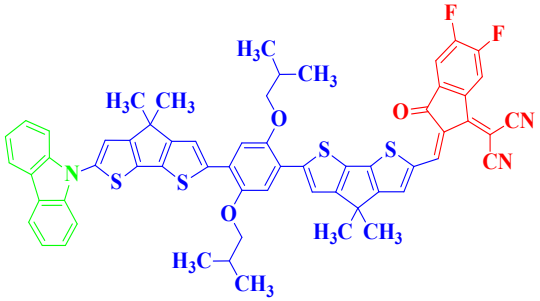


Figure S1: Comparison between DFT and experimental UV-Vis results of **PMD-1** at various functionals in dichloromethane (DCM) solvent



PMD-1



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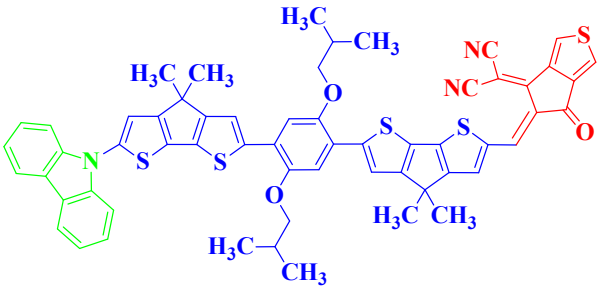

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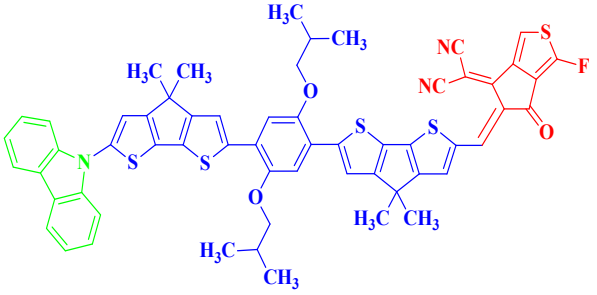

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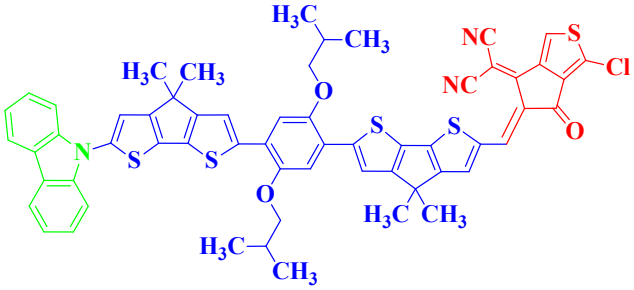

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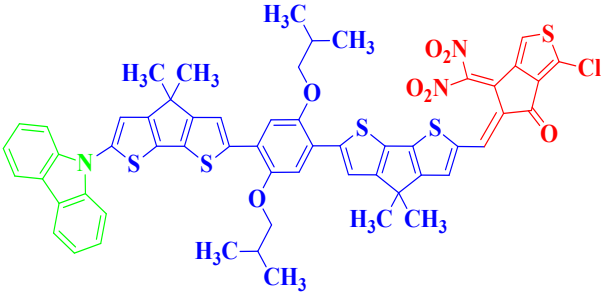

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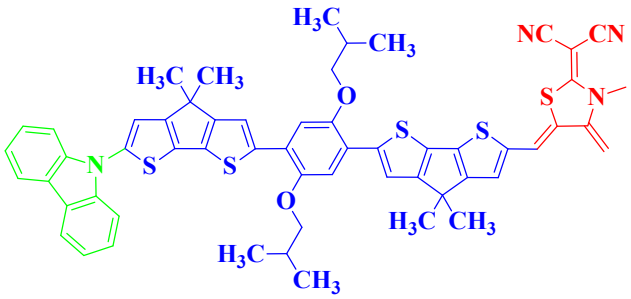

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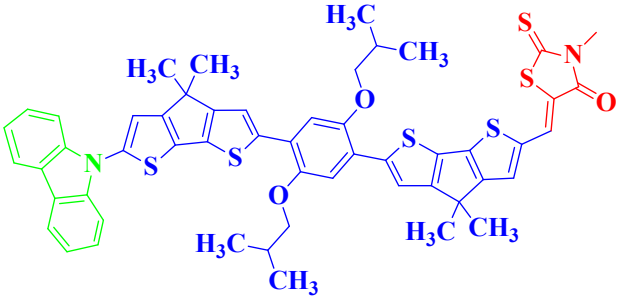
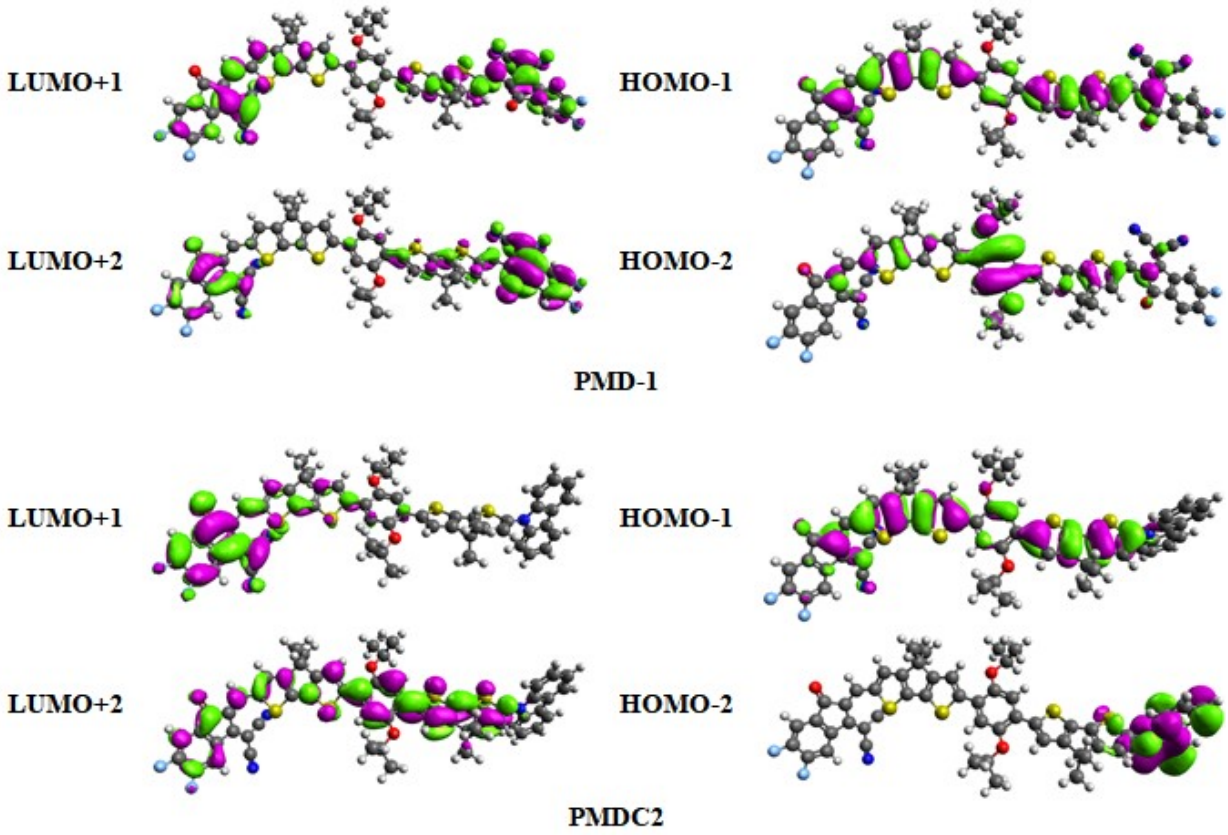
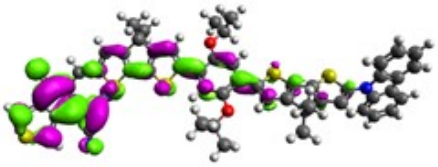
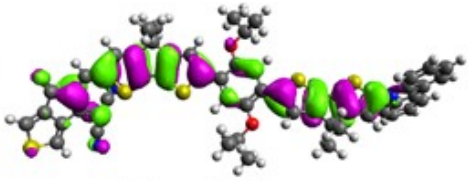


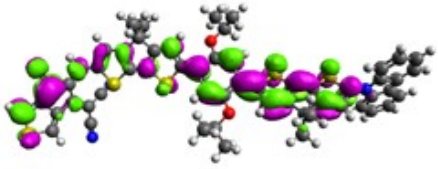
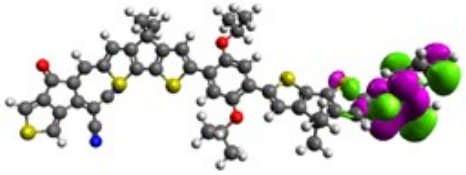
PMDC8

Depicts Donor Depicts π-spacer Depicts Acceptor

Figure S2: The display of donor, π-spacer and acceptor structures with green, blue and red colors respectively, in **PMD-1**and its derivatives (**PMDC2-PMDC8**).



LUMO+1  HOMO-1 

LUMO+2  HOMO-2 

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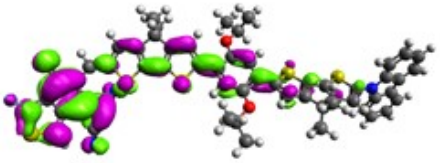
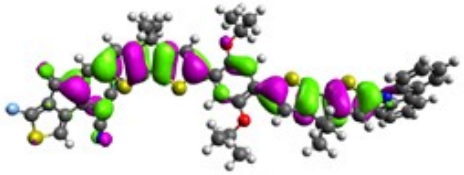
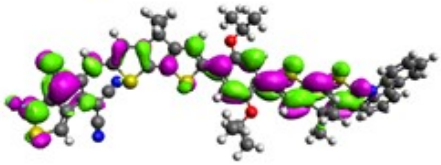
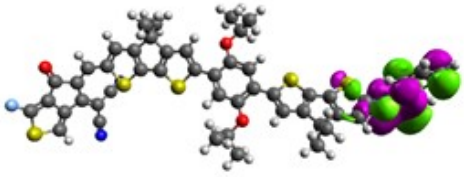
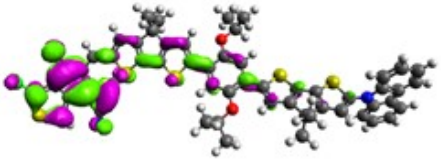
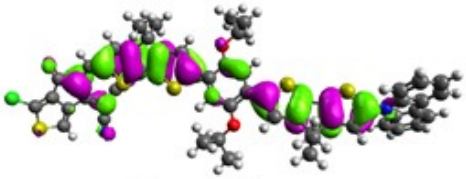
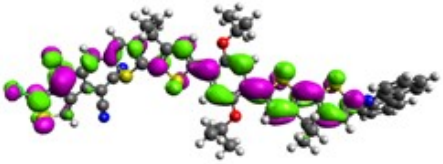
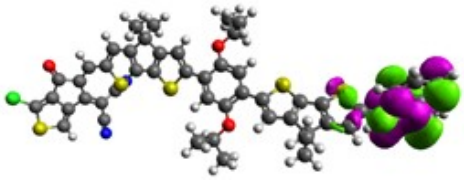
LUMO+1  HOMO-1 

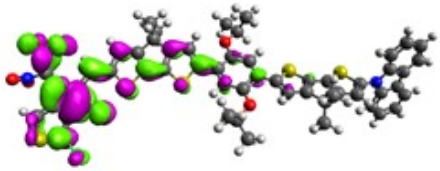
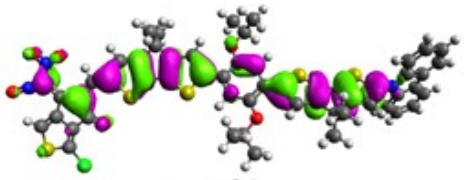
LUMO+2  HOMO-2 

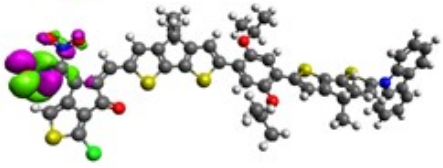
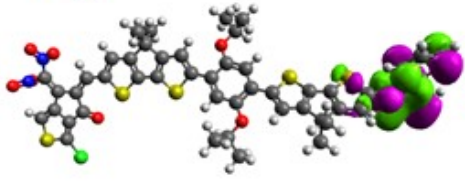
PMDC4

LUMO+1  HOMO-1 

LUMO+2  HOMO-2 

PMDC5

LUMO+1  HOMO-1 

LUMO+2  HOMO-2 

PMDC6

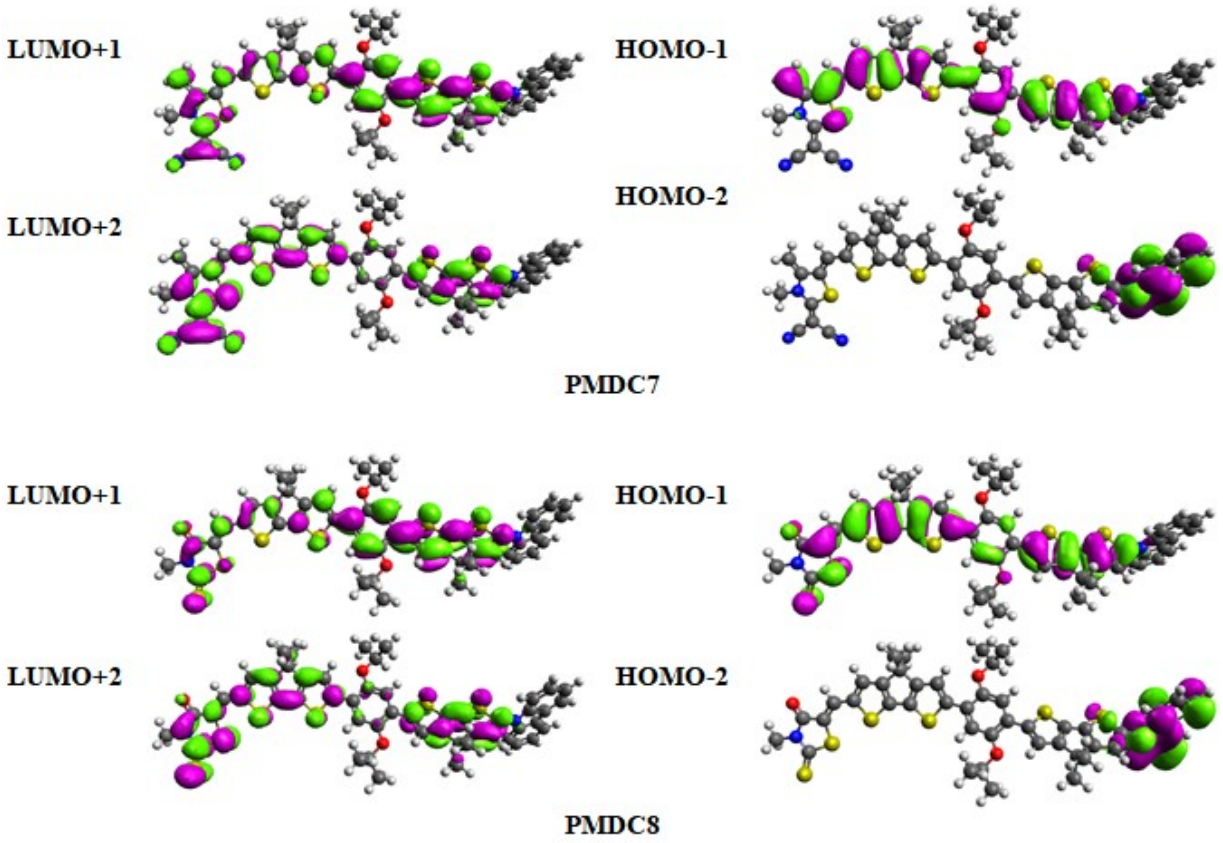
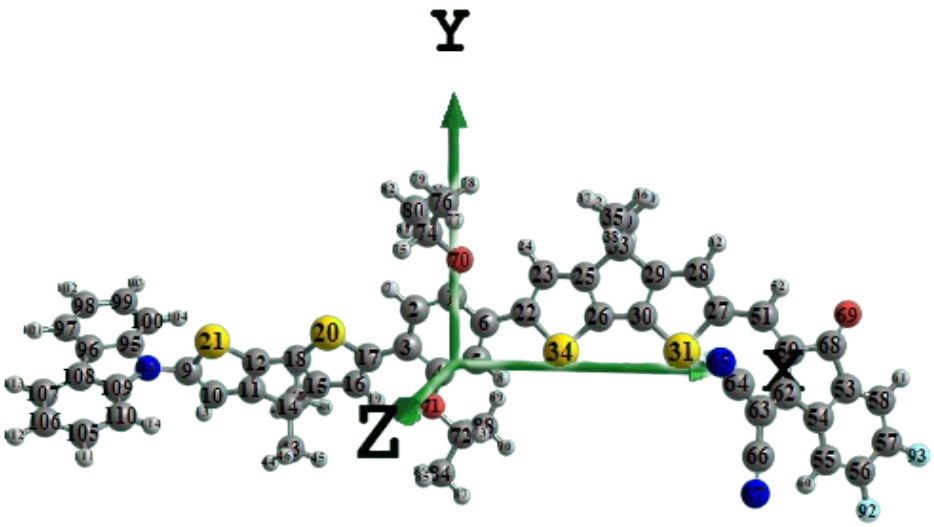
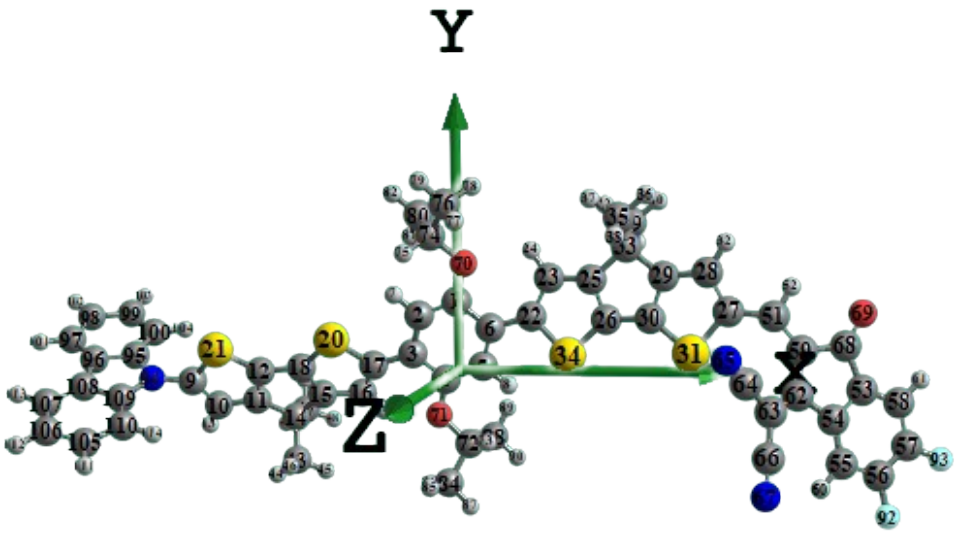


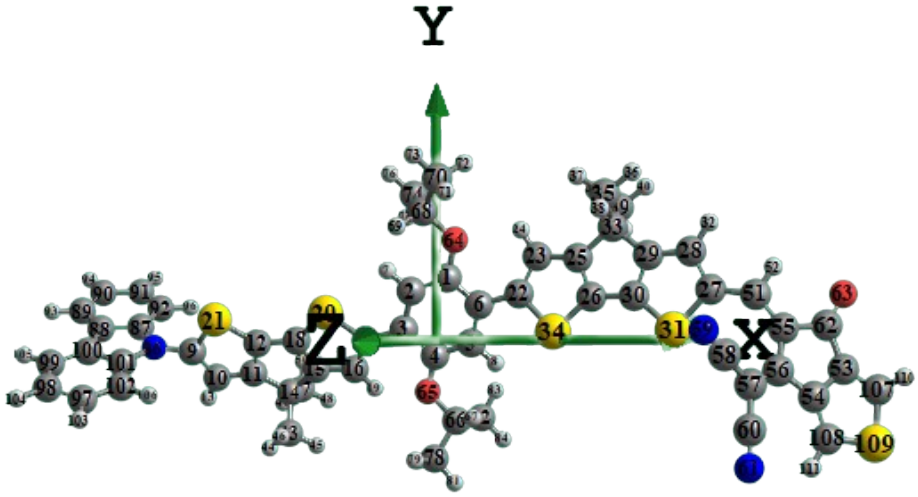
Figure S3: The 3D depiction of HOMO-1, LUMO+1, HOMO-2 and LUMO+2 of modified compound (**PMD-1** and **PMDC2-PMDC8**).



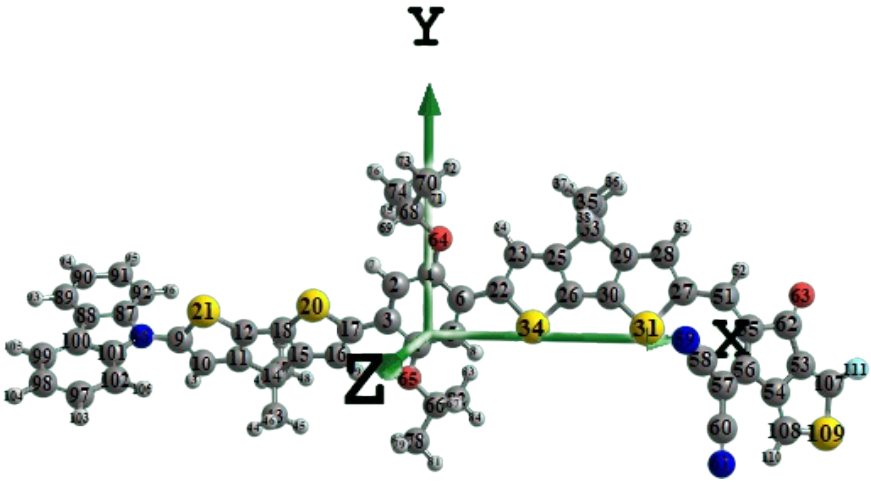
PMD-1



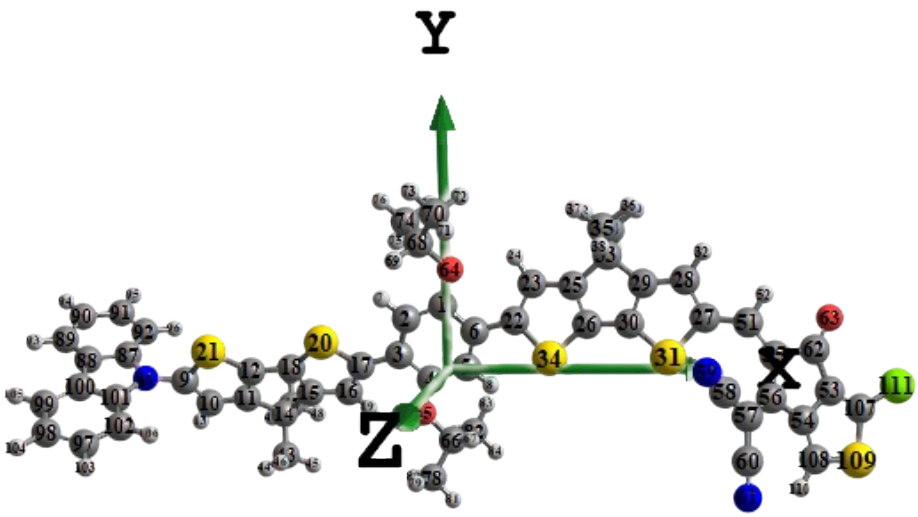
PMDC2



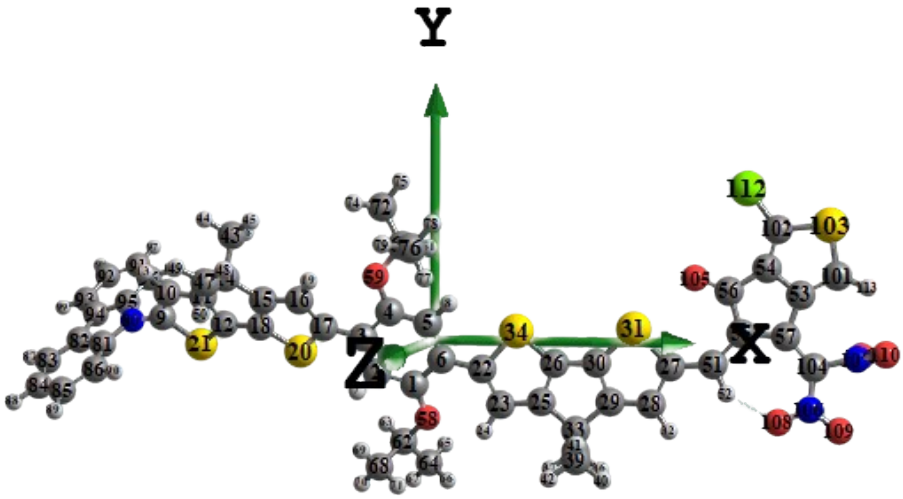
PMDC3



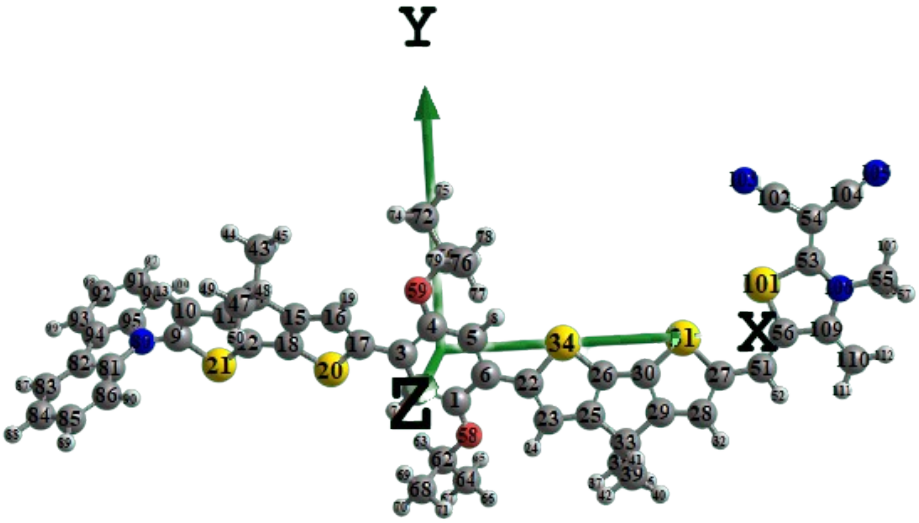
PMDC4



PMDC5



PMDC6



PMDC7

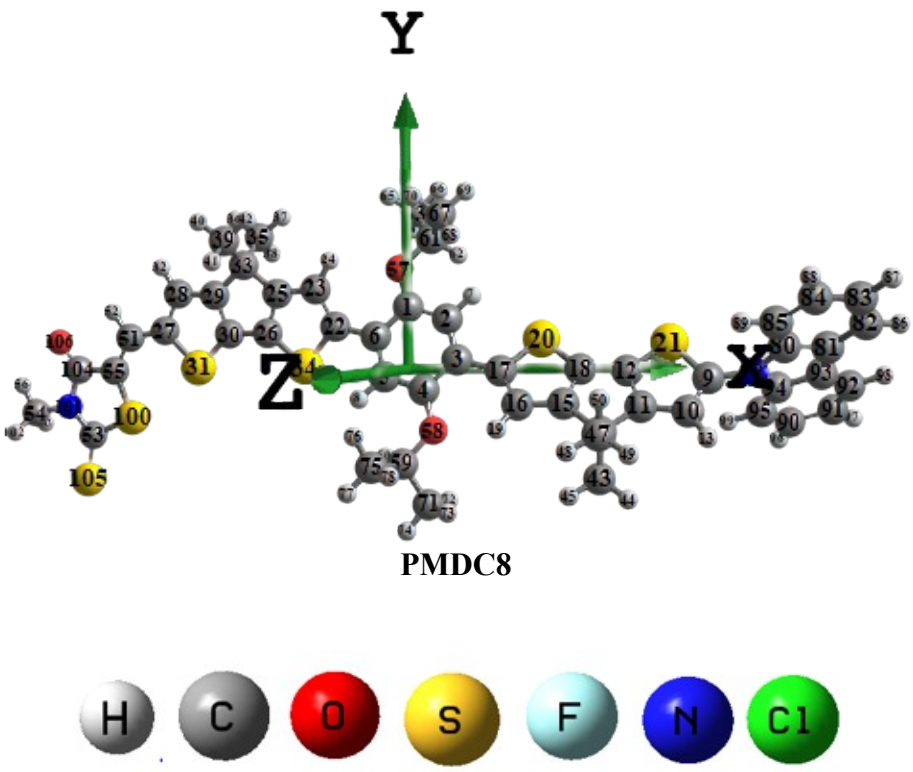
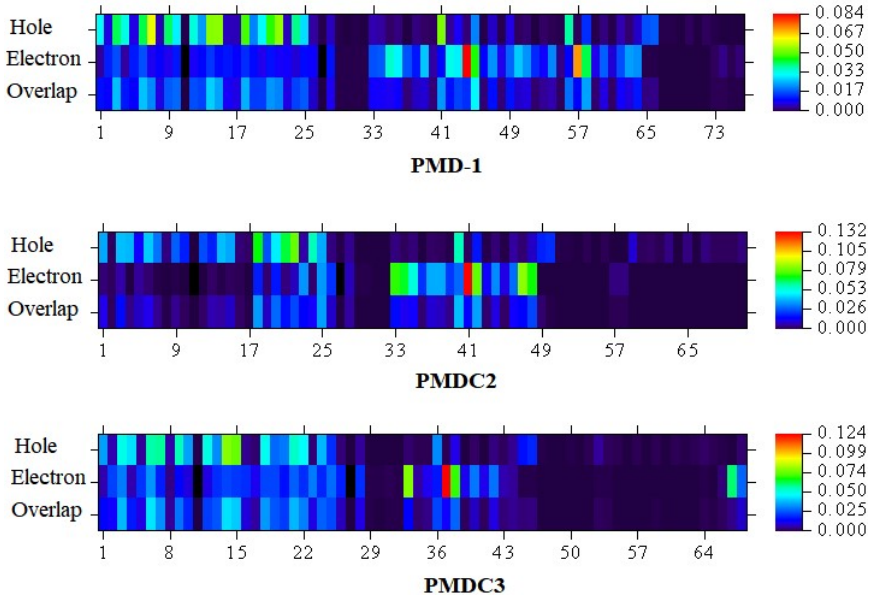


Figure S4: The optimized structures of all theoretically designed compounds.



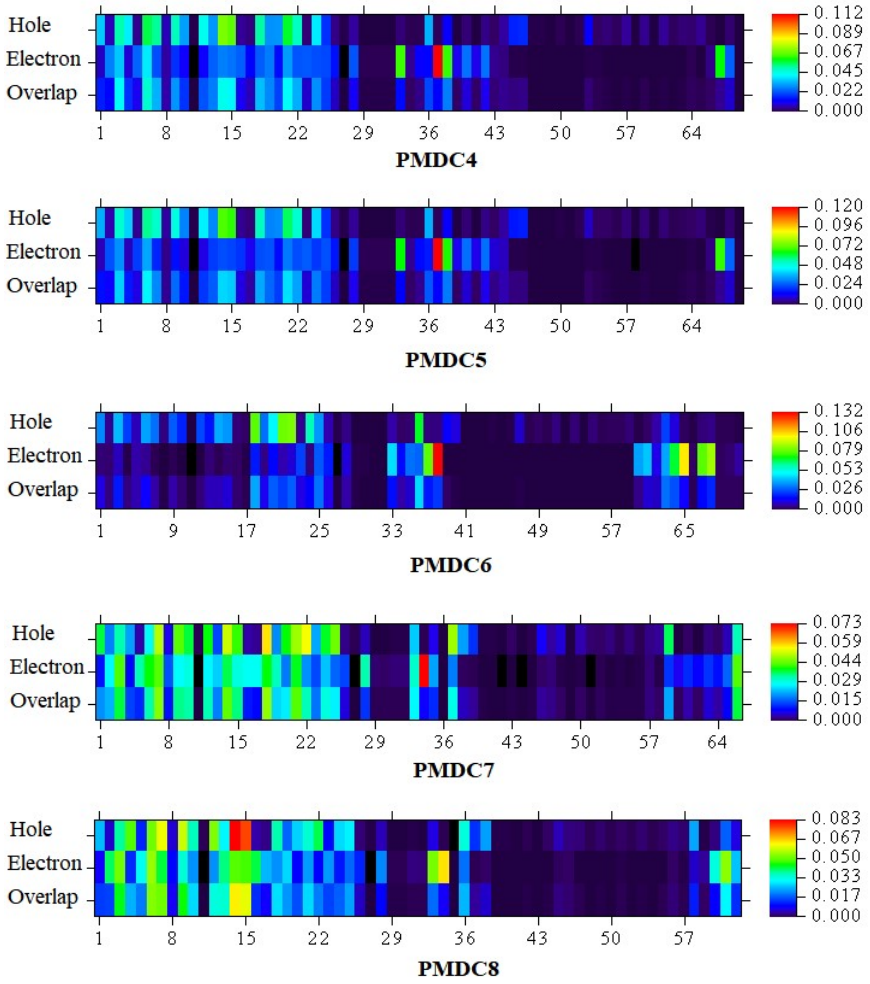
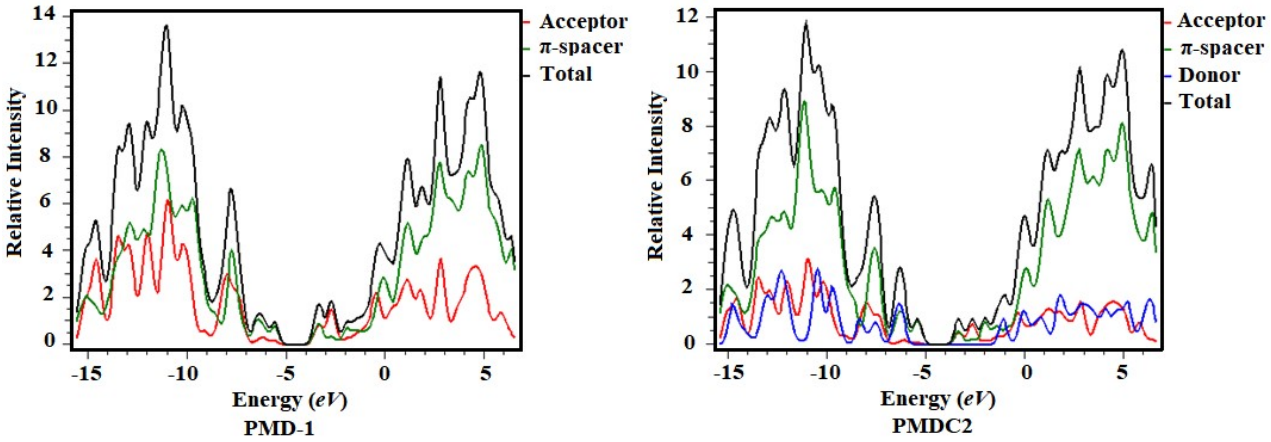


Figure S5. Pictorial representation of hole-electron transport analysis



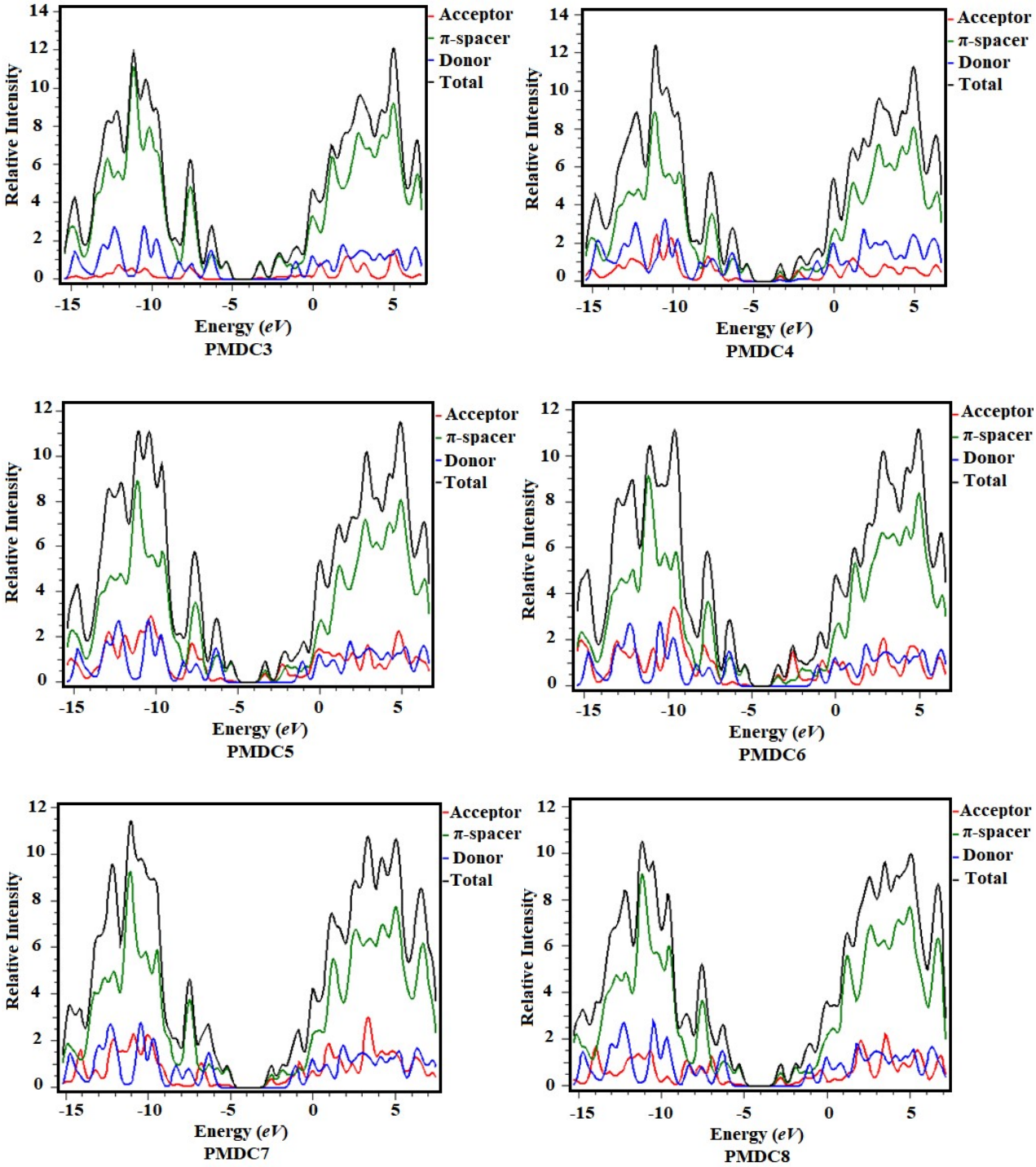


Figure S6: DOS pictographs of the **PMD-1** and **PMDC2-PMDC8**.

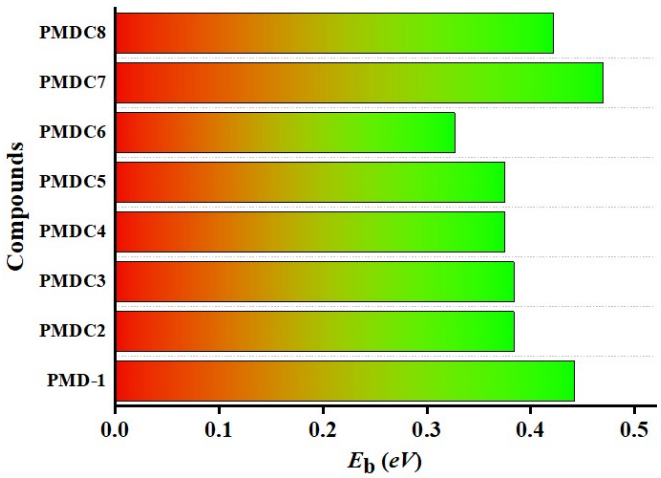


Figure S7: Graphical representation of the binding energies of **PMD-1** and its derivatives

$$\mu = (\mu^2_x+\mu^2_y+\mu^2_z)^{1/2} \qquad \text{(Equation S1)}$$

$$\langle\alpha\rangle = (a_{xx}+a_{yy}+a_{zz})/3 \qquad \text{(Equation S2)}$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad \text{(Equation S3)}$$

Where $\beta_x = \beta_{xxx}+\beta_{xyy}+\beta_{xzz}$; $\beta_y = \beta_{yxx}+\beta_{yyy}+\beta_{yzz}$ and $\beta_z = \beta_{zxx}+\beta_{zyy}+\beta_{zzz}$.

$$\gamma_{tot} = \sqrt{\gamma_x^2 + \gamma_y^2 + \gamma_z^2} \qquad \text{(Equation S4)}$$

Where $\gamma_i = \frac{1}{15}\sum_j (\gamma_{ijji} + \gamma_{ijij} + \gamma_{iijj}) \qquad i,j = \{x, y, z\}$