

Supporting Information

Photoelectrochemical Properties of Porphyrin Dyes with a Molecular Dipole in the Linker

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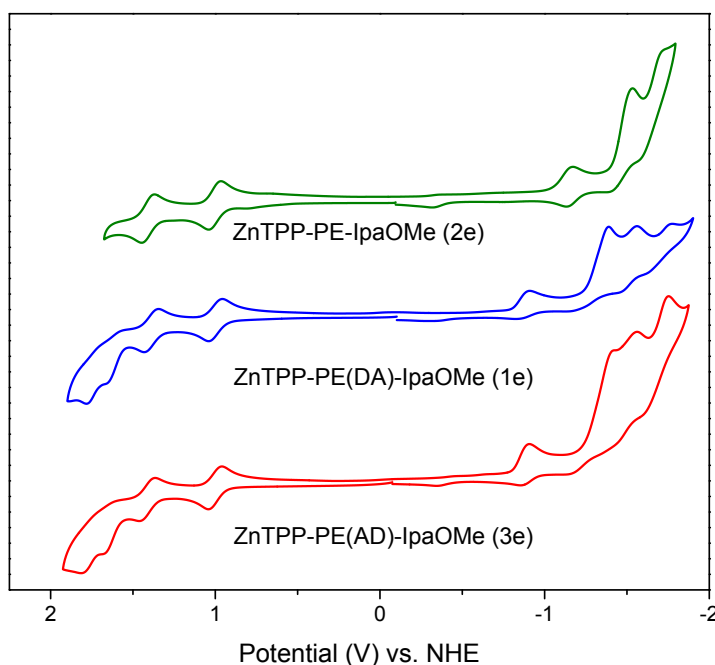


Figure S1. Cyclic voltammograms of porphyrins **1e**, **2e** and **3e** recorded in 0.1 M Bu₄NPF₆ 1,2-dichloroethane electrolyte (sample concentration = 1 mM; scan rate = 100 mV s⁻¹; glassy carbon working electrode; Ag-wire reference electrode; Pt wire counter electrode).

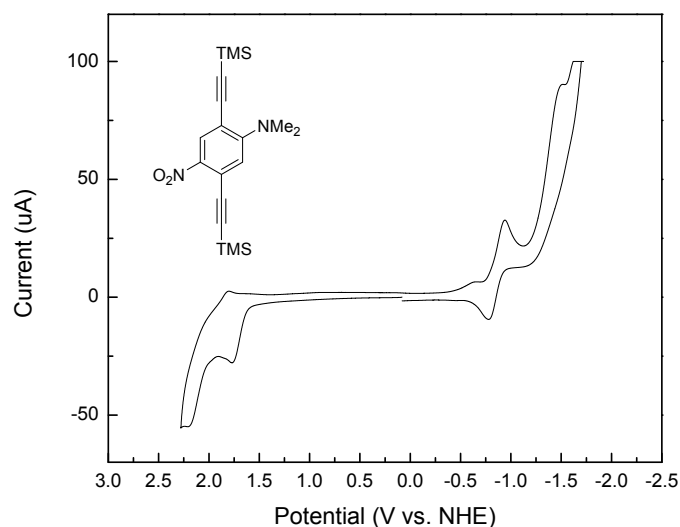


Figure S2. Cyclic voltammogram of the bridge intermediate (inset) recorded in 0.1 M Bu₄NPF₆ 1,2-dichloroethane electrolyte (sample concentration = 1 mM; scan rate = 100 mV s⁻¹; glassy carbon working electrode; Ag-wire reference electrode; Pt wire counter electrode).

Table 1. Cartesian coordinates of geometry optimized structure for **1a**.

#	atom	X	Y	Z
1	C	7.15915	-20.5499	-3.67814
2	C	5.925424	-19.7987	-3.74082
3	C	5.769979	-19.3936	-5.0309
4	H	5.274987	-19.5937	-2.90396
5	C	6.906534	-19.8942	-5.77202
6	N	7.741565	-20.5862	-4.9252
7	C	8.27371	-20.072	-7.85747
8	C	8.45485	-19.9081	-9.28292
9	N	9.37435	-20.7001	-7.32093
10	C	9.671352	-20.4339	-9.59327
11	C	10.24684	-20.9264	-8.36174
12	H	10.13135	-20.4971	-10.5679
13	Zn	9.56648	-21.3982	-5.39782
14	C	12.03213	-22.1213	-7.08685
15	C	13.35876	-22.685	-6.97559
16	C	13.51119	-23.0956	-5.68678
17	H	14.08305	-22.7417	-7.77408
18	C	12.27966	-22.7866	-4.99502
19	N	11.39741	-22.1899	-5.86742
20	C	10.89548	-22.6441	-2.91966

21	C	10.63107	-22.975	-1.53715
22	N	9.840844	-21.9227	-3.43179
23	C	9.416845	-22.4445	-1.22516
24	C	8.925441	-21.7836	-2.41347
25	H	8.89402	-22.5071	-0.28272
26	C	13.11807	-23.759	-2.8658
27	C	15.12604	-25.1232	-1.43816
28	C	13.43056	-25.0952	-3.16506
29	C	13.82976	-23.1187	-1.83807
30	C	14.82566	-23.7943	-1.13128
31	C	14.42485	-25.7719	-2.45695
32	H	12.88398	-25.6051	-3.95265
33	H	15.36891	-23.2805	-0.34359
34	H	13.60427	-22.0835	-1.60003
35	H	14.64838	-26.8066	-2.6996
36	C	13.62956	-20.5629	-11.2617
37	C	12.60945	-22.8866	-10.1057
38	C	12.8532	-20.485	-10.1044
39	C	13.89648	-21.803	-11.8458
40	C	13.38339	-22.9646	-11.2645
41	C	12.33233	-21.6456	-9.50932
42	C	5.289183	-20.8779	1.077648
43	C	6.851973	-21.0379	-1.25971
44	C	4.856424	-21.6465	-0.00516
45	C	6.501376	-20.1893	0.994478
46	C	7.276444	-20.2696	-0.16362
47	C	5.630632	-21.7245	-1.16382
48	C	7.125921	-19.6686	-7.14594
49	C	11.50043	-21.5617	-8.26583
50	C	12.0509	-23.0328	-3.62648
51	C	7.682432	-21.1259	-2.50408
52	H	11.28151	-23.5508	-0.8963
53	H	14.38301	-23.5489	-5.23975
54	H	4.969152	-18.7957	-5.43938
55	H	7.739616	-19.465	-9.95935
56	H	12.20829	-23.7919	-9.6601
57	H	12.65327	-19.5191	-9.65038
58	H	14.02822	-19.6546	-11.7039
59	H	14.4997	-21.8637	-12.7467
60	H	13.58227	-23.933	-11.7143
61	H	8.215601	-19.728	-0.22544
62	H	6.843845	-19.5857	1.829895
63	H	4.686743	-20.8161	1.979009
64	H	3.917396	-22.1892	0.05178
65	H	5.292933	-22.3279	-2.00106

66	C	6.058376	-18.946	-7.90581
67	C	6.299797	-17.6781	-8.46193
68	C	4.785575	-19.5163	-8.08076
69	C	5.309674	-17.0004	-9.16438
70	H	7.273054	-17.2157	-8.3311
71	C	3.789507	-18.8505	-8.78639
72	H	4.580679	-20.4979	-7.66524
73	C	4.035333	-17.5774	-9.34017
74	H	5.512152	-16.0184	-9.57891
75	H	2.81583	-19.3109	-8.91706
76	H	15.90041	-25.6491	-0.88768
77	C	3.020868	-16.885	-10.0603
78	C	2.147222	-16.2986	-10.674
79	C	1.169196	-15.5208	-11.3532
80	C	-0.17082	-15.9799	-11.6235
81	C	1.506065	-14.2019	-11.6669
82	C	-1.08896	-15.0317	-12.1284
83	C	0.585547	-13.299	-12.1931
84	H	2.508538	-13.8514	-11.4624
85	C	-0.7571	-13.7027	-12.4176
86	H	-2.10151	-15.3404	-12.3467
87	C	-1.78825	-12.8815	-12.95
88	C	-2.76689	-12.3091	-13.3906
89	C	-3.8794	-11.5902	-13.9139
90	C	-5.12263	-12.2225	-14.0929
91	C	-3.75179	-10.2334	-14.2631
92	C	-6.21138	-11.5152	-14.6086
93	H	-5.24705	-13.267	-13.8321
94	C	-4.84173	-9.52781	-14.7776
95	H	-2.80395	-9.72414	-14.1346
96	C	-6.07535	-10.1656	-14.9526
97	H	-6.9188	-9.61846	-15.3518
98	C	-7.50188	-12.2443	-14.776
99	O	-7.66685	-13.4177	-14.4971
100	O	-8.48367	-11.466	-15.2715
101	H	-9.28085	-12.0183	-15.3464
102	C	-4.64055	-8.09163	-15.1265
103	O	-3.58795	-7.49528	-14.9931
104	O	-5.75488	-7.5093	-15.611
105	H	-5.53442	-6.58295	-15.8095
106	N	1.04636	-11.9579	-12.4664
107	O	0.231854	-11.1131	-12.8579
108	O	2.249319	-11.7043	-12.2993
109	N	-0.57918	-17.2631	-11.367
110	C	-2.00205	-17.5865	-11.3221

111	H	-2.44004	-17.7028	-12.3236
112	H	-2.11885	-18.5325	-10.789
113	H	-2.55472	-16.8197	-10.7765
114	C	0.27411	-18.4323	-11.5927
115	H	1.275806	-18.137	-11.8901
116	H	0.340956	-19.0474	-10.6894
117	H	-0.15879	-19.0416	-12.3957

Table 2. Cartesian coordinates of geometry optimized structure for **2a**.

#	atom	X	Y	Z
1	C	7.213091	-20.5944	-3.56829
2	C	5.99871	-19.8101	-3.56322
3	C	5.830973	-19.3257	-4.82411
4	H	5.368025	-19.6394	-2.7039
5	C	6.941079	-19.8091	-5.61494
6	N	7.774096	-20.5683	-4.82561
7	C	8.26599	-19.899	-7.73349
8	C	8.418325	-19.6768	-9.15437
9	N	9.370349	-20.562	-7.24897
10	C	9.622528	-20.2002	-9.51319
11	C	10.21894	-20.7506	-8.31682
12	H	10.06038	-20.2269	-10.4996
13	Zn	9.59463	-21.3436	-5.36607
14	C	12.01532	-22.0231	-7.13552
15	C	13.33495	-22.611	-7.07813
16	C	13.50124	-23.0959	-5.81706
17	H	14.04499	-22.6346	-7.89095
18	C	12.28457	-22.8109	-5.08947
19	N	11.40035	-22.1484	-5.91066
20	C	10.91739	-22.8008	-2.99813
21	C	10.6607	-23.2239	-1.63957
22	N	9.866672	-22.0349	-3.44941
23	C	9.457687	-22.6988	-1.27871
24	C	8.965777	-21.9487	-2.41282
25	H	8.943479	-22.8185	-0.33709
26	C	13.13341	-23.9285	-3.03628
27	C	15.14301	-25.393	-1.71404
28	C	13.43313	-25.2455	-3.42096
29	C	13.85867	-23.3585	-1.97715
30	C	14.85543	-24.0836	-1.32249
31	C	14.42831	-25.9719	-2.765
32	H	12.87596	-25.7017	-4.23369
33	H	15.40905	-23.6236	-0.50922

34	H	13.64278	-22.3387	-1.67305
35	H	14.64187	-26.9911	-3.07333
36	C	13.5395	-20.2988	-11.2758
37	C	12.51695	-22.6577	-10.196
38	C	12.79297	-20.2617	-10.097
39	C	13.77506	-21.5156	-11.9196
40	C	13.26093	-22.6949	-11.3762
41	C	12.27108	-21.4405	-9.53983
42	C	5.416995	-21.1607	1.194476
43	C	6.931858	-21.2231	-1.17896
44	C	4.93627	-21.8386	0.072074
45	C	6.65329	-20.5139	1.133043
46	C	7.404539	-20.5461	-0.04282
47	C	5.686696	-21.8684	-1.10436
48	C	7.138216	-19.5149	-6.97975
49	C	11.46775	-21.4014	-8.27546
50	C	12.06511	-23.1473	-3.7388
51	C	7.738276	-21.257	-2.44145
52	H	11.30899	-23.8517	-1.04715
53	H	14.372	-23.5884	-5.41137
54	H	5.03846	-18.6853	-5.18089
55	H	7.693055	-19.1998	-9.79612
56	H	12.11437	-23.5766	-9.78035
57	H	12.61684	-19.314	-9.59709
58	H	13.93923	-19.3772	-11.6884
59	H	14.35474	-21.5445	-12.8374
60	H	13.43534	-23.6452	-11.8722
61	H	8.362659	-20.0371	-0.08751
62	H	7.033209	-19.9804	1.999403
63	H	4.832942	-21.1365	2.109622
64	H	3.978078	-22.3483	0.111797
65	H	5.311536	-22.4019	-1.97253
66	C	6.065899	-18.743	-7.68125
67	C	6.32006	-17.4662	-8.21158
68	C	4.773787	-19.2772	-7.82795
69	C	5.324385	-16.7467	-8.86299
70	H	7.308327	-17.0311	-8.10168
71	C	3.771254	-18.5676	-8.47902
72	H	4.558813	-20.2653	-7.43352
73	C	4.030263	-17.2868	-9.0084
74	H	5.537489	-15.7594	-9.25926
75	H	2.781996	-18.9995	-8.58856
76	H	15.91785	-25.9577	-1.20428
77	C	3.006071	-16.5559	-9.67524
78	C	2.127799	-15.9337	-10.2449

79	C	1.098446	-15.2113	-10.9099
80	C	-0.20035	-15.7527	-11.0235
81	C	1.354659	-13.9408	-11.4691
82	C	-1.20516	-15.0503	-11.6718
83	C	0.350011	-13.2382	-12.1179
84	H	2.348927	-13.5147	-11.388
85	C	-0.9479	-13.7804	-12.231
86	H	-2.19954	-15.476	-11.753
87	C	-1.97865	-13.0607	-12.8977
88	C	-2.86073	-12.4469	-13.4685
89	C	-3.89472	-11.7311	-14.1381
90	C	-5.19081	-12.2688	-14.2359
91	C	-3.63994	-10.4738	-14.715
92	C	-6.20413	-11.5677	-14.894
93	H	-5.41556	-13.2354	-13.8005
94	C	-4.65474	-9.77426	-15.3727
95	H	-2.65078	-10.0353	-14.6547
96	C	-5.94103	-10.3176	-15.4655
97	H	-6.72593	-9.77536	-15.9753
98	C	-7.55477	-12.1962	-14.9612
99	O	-7.83259	-13.2781	-14.4768
100	O	-8.45355	-11.4391	-15.6208
101	H	-9.29733	-11.9229	-15.616
102	C	-4.31579	-8.44704	-15.9622
103	O	-3.21362	-7.93306	-15.9061
104	O	-5.36444	-7.86141	-16.5734
105	H	-5.05482	-7.00898	-16.925
106	H	0.558301	-12.2627	-12.5441
107	H	-0.40862	-16.7283	-10.5976

Table 3. Cartesian coordinates of geometry optimized structure for **3a**.

#	atom	X	Y	Z
1	C	-2.35553	1.73331	-0.56326
2	C	-3.12855	1.438527	-1.74894
3	C	-2.65179	0.268911	-2.25591
4	H	-3.92133	2.05293	-2.14816
5	C	-1.58052	-0.16431	-1.38651
6	N	-1.4105	0.74968	-0.37187
7	C	0.287751	-1.71781	-0.7968
8	C	1.01095	-2.9613	-0.94716
9	N	0.828726	-0.99095	0.238191
10	C	1.99395	-2.96677	-0.0056
11	C	1.880814	-1.72843	0.732338

12	H	2.718361	-3.74429	0.184141
13	Zn	0.079198	0.749397	1.034914
14	C	2.550841	-0.2015	2.592612
15	C	3.458516	0.209871	3.639961
16	C	2.971882	1.371555	4.156241
17	H	4.356715	-0.3136	3.930874
18	C	1.761568	1.684208	3.429846
19	N	1.532584	0.717739	2.476227
20	C	-0.1656	3.18373	2.90188
21	C	-1.02892	4.305441	3.197181
22	N	-0.63063	2.523978	1.787183
23	C	-2.00415	4.318899	2.247386
24	C	-1.74792	3.205026	1.361705
25	H	-2.82999	5.008823	2.16201
26	C	1.346959	3.715267	4.80337
27	C	2.065575	5.392801	6.948636
28	C	1.271987	3.258019	6.129233
29	C	1.788138	5.028371	4.571928
30	C	2.145472	5.859469	5.634744
31	C	1.626914	4.089512	7.192498
32	H	0.925765	2.247477	6.32425
33	H	2.489472	6.870041	5.434929
34	H	1.857778	5.393716	3.551757
35	H	1.556993	3.719329	8.211126
36	C	5.982222	-3.29805	1.556895
37	C	3.884344	-2.96721	3.363735
38	C	4.91817	-2.45056	1.244635
39	C	5.999881	-3.98411	2.773179
40	C	4.947007	-3.8167	3.675384
41	C	3.854098	-2.27199	2.143821
42	C	-5.81929	5.502475	-0.7297
43	C	-3.68234	3.782622	-0.09092
44	C	-6.07209	4.199521	-0.29512
45	C	-4.50063	5.947729	-0.84525
46	C	-3.44188	5.095705	-0.5273
47	C	-5.01296	3.347098	0.020358
48	C	-0.81911	-1.33466	-1.58085
49	C	2.712832	-1.36104	1.807977
50	C	0.964313	2.822602	3.662577
51	C	-2.54549	2.867968	0.249559
52	H	-0.91168	4.982212	4.02996
53	H	3.399789	1.970475	4.945902
54	H	-2.9839	-0.24396	-3.14599
55	H	0.786286	-3.73493	-1.66581
56	H	3.065025	-2.84467	4.065677

57	H	4.912191	-1.91462	0.300254
58	H	6.798624	-3.41882	0.850891
59	H	6.827333	-4.64412	3.015883
60	H	4.949627	-4.3499	4.621531
61	H	-2.41816	5.4445	-0.62447
62	H	-4.29407	6.957932	-1.18635
63	H	-6.6432	6.165537	-0.97607
64	H	-7.09432	3.845868	-0.19767
65	H	-5.21476	2.336848	0.363579
66	C	-1.22098	-2.24083	-2.70136
67	C	-0.36409	-2.46693	-3.79257
68	C	-2.46868	-2.88916	-2.68824
69	C	-0.73711	-3.30601	-4.83665
70	H	0.599883	-1.96934	-3.82432
71	C	-2.85021	-3.73291	-3.72447
72	H	-3.13984	-2.73399	-1.84965
73	C	-1.98879	-3.95398	-4.81903
74	H	-0.06715	-3.46303	-5.67548
75	H	-3.81319	-4.23169	-3.69682
76	H	2.342585	6.039565	7.775764
77	C	-2.38337	-4.81374	-5.88163
78	C	-2.78384	-5.5596	-6.7569
79	C	-3.09653	-6.38931	-7.86608
80	C	-4.27036	-7.18025	-7.99836
81	C	-2.14914	-6.46567	-8.8947
82	C	-4.46237	-7.95885	-9.13679
83	C	-2.30002	-7.26949	-10.0465
84	H	-1.23857	-5.89881	-8.76175
85	C	-3.52968	-8.01225	-10.1747
86	H	-5.38711	-8.5118	-9.23008
87	C	-3.91088	-8.70604	-11.3564
88	C	-4.32127	-9.28467	-12.3455
89	C	-4.79257	-9.95474	-13.5107
90	C	-6.01646	-10.6481	-13.491
91	C	-4.0472	-9.9344	-14.7035
92	C	-6.4818	-11.3022	-14.6343
93	H	-6.61153	-10.6809	-12.5859
94	C	-4.51497	-10.5889	-15.8455
95	H	-3.10081	-9.40854	-14.7492
96	C	-5.73412	-11.2753	-15.8169
97	H	-6.09561	-11.7815	-16.7018
98	C	-7.78726	-12.0176	-14.5434
99	O	-8.47068	-12.0723	-13.5375
100	O	-8.1438	-12.6072	-15.7016
101	H	-8.9987	-13.046	-15.5511

102	C	-3.67418	-10.5268	-17.0757
103	O	-2.6076	-9.9443	-17.1484
104	O	-4.21717	-11.1886	-18.1164
105	H	-3.60701	-11.0953	-18.8681
106	N	-5.31178	-7.1949	-6.99858
107	O	-6.25968	-7.98201	-7.14855
108	O	-5.22597	-6.42713	-6.03239
109	N	-1.32213	-7.28677	-11.0061
110	C	-0.27893	-6.26548	-11.0123
111	H	0.519536	-6.47325	-10.2861
112	H	0.166934	-6.24036	-12.0091
113	H	-0.70281	-5.28112	-10.8064
114	C	-0.96479	-8.49029	-11.761
115	H	-1.03912	-8.31591	-12.8394
116	H	0.070715	-8.76427	-11.5252
117	H	-1.60586	-9.32577	-11.4951

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