Supporting Information

Cyclo[8]pyrrole: An Androgynous Expanded Porphyrin that Acts as Both an Electron Donor and Acceptor in Anion-Bound Supramolecular Electron Donor-Acceptor Complexes

Kei Ohkubo,[†] Kentaro Mase,[†] Elizabeth Karnas,[‡] Jonathan L. Sessler,[*,‡] and Shunichi Fukuzumi[*,†]

[†] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan*

[‡] *Department of Chemistry, The University of Texas, Austin, Texas 78712-1224, USA*

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp, sessler@cm.utexas.edu

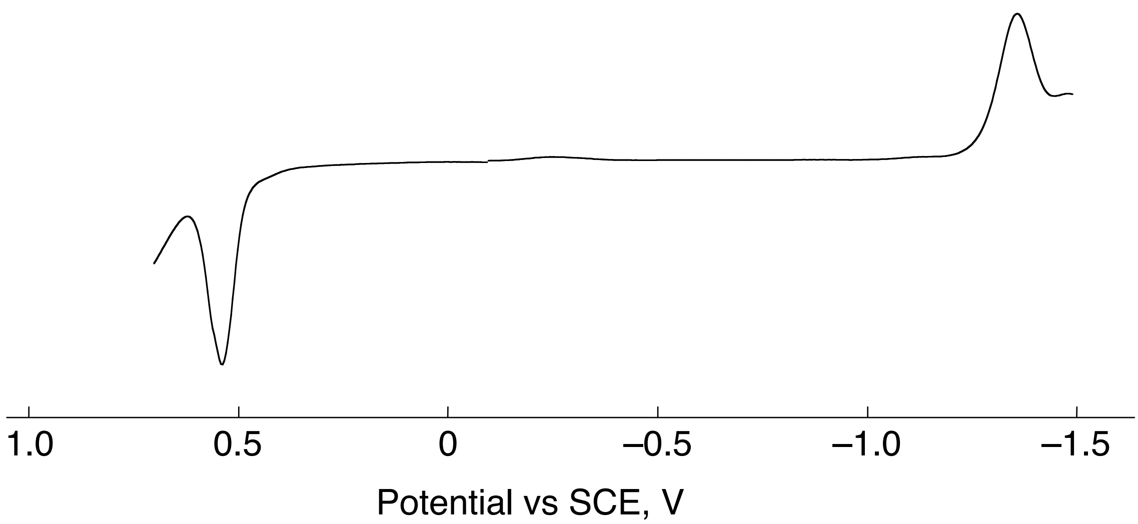

Figure S1. Differential pulse voltammogram of tetra-*n*-butylammonium zinc porphyrin carboxylate (ZnP: 1 mM) in deaerated MeCN containing tetra-*n*-butylammonium perchorate (0.10 M). Sweep rate: 4 mV s^{-1}.

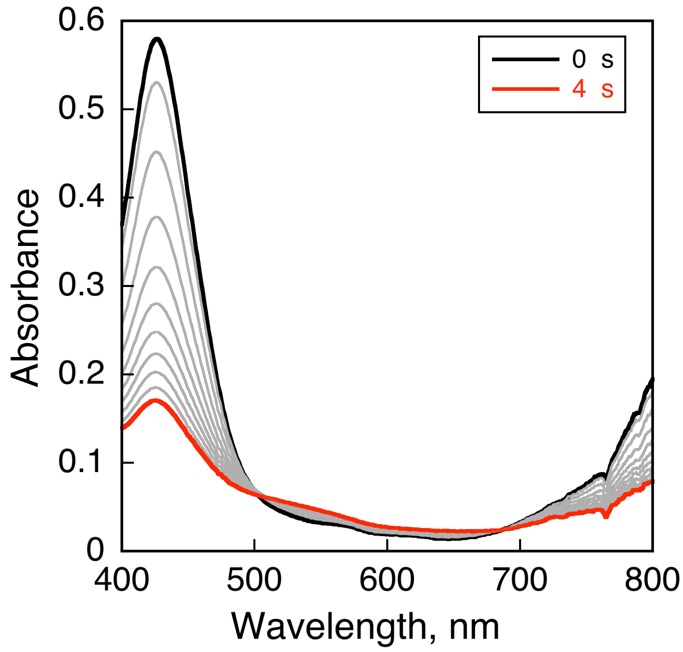

Figure S2. Absorption spectral changes associated with the reduction of C8 (1.0×10^{-5} M) by 1-benzyl-1,4-dihydronicotinamide dimer ($(BNA)_2$: 1.0×10^{-5} M) in deaerated MeCN.

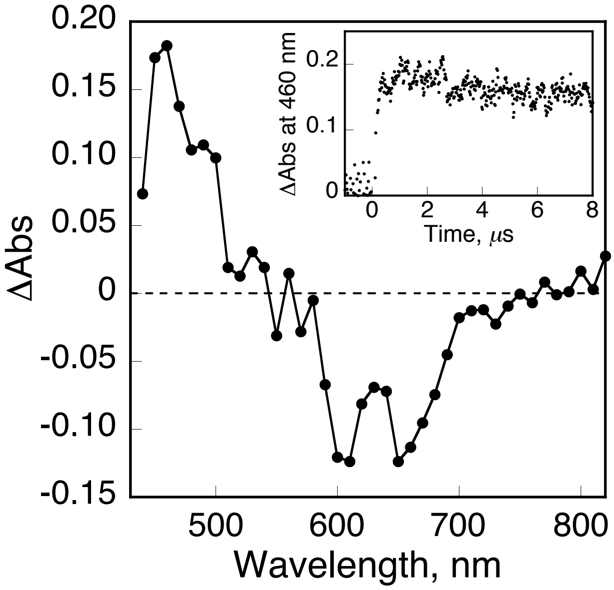

Figure S3. Transient absorption spectrum of $^3ZnP^*$ observed at 1 μs upon nanosecond laser excitation of a deaerated MeCN solution of ZnP (5.0×10^{-5} M) at 440 nm.

S4. Excitation Energies and Oscillator Strengths of C8 Radical Cation Calculated by TD-DFT B3LYP/6-31(d)

Excited State	1:	2.207-A	0.3129 eV	3962.13 nm	f=0.0002
Excited State	2:	3.243-A	0.4376 eV	2832.96 nm	f=0.0039
Excited State	3:	1.984-A	0.8545 eV	1450.97 nm	f=0.1244
Excited State	4:	2.244-A	1.4022 eV	884.22 nm	f=0.0891
Excited State	5:	2.143-A	1.7208 eV	720.52 nm	f=0.4356
Excited State	6:	2.465-A	1.8046 eV	687.04 nm	f=0.5264
Excited State	7:	2.979-A	1.8180 eV	681.97 nm	f=0.2069
Excited State	8:	3.227-A	1.8381 eV	674.53 nm	f=0.0066
Excited State	9:	2.140-A	2.0435 eV	606.72 nm	f=0.0030
Excited State	10:	2.399-A	2.0508 eV	604.57 nm	f=0.0028
Excited State	11:	2.297-A	2.0555 eV	603.18 nm	f=0.0014
Excited State	12:	2.216-A	2.0713 eV	598.58 nm	f=0.0001
Excited State	13:	2.310-A	2.0968 eV	591.30 nm	f=0.0019
Excited State	14:	2.456-A	2.1146 eV	586.33 nm	f=0.0004
Excited State	15:	2.368-A	2.1340 eV	581.00 nm	f=0.0032
Excited State	16:	2.347-A	2.1695 eV	571.49 nm	f=0.0008
Excited State	17:	3.082-A	2.2944 eV	540.39 nm	f=0.0010
Excited State	18:	3.007-A	2.3174 eV	535.02 nm	f=0.0002
Excited State	19:	2.146-A	2.4158 eV	513.22 nm	f=0.0043
Excited State	20:	2.683-A	2.4261 eV	511.04 nm	f=0.0034
Excited State	21:	3.144-A	2.4386 eV	508.41 nm	f=0.0431
Excited State	22:	2.980-A	2.4521 eV	505.62 nm	f=0.0212
Excited State	23:	2.750-A	2.4942 eV	497.10 nm	f=0.0005
Excited State	24:	2.905-A	2.5677 eV	482.86 nm	f=0.0026
Excited State	25:	2.951-A	2.5970 eV	477.41 nm	f=0.0023
Excited State	26:	2.474-A	2.6297 eV	471.48 nm	f=0.0033
Excited State	27:	2.857-A	2.6614 eV	465.86 nm	f=0.0755
Excited State	28:	2.522-A	2.6944 eV	460.15 nm	f=0.0002
Excited State	29:	2.423-A	2.7271 eV	454.64 nm	f=0.0497
Excited State	30:	2.596-A	2.7431 eV	451.98 nm	f=0.1336
Excited State	31:	2.300-A	2.7493 eV	450.97 nm	f=0.8208
Excited State	32:	2.580-A	2.7552 eV	450.01 nm	f=0.0193
Excited State	33:	2.504-A	2.8145 eV	440.51 nm	f=0.0094
Excited State	34:	2.502-A	2.8562 eV	434.09 nm	f=0.0008
Excited State	35:	2.740-A	2.9087 eV	426.25 nm	f=0.0147
Excited State	36:	2.749-A	2.9203 eV	424.56 nm	f=0.0105
Excited State	37:	2.745-A	2.9495 eV	420.35 nm	f=0.0138
Excited State	38:	2.599-A	2.9901 eV	414.65 nm	f=0.0356
Excited State	39:	2.979-A	3.0116 eV	411.69 nm	f=0.0823
Excited State	40:	2.326-A	3.0276 eV	409.52 nm	f=0.5544

S5. Excitation Energies and Oscillator Strengths of C8 Radical Anion Calculated by TD-DFT B3LYP/6-31(d)

Excited State	1:	2.001-A	0.8659 eV	1431.91 nm	f=0.3227
Excited State	2:	2.001-A	0.9179 eV	1350.70 nm	f=0.3183
Excited State	3:	2.008-A	1.8441 eV	672.34 nm	f=0.0002
Excited State	4:	2.008-A	1.8716 eV	662.45 nm	f=0.0003
Excited State	5:	2.025-A	2.2537 eV	550.13 nm	f=0.0015
Excited State	6:	2.028-A	2.2902 eV	541.37 nm	f=0.0032
Excited State	7:	2.029-A	2.2967 eV	539.83 nm	f=0.0077
Excited State	8:	2.015-A	2.3224 eV	533.86 nm	f=0.0000
Excited State	9:	2.018-A	2.3351 eV	530.96 nm	f=0.0008
Excited State	10:	2.017-A	2.3575 eV	525.92 nm	f=0.0006
Excited State	11:	2.017-A	2.3638 eV	524.52 nm	f=0.0005
Excited State	12:	2.017-A	2.3987 eV	516.88 nm	f=0.0000
Excited State	13:	2.412-A	2.5287 eV	490.32 nm	f=0.0009
Excited State	14:	3.087-A	2.6915 eV	460.65 nm	f=0.0258
Excited State	15:	2.028-A	2.7075 eV	457.94 nm	f=0.0004
Excited State	16:	2.029-A	2.7717 eV	447.33 nm	f=0.0004
Excited State	17:	3.123-A	2.7996 eV	442.86 nm	f=0.0228
Excited State	18:	2.016-A	3.0276 eV	409.52 nm	f=0.0110
Excited State	19:	3.254-A	3.2159 eV	385.53 nm	f=0.0001
Excited State	20:	3.270-A	3.2438 eV	382.22 nm	f=0.0004
Excited State	21:	2.598-A	3.4265 eV	361.84 nm	f=0.5312
Excited State	22:	2.955-A	3.4359 eV	360.85 nm	f=0.1618
Excited State	23:	2.458-A	3.5107 eV	353.16 nm	f=0.6681
Excited State	24:	2.190-A	3.5870 eV	345.65 nm	f=0.4763
Excited State	25:	2.208-A	3.6322 eV	341.35 nm	f=0.3740
Excited State	26:	3.093-A	3.6932 eV	335.71 nm	f=0.0068
Excited State	27:	3.257-A	3.7829 eV	327.75 nm	f=0.0001
Excited State	28:	3.269-A	3.8293 eV	323.78 nm	f=0.0002
Excited State	29:	2.171-A	3.9129 eV	316.86 nm	f=0.0009
Excited State	30:	2.530-A	3.9606 eV	313.05 nm	f=0.0011
Excited State	31:	3.106-A	4.0867 eV	303.39 nm	f=0.0002
Excited State	32:	2.375-A	4.1186 eV	301.04 nm	f=0.0035
Excited State	33:	2.374-A	4.1415 eV	299.37 nm	f=0.0009
Excited State	34:	2.373-A	4.1934 eV	295.66 nm	f=0.0002
Excited State	35:	2.324-A	4.2118 eV	294.38 nm	f=0.0001
Excited State	36:	3.290-A	4.3162 eV	287.25 nm	f=0.0882
Excited State	37:	3.309-A	4.3320 eV	286.20 nm	f=0.0624
Excited State	38:	3.323-A	4.3969 eV	281.98 nm	f=0.0017
Excited State	39:	3.188-A	4.3996 eV	281.81 nm	f=0.0002
Excited State	40:	2.303-A	4.4038 eV	281.54 nm	f=0.0006

S6: Full author list of ref 39

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.