Supplemental Information

Computational Methods and Results

The viologens and their reduced radical cation counterparts were optimized using the B3LYP exchange-correlation functional[1] and the 6-31G(d,p) basis set as implemented in the Gaussian03 suite of programs.[2] The radical cation species were computed using the unrestricted spin model. Stable structures were confirmed by computing analytic vibrational frequencies. Following the protocol of Baik and Friesner[3] for estimation of reduction potentials, we executed single-point B3LYP/cc-pVTZ calculations and used the CPCM model to obtain solvation corrections. Our best estimates for boroviologen and methyl viologen are 4.05 and 4.30 V, respectively. Details of these calculations are summarized in Tables S1; cartesian coordinates of the optimized structures are provided in Table S2.

[1] *(a)* Becke, A.D. *J. Chem. Phys.* 1993, **98**, 5648; *(b)* Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* 1988, **37**, 785; *(c)* Vosko, S.H.; Wilk, L.; Nusair, M. *Can. J. Phys.* 1980, **58**, 1200; *(d)* Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* 1994, **98**, 11623.

[2] *Gaussian 03, Revision E.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[3] M.-H. Baik, R.A. Friesner, *J. Phys. Chem. A*, 2002, **106**, 7407.

Electronic Supplementary Material (ESI) for Chemical Communications

Table S1. Computational Estimates of the Reduction Potentials of Boroviologen and Methyl Viologen.

	B^{2+}	+ e-	----->	B^{+}		kcal/mol	kcal/mol	E^0(red) Volts
H: B3LYP/6-31G(d,p)	-895.632349	0.002359		-895.917111			-180.1713	7.812994
E:	-896.1178884			-896.4005271		-177.359		
E: B3LYP/cc-pVTZ (sp)	-896.3787301			-896.6688544		-182.056	-184.86862	8.01669
Solvation corrections:								
ΔG_{solv} (kcal/mol)	-119.33			-27.84		91.49	-93.378623	4.049294
	C^{2+}	+ e-	----->	C^{+}				E^0(red) Volts
H: B3LYP/6-31G(d,p)	-574.429468	0.002359		-574.756066			-206.42381	8.951414
E:	-574.6835464			-575.0084789		-203.898		
E: B3LYP/cc-pVTZ (sp)	-574.8511861			-575.1828762		-208.139	-210.66424	9.135297
Solvation corrections:								
ΔG_{solv} (kcal/mol)	-150.97			-39.49		111.48	-99.184236	4.30105

B^{2+} and C^{2+} denote the parent boroviologen and methyl viologen species, respectively. Structures were optimized using the B3LYP/6-31G(d,p) model. Single-point energy corrections were obtained using the cc-pVTZ basis set. Energies are in Hartrees unless otherwise labeled.

Electronic Supplementary Material (ESI) for Chemical Communications

Table S2. Cartesian Coordinates of Optimized Structures (Å).

Boroviologen
Charge = 2 Multiplicity = 1

7	0.42281	3.5225	-0.20254
6	-0.08034	-0.739	-0.18368
6	0.08034	0.739	-0.18368
6	-0.03719	2.87662	-1.29831
1	1.13065	3.35071	1.73636
6	0.55554	1.42224	0.94626
6	-0.22187	1.50295	-1.3216
1	-0.23119	3.49197	-2.16791
5	0.77761	5.09016	-0.2705
1	0.84049	0.89431	1.84904
1	-0.60766	1.04487	-2.22504
1	0.23119	-3.49197	-2.16791
6	-0.55554	-1.42224	0.94626
6	0.22187	-1.50295	-1.3216
1	-0.75625	8.1367	0.35084
6	-0.72185	-2.79797	0.89981
1	-0.84049	-0.89431	1.84904
1	0.60766	-1.04487	-2.22504
6	0.03719	-2.87662	-1.29831
1	-1.13065	-3.35071	1.73636
7	-0.42281	-3.5225	-0.20254
1	0.33077	7.62841	-0.97361
1	0.90136	7.57334	0.71064
5	-0.77761	-5.09016	-0.2705
6	0.72185	2.79797	0.89981
7	-0.46711	6.02935	0.18387
1	1.01781	5.34147	-1.41558
1	1.67072	5.2776	0.50351
6	-0.87821	5.79749	1.60601
6	-1.66394	5.87563	-0.70482
6	0.03719	7.44512	0.05956
1	-2.43835	6.58689	-0.409
1	-2.06131	4.86349	-0.61359
1	-1.36872	6.06888	-1.73645
1	-1.65776	6.50927	1.88698
1	-0.01184	5.9337	2.25382
1	-1.26976	4.78459	1.71377
7	0.46711	-6.02935	0.18387
1	-1.01781	-5.34147	-1.41558
1	-1.67072	-5.2776	0.50351
6	0.87821	-5.79749	1.60601
6	1.66394	-5.87563	-0.70482
6	-0.03719	-7.44512	0.05956
1	0.75625	-8.1367	0.35084
1	-0.33077	-7.62841	-0.97361
1	-0.90136	-7.57334	0.71064
1	1.65776	-6.50927	1.88698
1	0.01184	-5.9337	2.25382
1	1.26976	-4.78459	1.71377
1	2.43835	-6.58689	-0.409
1	2.06131	-4.86349	-0.61359
1	1.36872	-6.06888	-1.73645

Stoichiometry C16H30B2N4(2+)

Boroviologen Reduced Species
Charge = 1 Multiplicity = 2

7	0.59506	3.53384	-0.00148
6	-0.12447	-0.70475	-0.00158
6	0.12447	0.70475	-0.00158
6	0.49842	2.81813	-1.16932
1	0.64273	3.39003	2.07457
6	0.27218	1.47008	1.19995
6	0.26943	1.4706	-1.2031
1	0.63712	3.39108	-2.07775
5	0.90041	5.05495	-0.00148
1	0.22318	1.00023	2.1739
1	0.2176	1.00129	-2.17716
1	-0.63712	-3.39108	-2.07775
6	-0.27218	-1.47008	1.19995
6	-0.26943	-1.4706	-1.2031
1	-0.95638	8.03646	0.00272
6	-0.50129	-2.81758	1.16625
1	-0.22318	-1.00023	2.1739
1	-0.2176	-1.00129	-2.17716
6	-0.49842	-2.81813	-1.16932
1	-0.64273	-3.39003	2.07457
7	-0.59506	-3.53384	-0.00148
1	0.52576	7.58065	-0.88812
1	0.52936	7.5804	0.8874
5	-0.90041	-5.05495	-0.00148
6	0.50129	2.81758	1.16625
7	-0.49842	5.95379	0.00149
1	1.46611	5.35991	-1.01747
1	1.46983	5.35921	1.01264
6	-1.32088	5.69356	1.21991
6	-1.32577	5.69381	-1.2137
6	-0.07505	7.38939	0.00084
1	-2.2088	6.33908	-1.21317
1	-1.64169	4.65019	-1.21981
1	-0.7247	5.89708	-2.10044
1	-2.20331	6.33964	1.22355
1	-0.71592	5.89565	2.10428
1	-1.63778	4.65025	1.22663
7	0.49842	-5.95379	0.00149
1	-1.46611	-5.35991	-1.01747
1	-1.46983	-5.35921	1.01264
6	1.32088	-5.69356	1.21991
6	1.32577	-5.69381	-1.2137
6	0.07505	-7.38939	0.00084
1	0.95638	-8.03646	0.00272
1	-0.52576	-7.58065	-0.88812
1	-0.52936	-7.5804	0.8874
1	2.20331	-6.33964	1.22355
1	0.71592	-5.89565	2.10428
1	1.63778	-4.65025	1.22663
1	2.2088	-6.33908	-1.21317
1	1.64169	-4.65019	-1.21981
1	0.7247	-5.89708	-2.10044

Stoichiometry C16H30B2N4(1+,2)

Methyl Viologen

Charge = 2 Multiplicity = 1

7	3.52793	-0.00692	-0.00758
6	-0.74446	0.00107	-0.00357
6	0.74447	-0.00106	-0.00357
6	2.85668	1.09577	-0.41517
1	3.44984	-1.9522	0.72302
6	1.46877	-1.13014	0.41053
6	1.4725	1.12593	-0.41898
1	3.45642	1.93909	-0.73727
6	5.01843	0.00734	0.02335
1	0.97362	-2.02713	0.76471
1	0.97979	2.02304	-0.77626
1	-3.45641	-1.93909	-0.73725
6	-1.46877	1.13015	0.41053
6	-1.4725	-1.12592	-0.41898
6	-5.01844	-0.00736	0.02332
6	-2.85368	1.10607	0.40228
1	-0.97363	2.02714	0.76472
1	-0.97979	-2.02303	-0.77626
6	-2.85667	-1.09577	-0.41515
1	-3.44984	1.9522	0.72304
7	-3.52793	0.00692	-0.00755
1	-5.34864	-0.44956	0.96589
1	-5.38434	-0.59552	-0.81764
1	-5.38483	1.01467	-0.06011
6	2.85368	-1.10607	0.40226
1	5.38434	0.59592	-0.8173
1	5.38485	-1.01464	-0.06061
1	5.34857	0.44907	0.96617

Stoichiometry C12H14N2(2+)

Methyl Viologen Reduced Species

Charge = 1 Multiplicity = 2

7	3.5563	0.00199	0.04303
6	-0.71598	0.00019	-0.00222
6	0.71594	0.00077	0.01057
6	2.85575	1.18041	0.03168
1	3.45176	-2.08186	0.03701
6	1.4917	-1.20309	0.01881
6	1.49066	1.20536	0.0188
1	3.45002	2.08578	0.03698
6	5.02384	0.00368	-0.01469
1	1.02108	-2.17732	0.01883
1	1.01912	2.17915	0.0187
1	-3.45002	-2.08481	-0.02921
6	-1.49173	1.20408	-0.01006
6	-1.4907	-1.20437	-0.01084
6	-5.02388	-0.00167	0.0231
6	-2.85684	1.17794	-0.02288
1	-1.02107	2.17829	-0.00979
1	-1.0192	-2.17817	-0.01131
6	-2.85583	-1.1794	-0.02367
1	-3.45181	2.08284	-0.02777
7	-3.55634	-0.00103	-0.03457
1	-5.36862	-0.00199	1.06153
1	-5.40577	-0.88796	-0.48482
1	-5.40654	0.88446	-0.48453
6	2.85684	-1.17694	0.0317
1	5.40588	0.88233	0.50636
1	5.36842	0.01933	-1.05304
1	5.40647	-0.88992	0.47954

Stoichiometry C12H14N2(1+,2)