SUPPORTING INFORMATION

Phosphonic anchoring groups in organic dyes for solid-state solar cells

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KEYWORDS. Organic dyes, solid-state dye-sensitized solar cells, phosphonic acid anchoring group

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Computational details

Pyt-COOH

Optimized ground state geometry in DMF (CPCM-6-31G*/M06-2x)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.798066	0.896518	-0.087146
2	6	0	0.778068	0.010224	-0.176956
3	6	0	1.016905	-1.412104	-0.122982
4	6	0	2.414575	-1.772091	-0.055259
5	6	0	3.386909	-0.836087	0.004973
6	1	0	-0.211007	0.414028	-0.331489
7	1	0	2.688304	-2.819961	-0.021334
8	6	0	4.835748	-1.083030	0.091937
9	6	0	5.686691	-0.096104	0.604711
10	6	0	5.375101	-2.303168	-0.334330
11	6	0	7.053315	-0.335684	0.702961
12	1	0	5.274381	0.850981	0.936301
13	6	0	6.741035	-2.536941	-0.232821
14	1	0	4.731503	-3.062483	-0.767141
15	6	0	7.583591	-1.555281	0.287732
16	1	0	7.705186	0.432023	1.107188
17	1	0	7.149406	-3.483499	-0.571726
18	1	0	8.650553	-1.739145	0.363847
19	6	0	1.670209	2.363773	-0.120227
20	6	0	2.779781	3.154575	-0.444305
21	6	0	0.446296	2.980971	0.169163
22	6	0	2.660295	4.539334	-0.492417
23	1	0	3.730015	2.681353	-0.667162
24	6	0	0.332727	4.364774	0.117097
25	1	0	-0.416036	2.387227	0.456925
26	6	0	1.438097	5.147587	-0.214824
27	1	0	3.524168	5.143149	-0.750568
28	1	0	-0.619096	4.833265	0.345344
29	1	0	1.346824	6.228450	-0.252112
30	8	0	3.085274	0.491457	0.021018
31	6	0	0.066277	-2.407322	-0.135815
32	1	0	0.417411	-3.434997	-0.134441
33	6	0	-1.354783	-2.315800	-0.129041
34	16	0	-2.288528	-0.835714	-0.015273
35	6	0	-3.414521	-3.113500	-0.136886
36	6	0	-3.759226	-1.773365	-0.046403
37	1	0	-4.154107	-3.908028	-0.174168
38	6	0	-5.094579	-1.298314	0.002358
39	6	0	-5.559298	-0.018510	0.096203
40	1	0	-5.851427	-2.078371	-0.042441
41	6	0	-4.694579	1.117634	0.169629
42	7	0	-3.986024	2.033478	0.230287
43	6	0	-7.001980	0.299376	0.133098
44	8	0	-7.443200	1.424029	0.222946
45	8	0	-7.777989	-0.791248	0.055873
46	1	0	-8.704245	-0.492263	0.089567
47	7	0	-2.109174	-3.416192	-0.179376

Pyt-COOH

Optimized first excited state geometry in DMF (CPCM-TD-6-31G*/M06-2x)

Standard orientation:

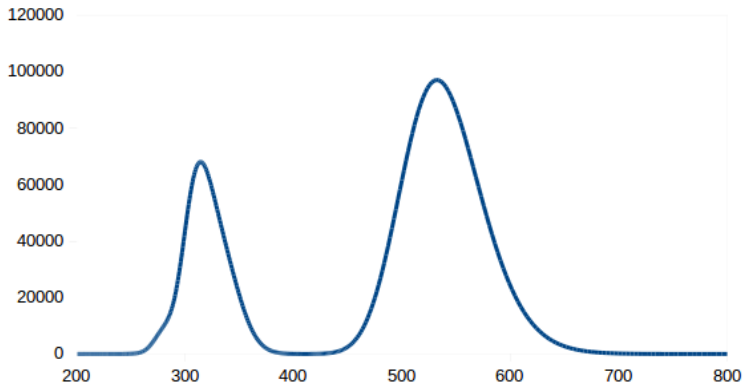
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.782775	0.908636	-0.216962
2	6	0	0.774282	0.004616	-0.390528
3	6	0	1.030083	-1.392966	-0.319898
4	6	0	2.390973	-1.773053	-0.141575
5	6	0	3.372093	-0.834610	-0.001541
6	1	0	-0.205806	0.386426	-0.640504
7	1	0	2.651148	-2.823435	-0.087684
8	6	0	4.798696	-1.083071	0.197692
9	6	0	5.631002	-0.058442	0.674925
10	6	0	5.353190	-2.341684	-0.085427
11	6	0	6.985602	-0.295443	0.874935
12	1	0	5.210220	0.915451	0.900069
13	6	0	6.707181	-2.569648	0.116694
14	1	0	4.733403	-3.137122	-0.486102
15	6	0	7.527964	-1.549160	0.598489
16	1	0	7.619401	0.501626	1.249915
17	1	0	7.125998	-3.544730	-0.109875
18	1	0	8.586538	-1.730961	0.754078
19	6	0	1.651997	2.363603	-0.259477
20	6	0	2.787426	3.167138	-0.445210
21	6	0	0.394786	2.973261	-0.114351
22	6	0	2.662588	4.549836	-0.499797
23	1	0	3.760768	2.703321	-0.562251
24	6	0	0.279110	4.355140	-0.172014
25	1	0	-0.491923	2.374202	0.070381
26	6	0	1.410533	5.148209	-0.366315
27	1	0	3.545899	5.161923	-0.651360
28	1	0	-0.696440	4.815253	-0.053530
29	1	0	1.316138	6.228553	-0.408635
30	8	0	3.056791	0.488599	-0.007585
31	6	0	0.043739	-2.414063	-0.431489
32	1	0	0.409357	-3.430870	-0.552342
33	6	0	-1.338987	-2.322306	-0.377978
34	16	0	-2.271488	-0.850852	-0.018615
35	6	0	-3.399797	-3.127907	-0.434798
36	6	0	-3.746541	-1.771077	-0.145031
37	1	0	-4.156449	-3.898049	-0.552038
38	6	0	-5.055686	-1.305399	0.000381
39	6	0	-5.501960	-0.011930	0.261050
40	1	0	-5.828849	-2.061094	-0.110713
41	6	0	-4.626493	1.096796	0.415156
42	7	0	-3.911134	2.005725	0.538821
43	6	0	-6.923805	0.315528	0.384456
44	8	0	-7.362417	1.430554	0.600549
45	8	0	-7.726489	-0.756769	0.231656
46	1	0	-8.642047	-0.440114	0.326434
47	7	0	-2.129031	-3.419702	-0.555002

Pyt-COOH

Calculated Absorption Spectrum in DMF

(CPCM-TD-M06-2x/6-311+G(2d,p)//CPCM-M06-2x/6-31G*):

No.	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	18800.10704	531.911865115	1.3394	HOMO->LUMO (97%)
2	29513.64352	338.826346304	0.305	HOMO->L+1 (60%), HOMO->L+2 (25%) H-1->LUMO (6%)
3	31308.23952	319.404736686	0.4342	HOMO->L+1 (28%), HOMO->L+2 (47%) H-2->LUMO (9%), H-1->LUMO (9%)
4	32570.50592	307.026240997	0.5679	H-1->LUMO (69%), HOMO->L+2 (14%) H-2->LUMO (3%), H-1->L+1 (7%)
5	35591.07312	280.969330885	0.1103	H-2->LUMO (76%) H-5->LUMO (5%), HOMO->L+1 (7%), HOMO->L+2 (7%)
6	38543.08272	259.44992705	0.0021	H-7->LUMO (90%) H-7->L+7 (3%)



Pyt-PO(OH)$_2$

Optimized ground state geometry in DMF (CPCM-6-31G*/M06-2x)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.369167	0.895625	-0.072787
2	6	0	1.366329	-0.010068	-0.156846
3	6	0	1.633057	-1.428463	-0.107874
4	6	0	3.038776	-1.759968	-0.044378
5	6	0	3.992624	-0.805401	0.009150
6	1	0	0.368024	0.375252	-0.298388
7	1	0	3.333488	-2.802157	-0.010755
8	6	0	5.446806	-1.023173	0.088518
9	6	0	6.280621	-0.016879	0.591577
10	6	0	6.008971	-2.233663	-0.335786
11	6	0	7.652630	-0.227238	0.681734
12	1	0	5.851223	0.923104	0.921681
13	6	0	7.380175	-2.438406	-0.242151
14	1	0	5.379018	-3.008450	-0.761261
15	6	0	8.205672	-1.437248	0.268316
16	1	0	8.290646	0.556060	1.078165
17	1	0	7.805835	-3.377925	-0.579487
18	1	0	9.276722	-1.598562	0.337971
19	6	0	2.212900	2.360562	-0.099989
20	6	0	3.305944	3.173080	-0.426221
21	6	0	0.979639	2.954290	0.198531
22	6	0	3.161586	4.555748	-0.466639
23	1	0	4.263436	2.718312	-0.656274
24	6	0	0.841125	4.336161	0.154256
25	1	0	0.129627	2.343619	0.487543
26	6	0	1.930367	5.140598	-0.179159
27	1	0	4.013305	5.176032	-0.726204
28	1	0	-0.117747	4.786296	0.389992
29	1	0	1.819427	6.219816	-0.209910
30	8	0	3.665703	0.516490	0.024292
31	6	0	0.704732	-2.442906	-0.119094
32	1	0	1.078338	-3.462651	-0.111351
33	6	0	-0.719907	-2.385306	-0.118765
34	16	0	-1.689461	-0.925456	-0.042195
35	6	0	-2.761641	-3.229767	-0.122259
36	6	0	-3.136288	-1.898658	-0.061797
37	1	0	-3.481261	-4.042742	-0.146376
38	6	0	-4.483455	-1.445288	-0.028176
39	6	0	-4.970428	-0.173661	0.024999
40	6	0	-4.141584	0.985755	0.062614
41	7	0	-3.490724	1.946093	0.096587
42	15	0	-6.742215	0.066897	0.078019
43	8	0	-7.494155	-1.206501	0.068398
44	8	0	-6.956034	1.086534	-1.136667
45	1	0	-7.840678	1.492827	-1.151024
46	8	0	-7.056681	1.032093	1.326352
47	1	0	-7.268358	0.533700	2.134035
48	1	0	-5.230098	-2.238605	-0.049074
49	7	0	-1.446978	-3.502289	-0.152312

Pyt-PO(OH)$_2$

Optimized first excited state geometry in DMF (CPCM-TD-6-31G*/M06-2x)

Standard orientation:

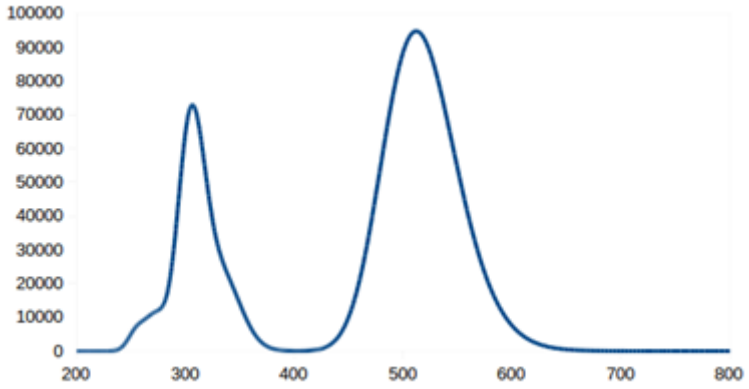
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.333299	0.899767	-0.297492
2	6	0	1.358901	-0.029517	-0.525680
3	6	0	1.645965	-1.419464	-0.439393
4	6	0	3.004094	-1.767493	-0.191129
5	6	0	3.952914	-0.805275	0.003508
6	1	0	0.384327	0.325804	-0.831458
7	1	0	3.285842	-2.811600	-0.124435
8	6	0	5.371640	-1.014925	0.284396
9	6	0	6.151531	0.042386	0.779028
10	6	0	5.972635	-2.265761	0.066782
11	6	0	7.498527	-0.152793	1.058162
12	1	0	5.695361	1.010061	0.955523
13	6	0	7.318650	-2.452152	0.348615
14	1	0	5.396629	-3.088818	-0.343454
15	6	0	8.086717	-1.398491	0.845958
16	1	0	8.090044	0.670804	1.444900
17	1	0	7.773000	-3.421736	0.172868
18	1	0	9.139356	-1.548701	1.063191
19	6	0	2.168966	2.350572	-0.341580
20	6	0	3.292898	3.182842	-0.460580
21	6	0	0.891341	2.929133	-0.260214
22	6	0	3.137763	4.562486	-0.511715
23	1	0	4.282069	2.743520	-0.529185
24	6	0	0.745574	4.308290	-0.314368
25	1	0	0.011419	2.306511	-0.127464
26	6	0	1.866317	5.129861	-0.441602
27	1	0	4.012873	5.196900	-0.609125
28	1	0	-0.245671	4.744278	-0.244395
29	1	0	1.748125	6.207985	-0.480266
30	8	0	3.604914	0.510016	-0.020790
31	6	0	0.686196	-2.462853	-0.596674
32	1	0	1.076876	-3.468003	-0.735941
33	6	0	-0.697339	-2.398703	-0.556354
34	16	0	-1.654204	-0.953520	-0.152953
35	6	0	-2.745251	-3.235221	-0.638635
36	6	0	-3.111730	-1.896441	-0.303425
37	1	0	-3.489701	-4.013601	-0.778277
38	6	0	-4.426004	-1.449474	-0.129023
39	6	0	-4.881718	-0.172574	0.177041
40	6	0	-4.038864	0.950688	0.356233
41	7	0	-3.379031	1.898569	0.510073
42	15	0	-6.629058	0.084926	0.374715
43	8	0	-7.423189	-1.154821	0.210739
44	8	0	-6.915527	1.293619	-0.641475
45	1	0	-7.781420	1.714566	-0.496138
46	8	0	-6.870324	0.852677	1.774156
47	1	0	-7.000598	0.233896	2.512603
48	1	0	-5.197336	-2.207762	-0.251738
49	7	0	-1.469996	-3.503274	-0.770482

Pyt-PO(OH)$_2$

Calculated Absorption Spectrum in DMF

(CPCM-TD-M06-2x/6-311+G(2d,p)//CPCM-M06-2x/6-31G*):

No.	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	19541.33568	511.735746407	1.309	HOMO->LUMO (97%)
2	29548.3256	338.428651944	0.2418	HOMO->L+1 (79%) H-1->LUMO (5%), HOMO->L+2 (7%)
3	32050.27472	312.009806074	0.3965	H-1->LUMO (12%), HOMO->L+1 (11%), HOMO->L+2 (63%) H-2->LUMO (6%)
4	33035.89104	302.701083131	0.6678	H-1->LUMO (68%), HOMO->L+2 (14%) H-2->LUMO (3%), H-1->L+1 (4%), H-1->L+2 (4%)
5	36524.26304	273.790602949	0.1353	H-2->LUMO (78%) H-5->LUMO (6%), HOMO->L+2 (9%)
6	39059.28112	256.02109699	0.0884	H-4->LUMO (41%), H-4->L+1 (23%) H-7->LUMO (3%), H-3->LUMO (4%), H-1->L+1 (4%), H-1->L+4 (3%), H-1->L+5 (2%), HOMO->L+4 (3%), HOMO->L+5 (3%)



Pyt-PO(OEt)OH

Optimized ground state geometry in DMF (CPCM-6-31G*/M06-2x)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.808704	0.887389	-0.171869
2	6	0	1.833806	-0.045755	-0.281242
3	6	0	2.128050	-1.452988	-0.144687
4	6	0	3.532918	-1.746421	0.030628
5	6	0	4.459278	-0.766851	0.107359
6	1	0	0.840307	0.306534	-0.515050
7	1	0	3.847157	-2.778319	0.133425
8	6	0	5.908523	-0.940398	0.302506
9	6	0	6.678224	0.116908	0.803034
10	6	0	6.529953	-2.156507	-0.007375
11	6	0	8.044736	-0.047142	1.003479
12	1	0	6.202160	1.061678	1.042811
13	6	0	7.895447	-2.314900	0.196380
14	1	0	5.952983	-2.973283	-0.429675
15	6	0	8.656422	-1.262315	0.703511
16	1	0	8.631693	0.776801	1.396568
17	1	0	8.368566	-3.259753	-0.050757
18	1	0	9.723201	-1.388441	0.858956
19	6	0	2.625397	2.344697	-0.285507
20	6	0	3.719920	3.163103	-0.590989
21	6	0	1.364993	2.924896	-0.091264
22	6	0	3.551349	4.537908	-0.714189
23	1	0	4.697712	2.718373	-0.741192
24	6	0	1.202607	4.299106	-0.217591
25	1	0	0.512615	2.309658	0.180795
26	6	0	2.293885	5.109121	-0.530164
27	1	0	4.404316	5.162975	-0.957759
28	1	0	0.223161	4.739530	-0.062015
29	1	0	2.164064	6.182525	-0.625344
30	8	0	4.102363	0.545198	0.036789
31	6	0	1.225879	-2.490729	-0.170155
32	1	0	1.622221	-3.498881	-0.092617
33	6	0	-0.196742	-2.470339	-0.259267
34	16	0	-1.203532	-1.034397	-0.289462
35	6	0	-2.213407	-3.367864	-0.344385
36	6	0	-2.623443	-2.045576	-0.353764
37	1	0	-2.910753	-4.199574	-0.377764
38	6	0	-3.981031	-1.628192	-0.411877
39	6	0	-4.503462	-0.369037	-0.429342
40	6	0	-3.707233	0.812760	-0.377916
41	7	0	-3.083349	1.790518	-0.333073
42	15	0	-6.281645	-0.170222	-0.481769
43	8	0	-7.004659	-1.461566	-0.458622
44	8	0	-6.470676	0.768338	-1.764408
45	1	0	-7.386686	1.073504	-1.889246
46	8	0	-6.655613	0.848827	0.696340
47	1	0	-4.704805	-2.442034	-0.448073
48	7	0	-0.893457	-3.606797	-0.291987
49	6	0	-6.687659	0.337102	2.048979
50	6	0	-6.947792	1.504606	2.972971
51	1	0	-5.723908	-0.136882	2.269202
52	1	0	-7.474010	-0.419455	2.116282
53	1	0	-6.978515	1.155982	4.008316
54	1	0	-6.154704	2.250338	2.877842
55	1	0	-7.905217	1.974491	2.734274

Pyt-PO(OEt)OH

Optimized first excited state geometry in DMF (CPCM-TD-6-31G*/M06-2x)

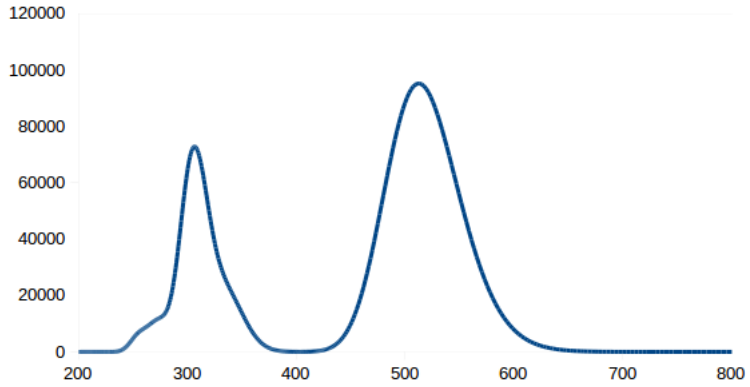
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.786587	0.890434	-0.359773
2	6	0	1.841766	-0.061833	-0.616938
3	6	0	2.142155	-1.443161	-0.465850
4	6	0	3.486055	-1.761393	-0.119208
5	6	0	4.406207	-0.777982	0.104176
6	1	0	0.883322	0.266353	-0.995569
7	1	0	3.777749	-2.798076	-0.000060
8	6	0	5.806467	-0.955795	0.482707
9	6	0	6.537983	0.126860	0.995800
10	6	0	6.437045	-2.202773	0.340875
11	6	0	7.865996	-0.040388	1.368356
12	1	0	6.058480	1.092047	1.115027
13	6	0	7.763882	-2.361145	0.715381
14	1	0	5.900346	-3.045179	-0.083159
15	6	0	8.483294	-1.282581	1.231610
16	1	0	8.419654	0.802407	1.769636
17	1	0	8.241304	-3.328166	0.595778
18	1	0	9.521208	-1.410296	1.521958
19	6	0	2.608598	2.335884	-0.472873
20	6	0	3.729056	3.179574	-0.532061
21	6	0	1.322304	2.898840	-0.523738
22	6	0	3.563505	4.553356	-0.655880
23	1	0	4.725396	2.752846	-0.496712
24	6	0	1.166405	4.272069	-0.649939
25	1	0	0.440572	2.270289	-0.441531
26	6	0	2.284570	5.104346	-0.717982
27	1	0	4.436768	5.195565	-0.706397
28	1	0	0.168006	4.695755	-0.685294
29	1	0	2.157839	6.177951	-0.814075
30	8	0	4.042254	0.530126	0.013065
31	6	0	1.210300	-2.505889	-0.657573
32	1	0	1.624007	-3.507060	-0.751863
33	6	0	-0.173702	-2.462925	-0.708497
34	16	0	-1.176209	-1.026651	-0.387933
35	6	0	-2.199094	-3.327935	-0.928540
36	6	0	-2.605691	-1.989638	-0.641735
37	1	0	-2.921773	-4.117888	-1.111420
38	6	0	-3.934489	-1.555453	-0.585900
39	6	0	-4.428799	-0.280811	-0.333629
40	6	0	-3.616265	0.849920	-0.074821
41	7	0	-2.981542	1.801880	0.145044
42	15	0	-6.190091	-0.032858	-0.313108
43	8	0	-6.957571	-1.285530	-0.512796
44	8	0	-6.399641	1.136023	-1.393812
45	1	0	-7.293048	1.522224	-1.366839
46	8	0	-6.546372	0.769368	1.033346
47	1	0	-4.685107	-2.322802	-0.767831
48	7	0	-0.914399	-3.580638	-0.962002
49	6	0	-6.581572	0.026217	2.271062
50	6	0	-6.872508	1.004559	3.386401
51	1	0	-5.611444	-0.463465	2.415329
52	1	0	-7.354173	-0.743937	2.194603
53	1	0	-6.909169	0.475323	4.342061
54	1	0	-6.092006	1.767697	3.439325
55	1	0	-7.835341	1.494944	3.222256

Pyt-PO(OEt)OH

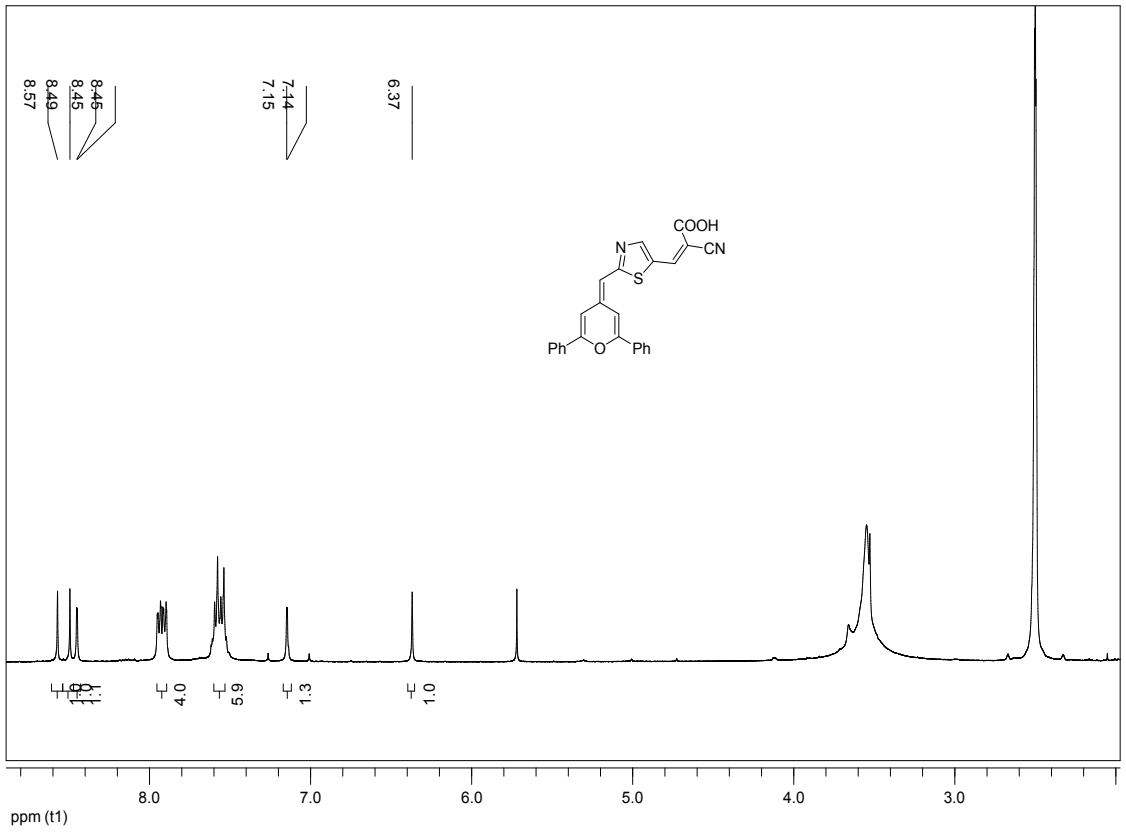
Calculated Absorption Spectrum in DMF
(CPCM-TD-M06-2x/6-311+G(2d,p)//CPCM-M06-2x/6-31G*):

No.	Energy (cm-1)	Wavelength (nm)	*f*	Major contribs
1	19519.55856	512.306667657	1.3148	HOMO->LUMO (97%)
2	29541.06656	338.511813028	0.2377	HOMO->L+1 (80%) H-1->LUMO (5%), HOMO->L+2 (7%)
3	32034.95008	312.159062993	0.3998	H-1->LUMO (12%), HOMO->L+1 (11%),HOMO->L+2 (64%) H-2->LUMO (6%)
4	33024.5992	302.804583318	0.664	H-1->LUMO (68%), HOMO->L+2 (14%), H-2->LUMO (3%), H-1->L+1 (4%), H-1->L+2 (4%)
5	36491.19408	274.038716795	0.1375	H-2->LUMO (78%), H-5->LUMO (6%),HOMO->L+2 (9%)
6	39071.37952	255.941820403	0.0822	H-7->LUMO (15%), H-4->LUMO (34%), H-4->L+1 (19%) H-3->LUMO (4%),H-1->L+1 (4%), H-1->L+4 (3%), HOMO->L+4 (3%), HOMO->L+5 (2%)

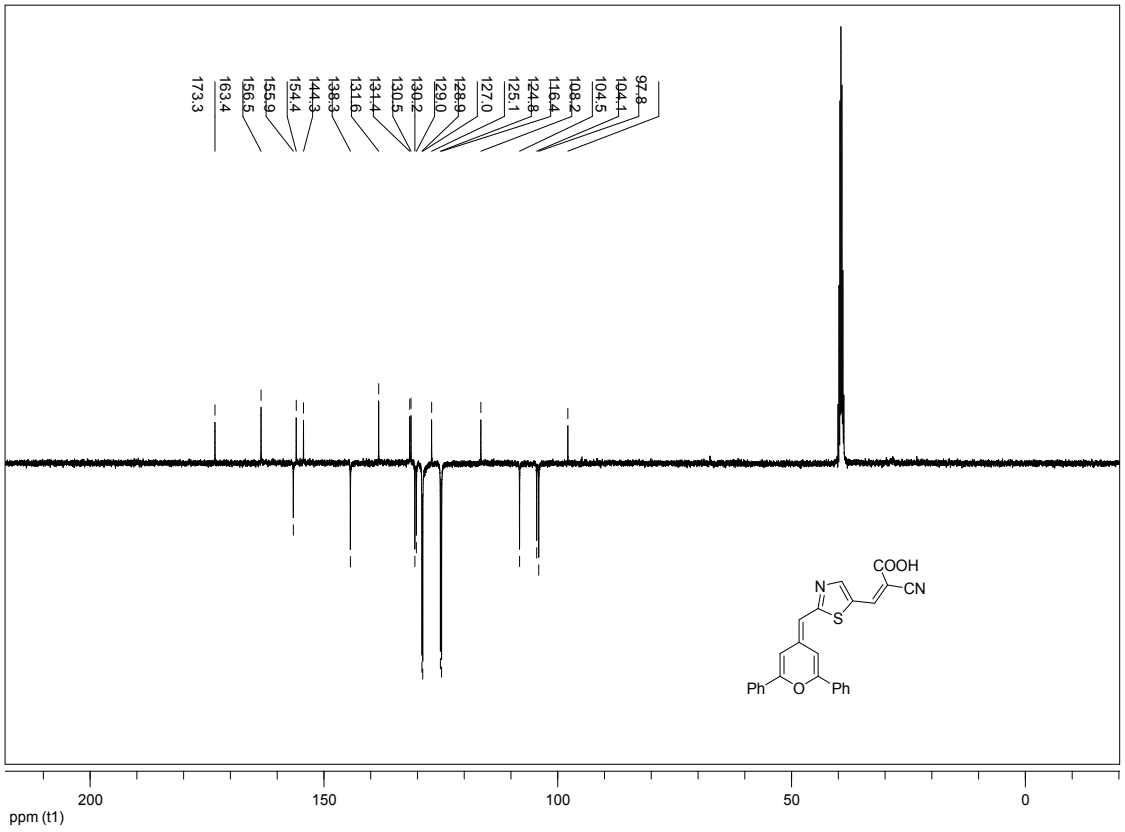


NMR spectra

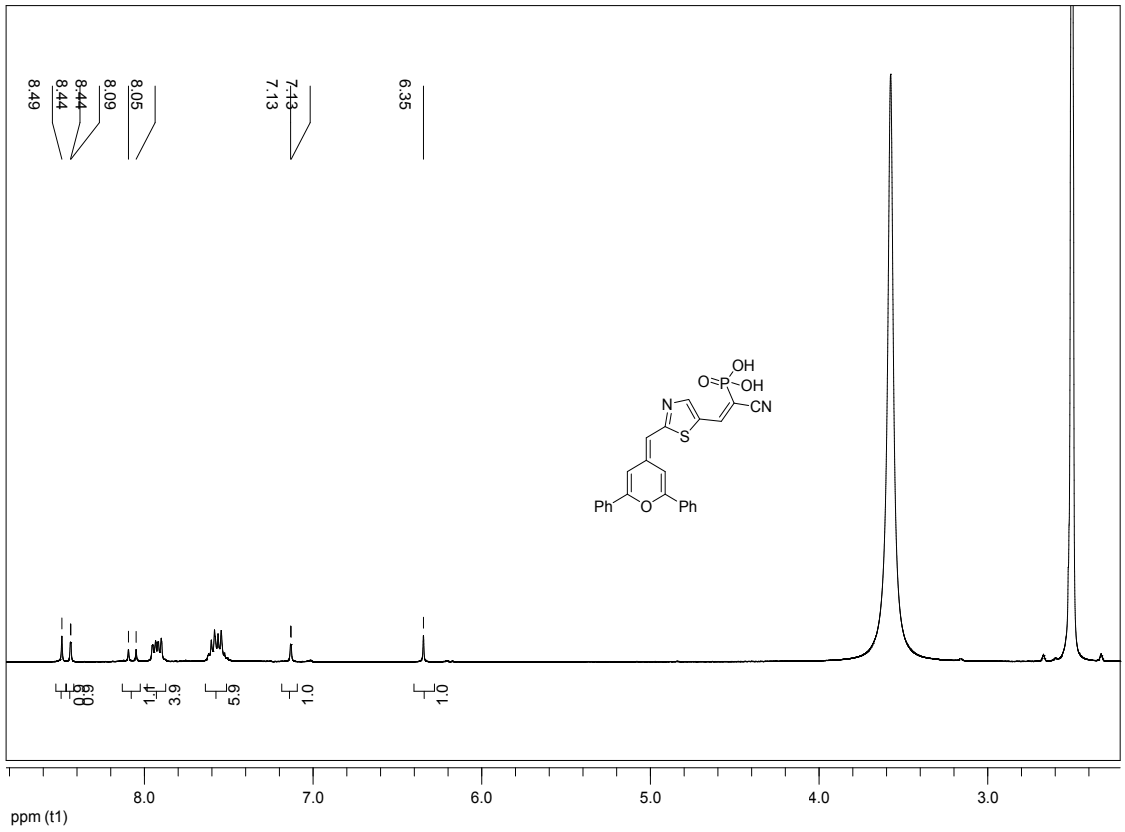
^{1}H NMR spectrum of compound pyt-COOH (400 MHz, dmso-d^{6}).



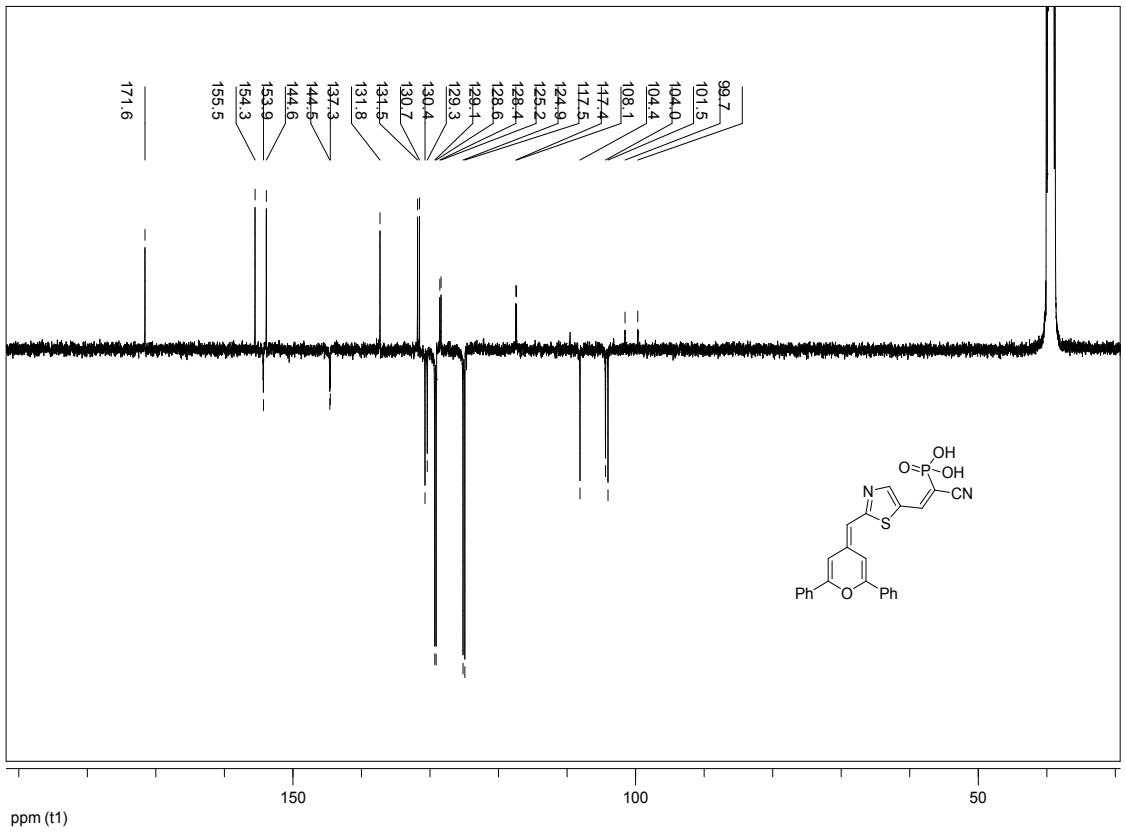
^{13}C NMR (APT) spectrum of compound pyt-COOH (100 MHz, dmso-d^{6})



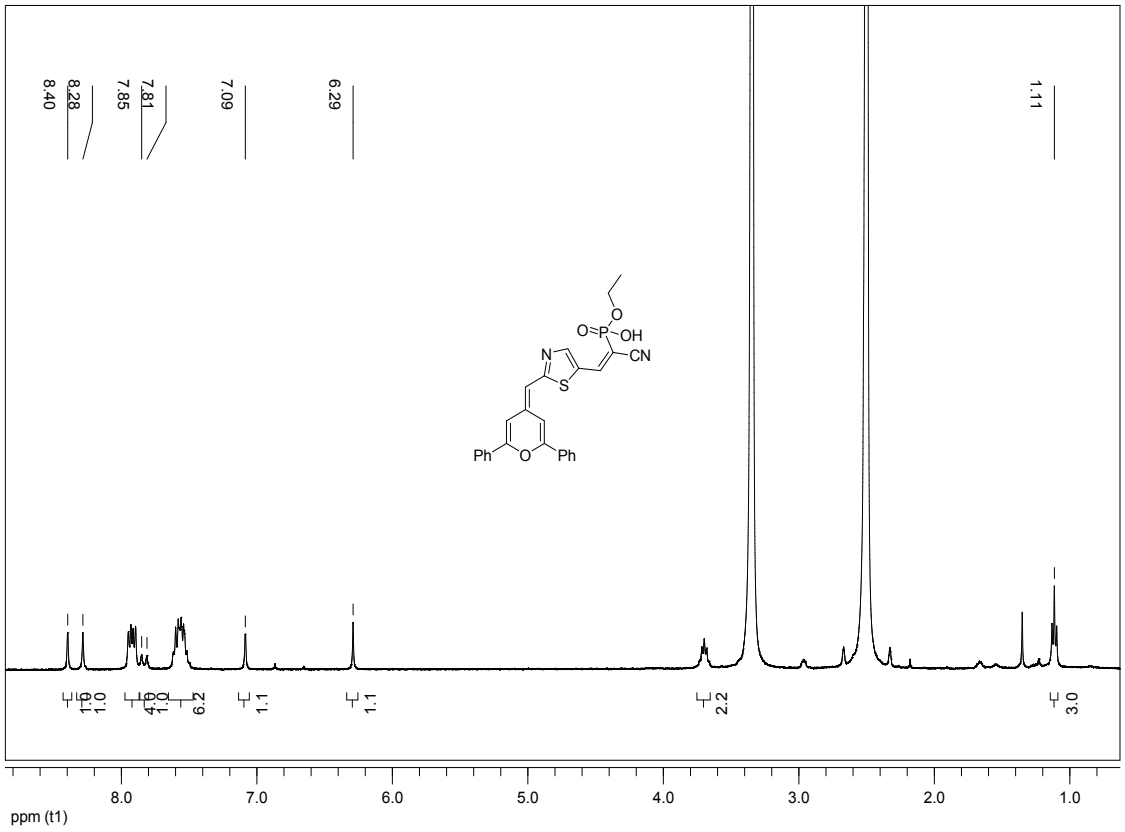
^{1}H NMR spectrum of compound pyt-PO(OH)$_2$ (400 MHz, dmso-d^{6})



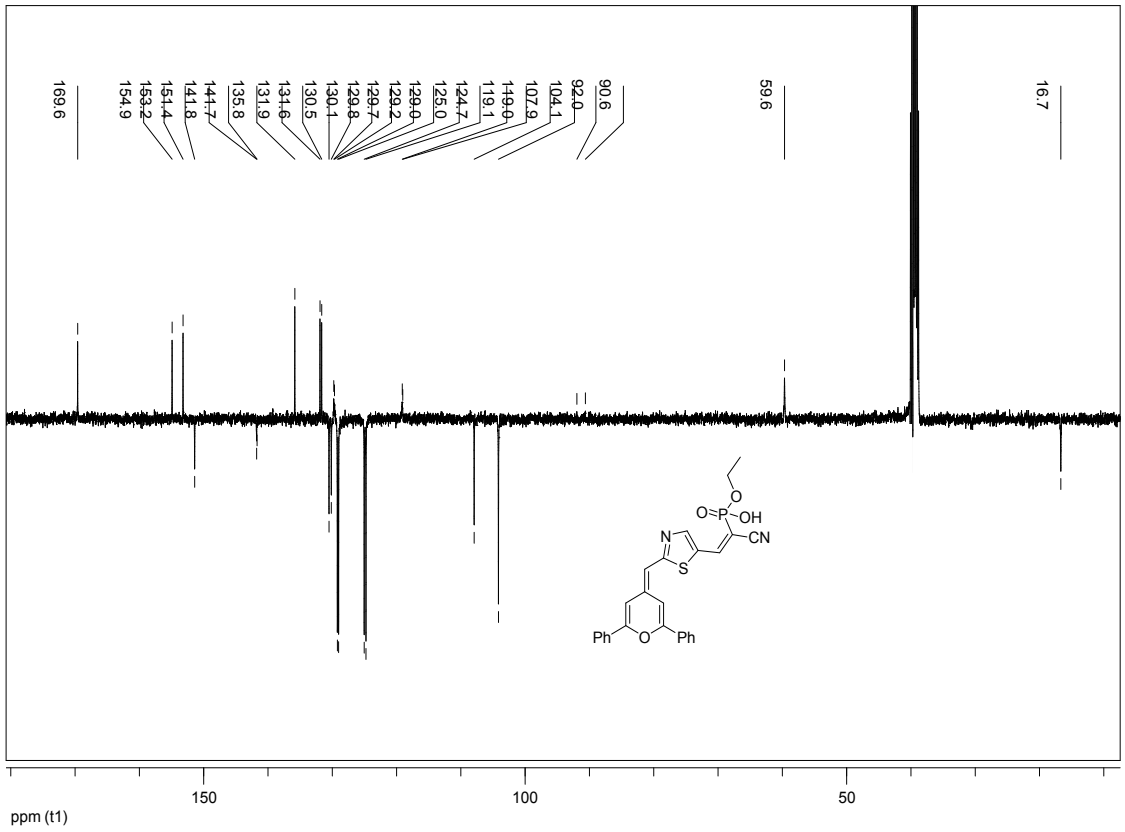
^{13}C NMR (APT) spectrum of compound pyt-PO(OH)$_2$ (100 MHz, dmso-d^6)



^{1}H NMR spectrum of compound pyt-PO(OEt)OH (400 MHz, dmso-d^{6})

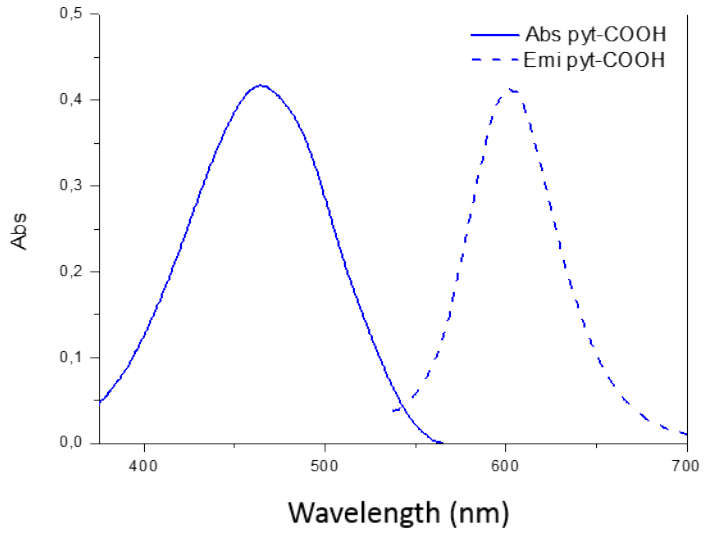


^{13}C NMR (APT) spectrum of compound pyt-PO(OEt)OH (100 MHz, dmso-d^{6})

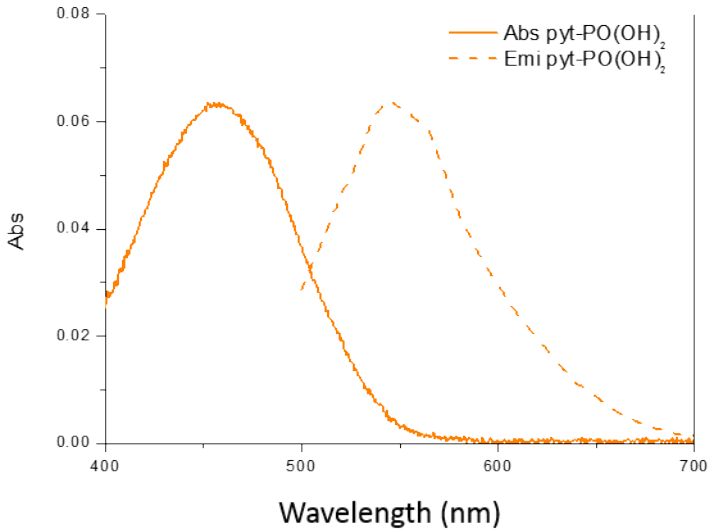


Absorption and emission spectra in $^{t}BuOH:CH_3CN$ (1:1)

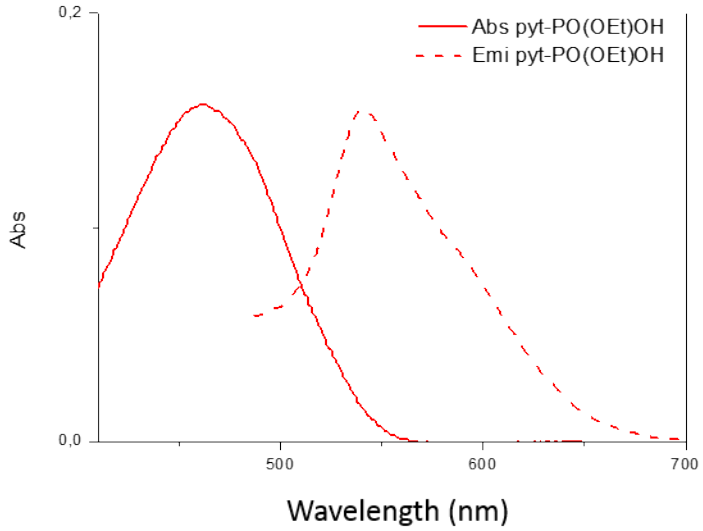
Absorption-Emission spectra 10^{-5}M in $^{t}BuOH:CH_3CN$ (1:1) pyt-COOH



Absorption-Emission spectra 10^{-5}M in $^{t}BuOH:CH_3CN$ (1:1) pyt-$PO(OH)_2$

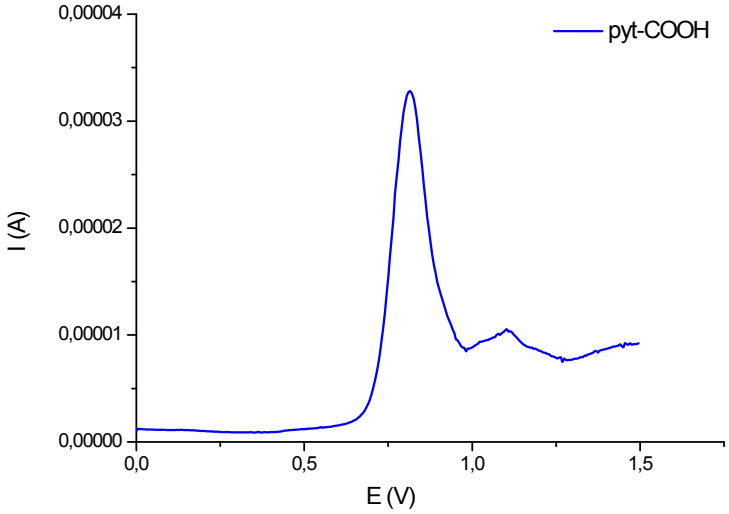


Absorption-Emission spectra 10^{-5}M in ^{t}BuOH:CH_3CN (1:1) pyt-PO(OEt)OH

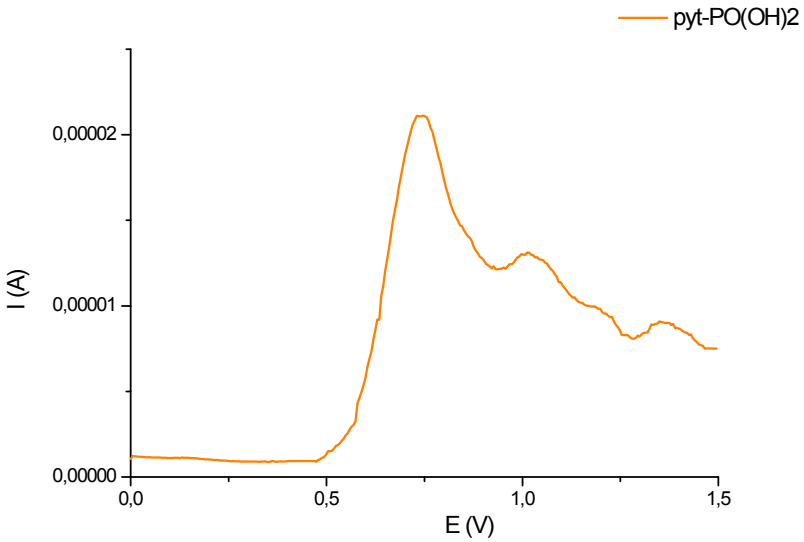


Electrochemical characterization

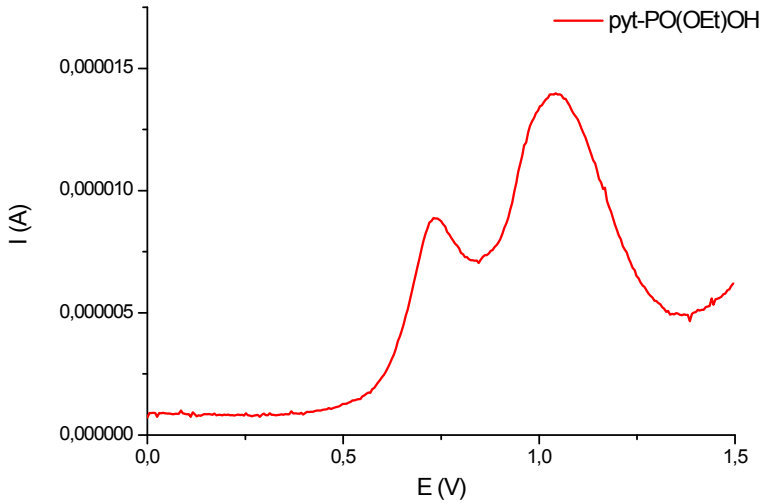
Differential pulse voltammetry (DPV) pyt-COOH in DMF



Differential pulse voltammetry (DPV) pyt-$PO(OH)_2$ in DMF



Differential pulse voltammetry (DPV) pyt-PO(OEt)OH in DMF



Relative dye concentration on the TiO_2 surface

To estimate the dye surface concentration on TiO_2 surface, we prepared three identical mesoporous TiO_2 films (thickness of the TiO_2 films 3 μm, area 0.36 cm^2) and about 0.1 mM dyeing solutions in 1:1 mixture of acetonitrile and *tert*-butyl alcohol of pyt-COOH and pyt-PO(OEt)OH. Then we measured the absorption of the dyeing solutions before and after soaking for 3 hours the TiO_2 films and made used of dye calibration curves (see next paragraph) to calculated the number of dye molecules left in solution and thus to estimate the relative dye concentration on TiO_2. All the details of the calculation are reported in the table below. As discussed in the main text pyt-$PO(OH)_2$ is not stable in the dyeing solution, therefore we could not extract the relative dye concentration for this dye.

	pyt-COOH		**pyt-PO(OEt)OH**	
	before soaking	after soaking	before soaking	after soaking
Absorption maximum	1.74	1.59	1.75	1.62
Molarity (M)	1.02E-4	9.37E-5	9.87E-5	9.34E-5
Moles in solution	3.56E-7	3.28E-7	3.45E-7	3.27E-7
Moles adsorbed on TiO_2 film	2.8E-8		1,9E-8	
Relative dye concentration on TiO_2	1		0.7	

Dye solution calibration curves

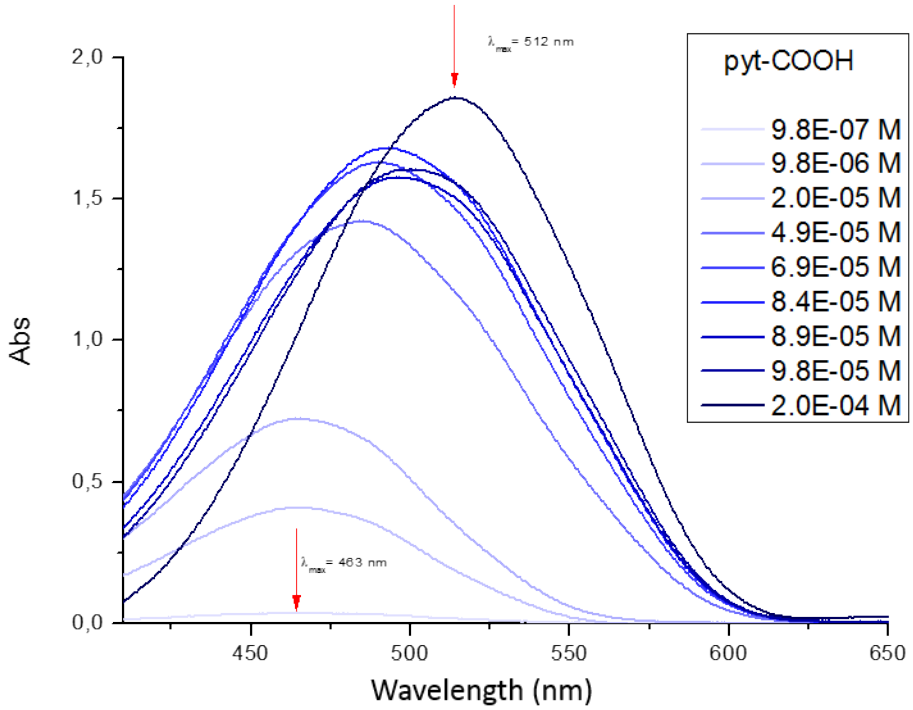


Figure 1

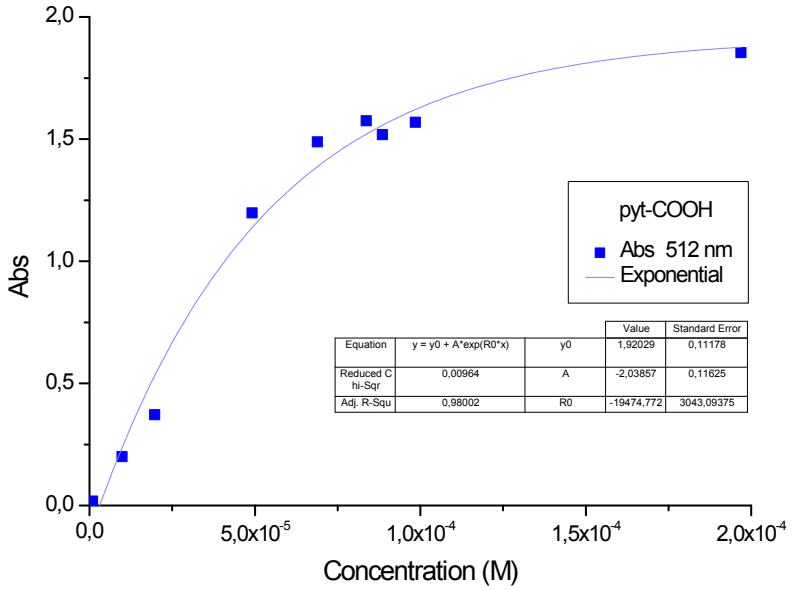


Figure 2

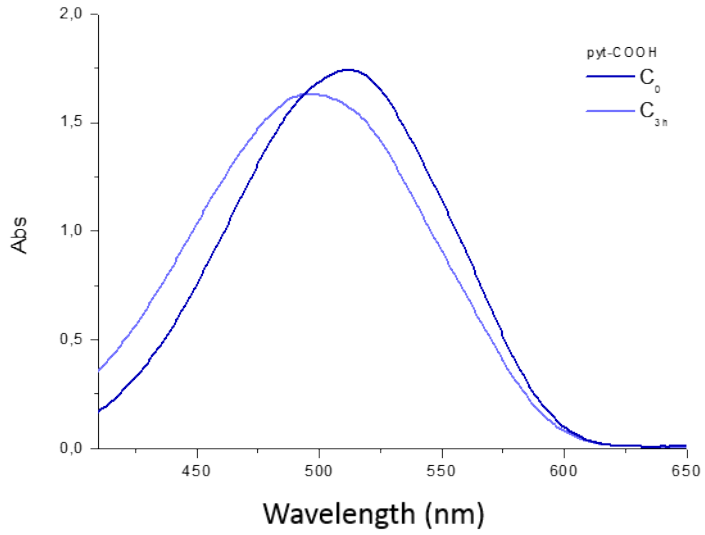


Figure 3

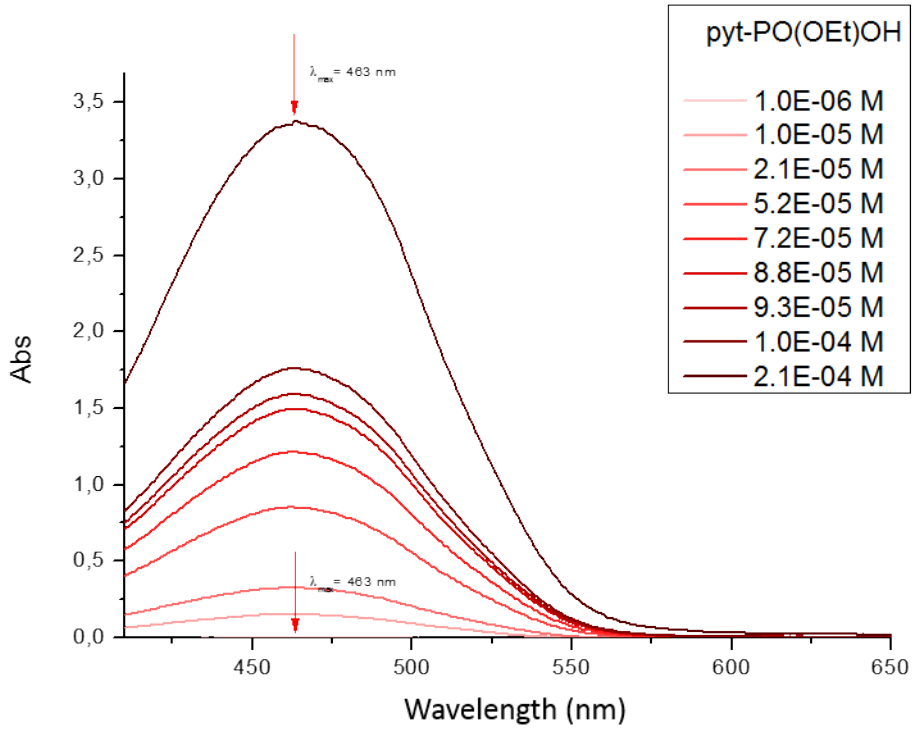


Figure 4

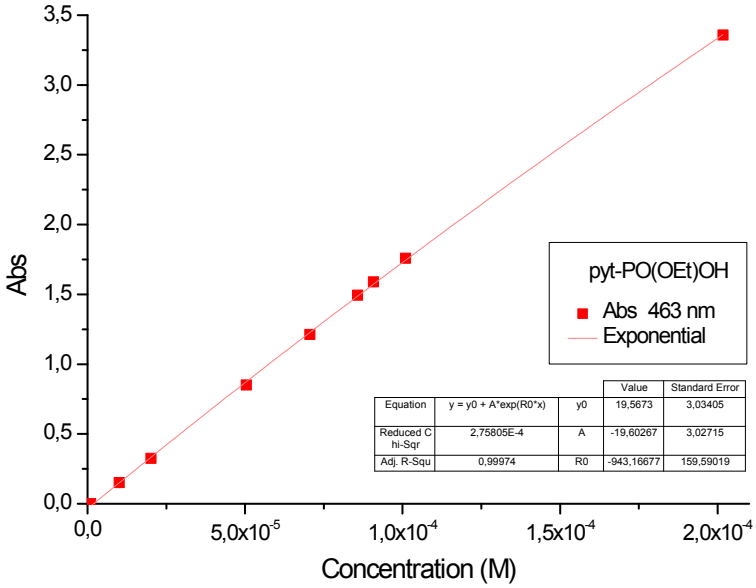


Figure 5

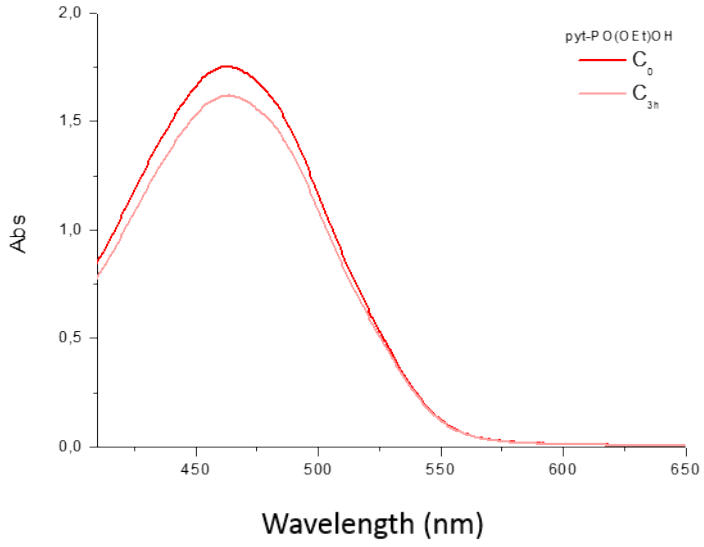


Figure 6

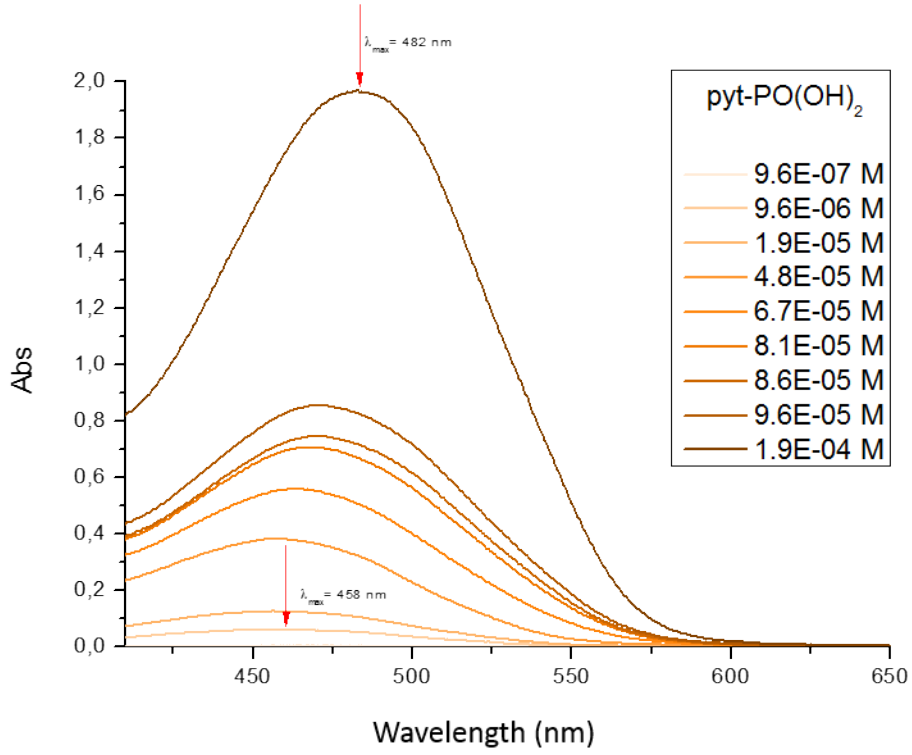
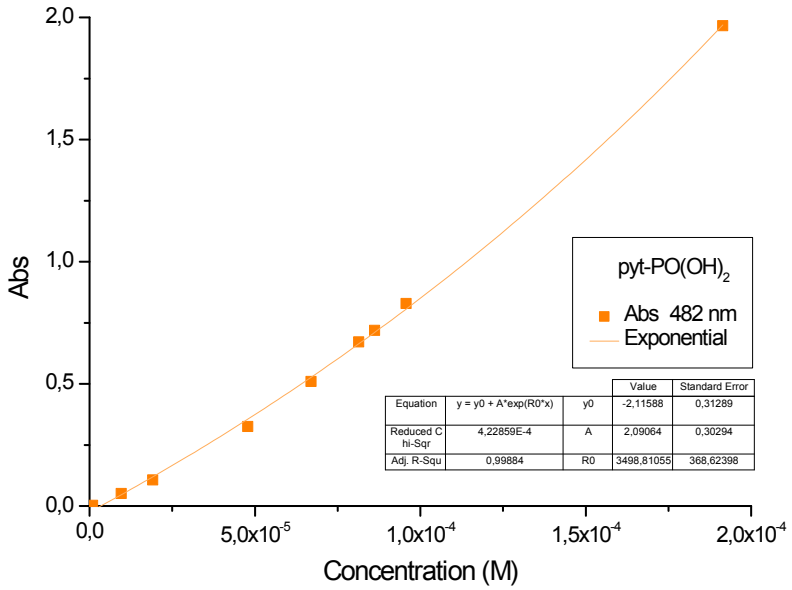


Figure 7



			Value	Standard Error
Equation	y = y0 + A*exp(R0*x)	y0	-2,11588	0,31289
Reduced Chi-Sqr	4,22859E-4	A	2,09064	0,30294
Adj. R-Squ	0,99884	R0	3498,81055	368,62398

Figure 8

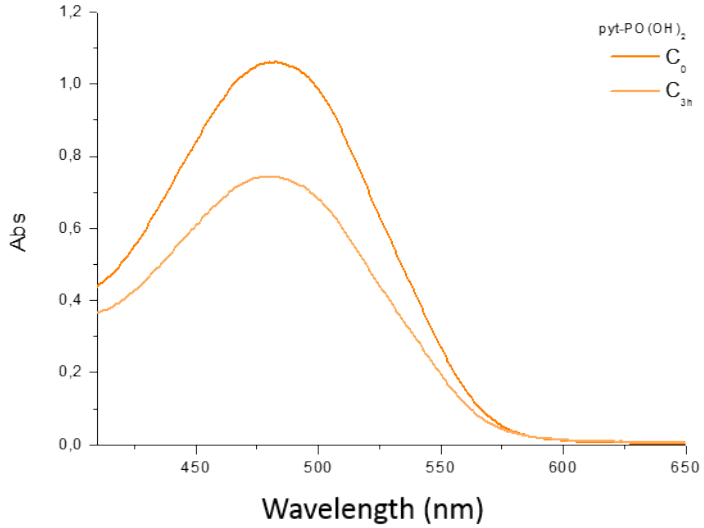
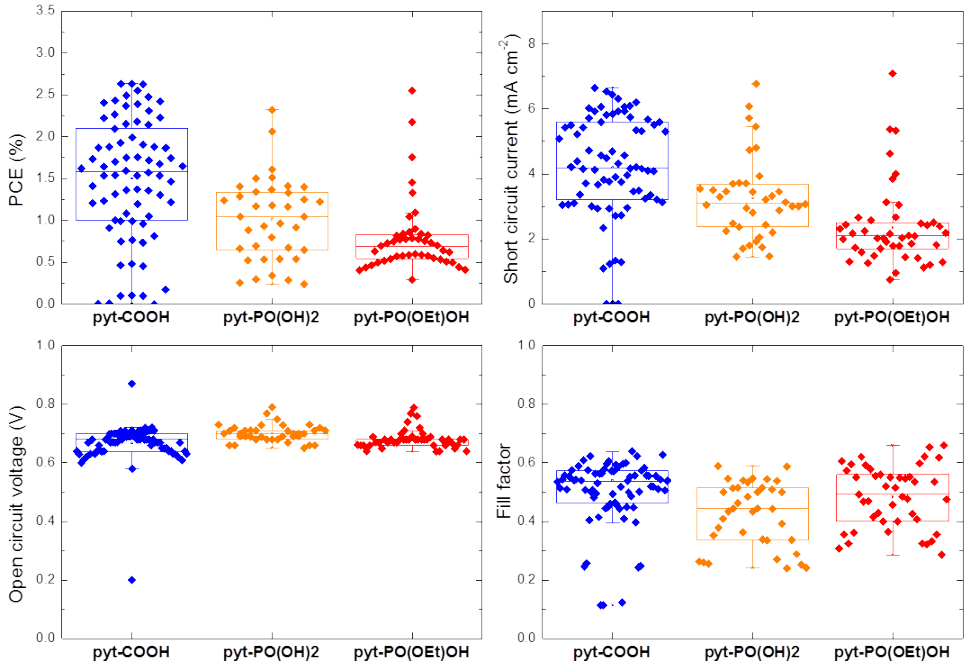

pyt-PO(OH)2
C0
C3h
Abs
1,2
1,0
0,8
0,6
0,4
0,2
0,0
450
500
550
600
650
Wavelength (nm)

Figure 9

Device performance parameters collected over 6 months of experiments



Box plot of the device performance parameters extracted from the current voltage curves collected under AM 1.5 simulated sunlight of 100 mW cm^{-2} equivalent solar irradiance, for over 40 devices prepared for each dye over a period of 6 months in several different experiments. We did plot the device performance parameters of all the devices in a single graph, which showed a relative narrow and a significant more spread data distribution for pyt-COOH and pyt-PO(OEt)OH respectively. The origin of such large data distribution is due to the fact that the device preparation procedure was constantly changed to optimize the performances. The best performance was achieved after tuning the concentration dying solution, the soaking time in the dying solution, the mesoporous TiO_2 thickness, the Spiro-OMeTAD concentration and additive composition. We kept track of all these change and we reported the optimized procedure in the Experimental section.