Supporting Information

Computational design of C-substituted paraquat/diquat derivatives for neutral aqueous organic redox flow batteries

Wei Jin [a], Yanli Chen *[a], Lai-Ke Chen [b], De-Yin Wu [b], Juan Xu [a] and Jianyu Cao *[a]

[a] *Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu 213164, China.*

[b] *State Key Laboratory of Physical Chemistry of Solid Surface, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China*

*Corresponding author. E-mail: jycao@cczu.edu.cn (J. Cao); chenyl@cczu.edu.cn (Y. Chen)

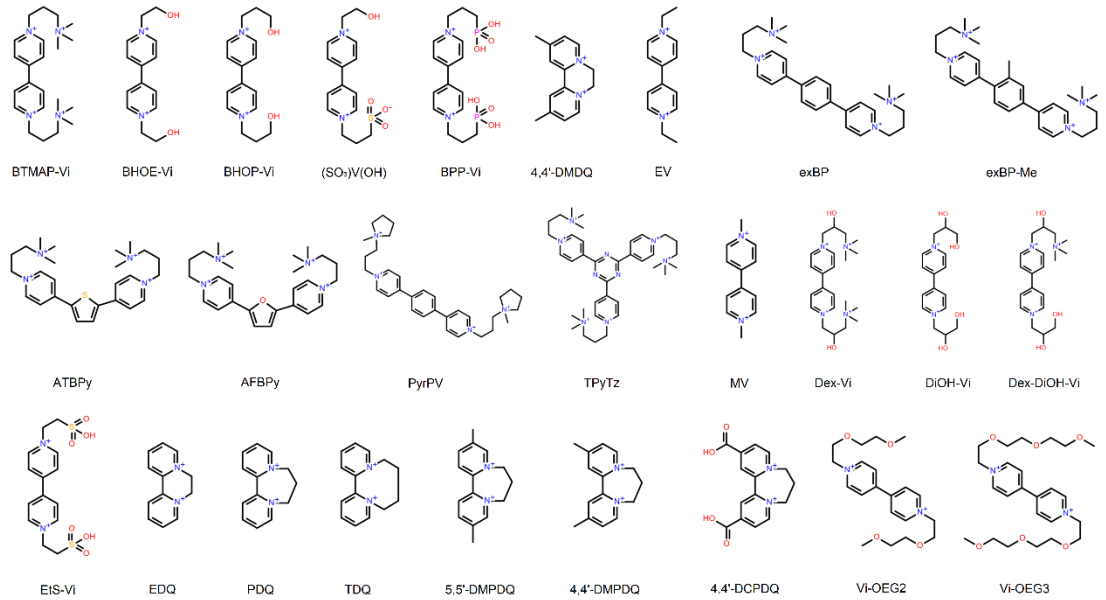

Fig. S1 Viologen (Vi) and diquat (DQ) derivatives for estimating the standard reduction potential. Bis(3-trimethylammonio)propyl viologen tetrachloride (BTMAP-Vi) [S1], 1,1′-di(2-ethanol)-4,4′-bipyridinium dichloride (BHOE-Vi) [S2], 1,1′-di(2-propanol)-4,4′-bipyridinium dichloride (BHOP-Vi) [S2], 3-(1'-(2-hydroxyethyl)-[4,4′-bipyridin]-1,1′-diium-1-yl)propane-1-sulfonate bromide ($(SO_3)V(OH)$) [S3], 1,1′-bis(3-phosphonopropyl)-(4,4′-bipyridine)-1,1′-diium (BPP-Vi) [S4], 4,4'-dimethyldiquat dichloride (4,4′-DMDQ) [S5], ethyl viologen dichloride (EV) [S6], exBP [S7], exBP-Me [S7], 1,1′-bis[3-(trimethylamonium)propyl]-4,4′-(2,5-thiophenediyl)bispyridinium tetrachloride (ATBPy) [S8], 1,1′-bis[3-(trimethylamonium)propyl]-4,4′-(2,5-furandiyl) bispyridinium tetrachloride (AFBPy) [S8], PyrPV [S9], 2,4,6-tris[1-(trimethylamonium)-propyl-4-pyridiniumyl]-1,3,5-triazine hexachloride (TPyTz) [S10], methyl viologen (MV) [S11], bis(3-trimethylammonio-2-hydroxy)propyl viologen tetrachloride (Dex-Vi) [S12], DiOH-Vi [S13], Dex-DiOH-Vi [S13], EtS-Vi [S13], EDQ [S14], PDQ [S14], TDQ [S14], 5,5'-DMPDQ [S14], 4,4'-DMPDQ [S14], 4,4'-DCPDQ [S14], 1,1′-bis(2-(2-methoxyethoxy)ethyl)-[4,4′-bipyridine]-1,1′-diium bromide (Vi-OEG2) [S15], 1,1′-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-[4,4′-bipyridine]-1,1′-diium bromide(Vi-OEG3) [S15].

Table S1 Experimental redox potential (E_{exp}^0) for 26 previously reported water-soluble viologen derivatives and their theoretical LUMO energies calculated using different functionals.

No.	Molecule	E_{exp}^0 (V)	LUMO (eV)	LUMO (eV)
			B3LYP	M06-2X
1	BTMAP-Vi	-0.350	-3.672	-2.902
2	BHOE-Vi	-0.396	-3.658	-2.723
3	BHOP-Vi	-0.433	-3.576	-2.469
4	$(SO_3)V(OH)$	-0.400	-3.742	-2.787
5	BPP-Vi	-0.460	-3.681	-2.832
6	4,4'-DMDQ	-0.400	-3.580	-2.577
7	EV	-0.380	-3.580	-2.724
8	exBP	-0.750	-3.326	-2.579
9	exBP-Me	-0.910	-3.178	-2.241
10	ATBPy	-0.560	-3.650	-2.716
11	AFBPy	-0.600	-3.491	-2.759
12	PyrPV	-0.760	-3.232	-2.298
13	TPyTz	-0.250	-3.958	-2.991
14	MV	-0.450	-3.541	-2.763
15	Dex-Vi	-0.322	-3.827	-2.789
16	DiOH-Vi	-0.366	-3.685	-2.772
17	Dex-DiOH-Vi	-0.342	-3.779	-2.944
18	EtS-Vi	-0.341	-3.665	-2.789
19	EDQ	-0.050	-4.106	-2.794
20	PDQ	-0.270	-3.962	-2.698
21	TDQ	-0.400	-3.626	-2.324
22	5,5'-DMPDQ	-0.410	-3.746	-2.456
23	4,4'-DMPDQ	-0.380	-3.746	-2.345
24	4,4'-DCPDQ	0.270	-4.484	-3.127
25	Vi-OEG2	-0.320	-3.833	-2.661
26	VI-OEG3	-0.330	-3.938	-2.943

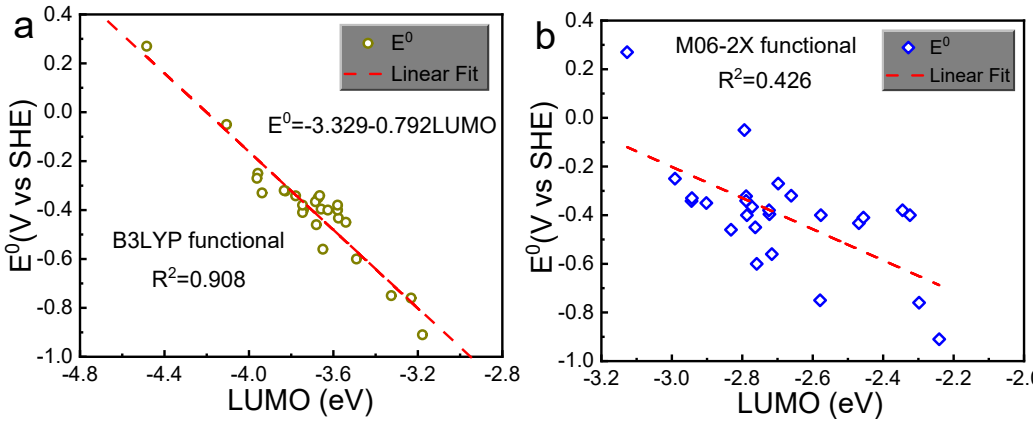

Fig. S2 The experimental redox potential (E_{exp}^{0}) versus the LUMO energy. (a) The LUMO energy calculated using the B3LYP functional. (b) The LUMO energy calculated using the M06-2X functional.

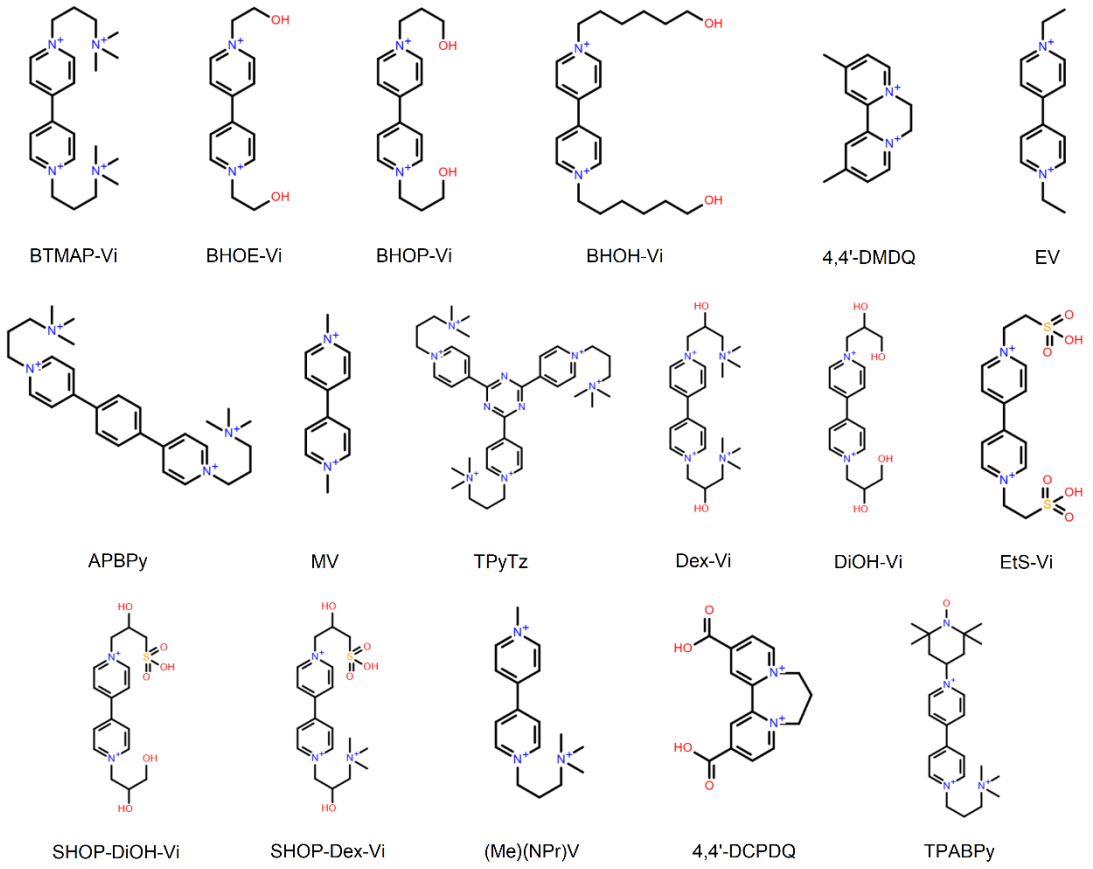

Fig. S3 Viologen (Vi) and diquat (DQ) derivatives for estimating the kinetic rate constant. (BHOH-Vi) [S2], (APBPy) [S16], (SHOP-DiOH-Vi) [S13], (SHOP-Dex-Vi) [S13], (Me)(NPr)V [S17], TPABPy [S18].

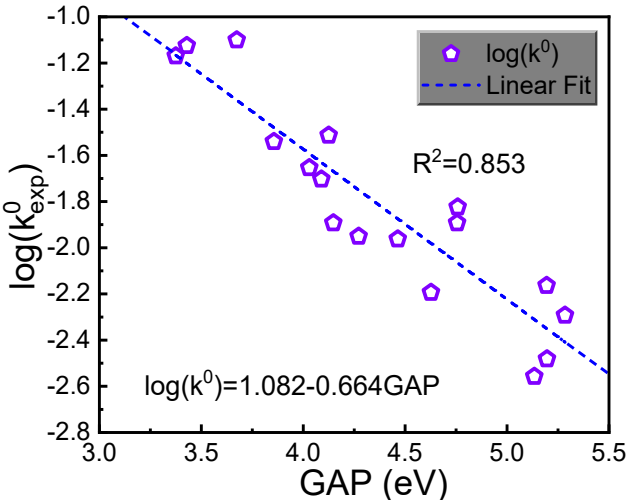

Fig. S4 The correlation plot between log (k^0_{exp}) and the B3LYP-calculated LUMO-HOMO GAP for 17 water-soluble viologen derivatives.

Table S2 The calculated E^0 and k^0 values of the 74 promising anolyte compounds for neutral AORFBs. Me, Et and Pr represent one, two and three methylene units within the substituent group, respectively. N represents terminal trimethyl quaternary ammonium group, P phosphonic acid group, S sulfonate and C carboxylic acid group, respectively.

No.	Parent structure	Substitution site	Substituent group	Number of substituents	$k^0\times10^{-3}$ (cm s^{-1})	E^0(V)
1	PQT	2	MeP	1	6.358	-0.44972
2	PQT	2	EtP	1	9.220	-0.52591
3	PQT	2	PrP	1	9.083	-0.42807
4	PQT	3	MeP	1	4.423	-0.42887
5	PQT	3	PrP	1	5.024	-0.51629
5	DQT	5	PrP	1	4.470	-0.67749
6	PQT	2,2’	EtP	2	6.610	-0.41523
7	PQT	2,2’	PrP	2	7.103	-0.41443
8	PQT	3,3’	MeP	2	5.154	-0.43689
9	PQT	3,3’	EtP	2	5.123	-0.52511
10	PQT	3,3’	PrP	2	5.017	-0.54516
11	DQT	6,6’	EtP?	2	8.129	-0.49864
12	DQT	5,5’	PrP	2	6.444	-0.62857
13	PQT	2,2’,6,6’	EtP	4	5.952	-0.40882
14	PQT	2,2’,6,6’	PrP	4	7.157	-0.34546
15	PQT	3,3’,5’	PrP	3	6.170	-0.35669
16	PQT	2,3’,5’	MeP	3	5.724	-0.4401
17	PQT	2,3’,5’	PrP	3	5.002	-0.49784

18	PQT	2,3',5',6	MeP	4	4.319	-0.53393
19	PQT	2,3',5',6	PrP	4	4.538	-0.71999
20	PQT	2,2',6	PrS	3	8.227	-0.33022
21	PQT	2	MeC	1	10.679	-0.53553
22	PQT	2	EtC	1	11.528	-0.55639
23	PQT	2	PrC	1	12.332	-0.55799
24	PQT	3	MeC	1	7.178	-0.44731
25	PQT	3	EtC	1	8.081	-0.46255
26	PQT	3	PrC	1	8.908	-0.49864
27	DQT	6	MeC	1	5.367	-0.62616
28	DQT	6	EtC	1	6.956	-0.66065
29	DQT	6	PrC	1	8.491	-0.6005
30	DQT	5	MeC	1	4.972	-0.6807
31	DQT	5	EtC	1	6.822	-0.65664
32	DQT	5	PrC	1	7.645	-0.65744
33	DQT	4	MeC	1	5.547	-0.59649
34	DQT	4	EtC	1	6.822	-0.65664
35	DQT	4	PrC	1	7.645	-0.65744
36	PQT	2,3',5',6	MeC	4	6.863	-0.43769
37	PQT	2,3',5',6	EtC	4	6.977	-0.75849
38	PQT	2,3',5',6	PrC	4	4.811	-0.8419
39	PQT	3,3',5,5'	MeC	4	6.966	-0.67187
40	PQT	3,3',5,5'	EtC	4	4.443	-0.8836
41	PQT	3,3',5,5'	PrC	4	5.407	-0.85393
42	PQT	2,2'	MeC	2	10.679	-0.52832
43	PQT	2,2'	EtC	2	10.955	-0.44651
44	PQT	2,2'	PrC	2	14.807	-0.46335
45	PQT	3,3'	MeC	2	5.699	-0.58045
46	PQT	3,3'	EtC	2	6.873	-0.64781
47	PQT	3,3'	PrC	2	4.338	-0.9213
48	DQT	6,6'	MeC	2	4.920	-0.53714
49	DQT	6,6'	EtC	2	5.514	-0.69754
50	DQT	6,6'	PrC	2	7.497	-0.6414
51	DQT	5,5'	MeC	2	6.329	-0.61814
52	DQT	5,5'	EtC	2	7.877	-0.60932
53	DQT	5,5'	PrC	2	7.520	-0.67669
54	DQT	3	MeC	1	4.358	-0.59729
55	DQT	3	EtC	1	6.198	-0.64781
56	DQT	3	PrC	1	7.588	-0.643
57	DQT	4,4'	MeC	2	5.367	-0.62616
58	DQT	4,4'	EtC	2	6.956	-0.66065
59	DQT	4,4'	PrC	2	8.491	-0.60050
60	PQT	3,3',5'	MeC	3	4.987	-0.55238

61	PQT	3,3’,5’	EtC	3	4.876	-0.81463
62	PQT	3,3’,5’	PrC	3	5.759	-0.83227
63	PQT	2,3’,6	MeC	3	7.509	-0.38315
64	PQT	2,3’,6	EtC	3	8.554	-0.53072
65	PQT	2,3’,6	PrC	3	8.961	-0.49223
66	PQT	2,2’,6	PrC	3	11.288	-0.4016
67	PQT	2,2’,6,6’	EtC	4	9.529	-0.46416
68	PQT	2,2’,6,6’	PrC	4	10.179	-0.50746
69	DQT	3,3’	MeC	2	4.504	-0.6013
70	DQT	3,3’	EtC	2	5.062	-0.71518
71	DQT	3.3’	PrC	2	6.791	-0.7232
72	PQT	2,3’,5’	MeC	3	5.688	-0.59911
73	PQT	2,3’,5’	EtC	3	7.579	-0.60029
74	PQT	2,3’,5’	PrC	3	7.963	-0.60111

References

[S1] E. S. Beh, D. D. Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon, M. J. Aziz, ACS Energy Lett., 2017, 2, 639-644.

[S2] Y. Liu, Y. Li, P. Zuo, Q. Chen, G. Tang, P. Sun, Z. Yang, T. Xu, ChemSusChem, 2020, 13, 2245-2249.

[S3] H. Wang, D. Li, J. Xu, Y. Wu, Y. Cui, L. Chen, J. Power Sources, 2021, 492, 229659.

[S4] S. Jin, E. M. Fell, L. Vina-Lopez, Y. Jing, P. W. Michalak, R. G. Gordon, M. J. Aziz, Adv. Energy Mater., 2020, 10, 2000100.

[S5] J. Huang, Z. Yang, V. Murugesan, E. Walter, A. Hollas, B. Pan, R. S. Assary, I. A. Shkrob, X. Wei, Z. Zhang, ACS Energy Lett., 2018, 3, 2533-2538.

[S6] L. Liu, Y. Yao, Z. Wang, Y.-C. Lu, Nano Energy, 2021, 84, 105897.

[S7] G. Tang, Y. Liu, Y. Li, K. Peng, P. Zuo, Z. Yang, T. Xu, JACS Au, 2022, 2, 1214-1222.

[S8] M. Huang, S. Hu, X. Yuan, J. Huang, W. Li, Z. Xiang, Z. Fu, Z. Liang, Adv. Funct. Mater., 2022, 32, 2111744.

[S9] M. Pan, L. Gao, J. Liang, P. Zhang, S. Lu, Y. Lu, J. Ma, Z. Jin, Adv. Energy Mater., 2022, 12, 2103478.

[S10] J. Huang, S. Hu, X. Yuan, Z. Xiang, M. Huang, K. Wan, J. Piao, Z. Fu, Z. Liang, Angew. Chem. Int. Ed., 2021, 60, 2-7.

[S11] T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, Adv. Energy Mater., 2016, 6, 1501449.

[S12] X.-L. Lv, P. Sullivan, H.-C.Fu, X. X. Hu, H. Liu, S. Jin, W. Li, D. Feng, ACS Energy Lett., 2022, 7, 2428-2434.

[S13] P. T. Sullivan, H. Liu, X.-L. Lv, S. Jin, W. Li, D. Feng, Adv. Energy Mater., 2023,13, 2203919.

[S14] J. Asenjo-Pascual, I. Salmeron-Sanchez, P. Mauleón, M. Agirre, A. C. Lopes, O. Zugazua, E. Sánchez-Díez, J. R. Avilés-Moreno, P. Ocon, J. Power Sources, 2023, 564, 232817.

[S15] Y. Yao, W. Ma, J. Lei, Z. Wang, Y.-C. Lu, L. Liu, J. Mater. Chem. A, 2023, 11, 12984-12991.
[S16] S. Hu, T. Li, M. Huang, J. Huang, W. Li, L. Wang, Z. Chen, Z. Fu, X. Li, Z. Liang, Adv. Mater., 2021, 33, 2005839.
[S17] C. DeBruler, B. Hu, J. Moss, X. Liu, J. Luo, Y. Sun, T. L. Liu, Chem, 2017, 3, 1-18.
[18] L. Wang, M. Huang, K. Wan, Z. Fu, Z. Xiang, Z. Liang, Adv. Funct. Mater., 2023, 2310620.