Supporting Information

Computational design of phenazine derivative molecules as redox-active electrolyte materials in alkaline aqueous organic flow batteries

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Table S1 The total change of Gibbs free energy (ΔG^*_{sol}), computed standard potentials (E^0_{cal}) and measured standard potentials (E^0_{exp} vs. SHE, V) of various phenazine derivatives in alkaline aqueous solution. Phenazine (PZ), 1-hydroxyphenazine (1-HPZ), 2-hydroxyphenazine (2-HPZ), 1-phenazinecarboxylic acid (PZ-1-C), phenazine-1-carboxyamide (PZ-1-CA), 2,3-dihydroxyphenazine (2,3-DHPZ), 2-hydroxy-3-aminophenazine (2,3-HAPZ), 2,3-diaminophenazine (2,3-DAPZ), 1,4-phenazinedicarboxylic acid (PZ-1,4-DC), 1,5-phenazinedicarboxylic acid (PZ-1,5-DC), 7,8-dihydroxy-2-phenazinesulfonic acid (7,8-DHPZ-2-S), 7,8-dihydroxy-2-phenazinecarboxylic acid (7,8-DHPZ-2-C), benzo[a]hydroxyphenazine-7-carboxylic acid (BHPC), 1,2:3,4-dibenzophenazine (DBPZ), dibenzo[a,c]phenazin-11-amine (DBPZ-11-A), dipyridophenazine (DPPZ), 1-nitrophenazine (1-NPZ), 2-nitrophenazine (2-NPZ), 2,3-dinitrophenazine (2,3-DNPZ).

No.	Compound	ΔG^*_{sol} (kJ mol^{-1})	E^0_{cal} (V)	E^0_{exp} (V)
P1	PZ	-932.82	-0.426	-0.36[S1]
P2	1-HPZ	-899.24	-0.600	-0.594[S2]
P3	2-HPZ	-894.03	-0.627	-0.67[S3]
P4	PZ-1-C	-906.96	-0.560	-0.536[S2]
P5	PZ-1-CA	-907.35	-0.558	-0.56[S2]
P6	2,3-DHPZ	-875.70	-0.722	-0.82[S1]
P7	2,3-HAPZ	-885.54	-0.671	-0.78[S3]
P8	2,3-DAPZ	-867.02	-0.767	-0.701[S2]
P9	PZ-1,4-DC	-991.87	-0.120	-0.04[S4]
P10	PZ-1,5-DC	-972.96	-0.218	-0.165[S4]
P11	7,8-DHPZ-2-S	-865.67	-0.774	-0.86[S1]
P12	7,8-DHPZ-2-C	-876.28	-0.719	-0.88[S1]
P13	BHPC	-886.70	-0.665	-0.78[S3]
P14	DBPZ	-862.58	-0.790	-0.778
P15	DBPZ-11-A	-852.35	-0.843	-0.825
P16	DPPZ	-866.44	-0.770	-0.732
P17	1-NPZ	-941.31	-0.382	-0.45[S5]
P18	2-NPZ	-928.96	-0.446	-0.39[S5]
P19	2,3-DNPZ	-958.29	-0.294	-0.20[S5]

Table S2 Comparison between the computed solvation free energy (ΔG_{solv}) and measured solubility (S) of various organic molecules in water. Alloxazine 7/8-carboxylic acid (ACA), 3,3'-(phenazine-1,6-diylbis(azanediyl))diacetic acid (1,6-DGAP), 3,3'-(phenazine-1,8-diylbis(azanediyl))diacetic acid (1,8-DGAP), 3,3'-(phenazine-2,7-diylbis(azanediyl))diacetic acid (2,7-DGAP), 3,3'-(phenazine-1,6-diylbis(azanediyl))dibutyric acid (1,6-DBAP), 6-(1H-pyrrol-1-yl) quinoxaline (6-PyQX), 7-bromo-2,3-phenazinediol (7-Br-DHPZ), 4-carboxy-TEMPO (4CaT), 4-cyano-TEMPO (4CyT), 2,5-dihydroxy-1,4-benzoquinone (DHBQ), 1,8-dihydroxyanthraquinone (1,8-DHAQ).

Compound	ΔG_{solv} (kJ mol^{-1})	S (mol L^{-1})
PZ	12.0	6.85×10^{-5}[S1]
2-HPZ	-44.0	1.7[S3]
PCA	-40.1	0.27×10^{-3}[S6]
2,3-DHPZ	-43.0	0.1[S1]
2,3-HAPZ	-44.3	0.43[S3]
7,8-DHPZ-2-S	-70.7	1.8[S1]
7,8-DHPZ-2-C	-77.0	0.95[S1]
BHPC	-51.1	1.55[S3]
ACA	-75.5	2[S7]
1,6-DGAP	-42.0	0.115[S8]
1,8-DGAP	-58.8	0.924[S8]
2,7-DGAP	-67.4	0.886[S8]
1,6-DBAP	-55.7	0.401[S8]
6-PyQX	-2.50	6.6×10^{-4}
7-Br-DHPZ	0.30	7.86×10^{-4}
4CaT	-29.0	0.021[S9]
4CyT	-18.0	0.026[S9]
DHBQ	-62.9	4.31[S10]
1,8-DHAQ	-50.0	0.08[S11]

The solubilities for 6-PyQX and 7-Br-DHPZ in water are obtained from solubility experiments. The experimental procedure is described as follows. The excess 6-PyQX (or 7-Br-DHPZ) was first equilibrated in water for 48 hours at room temperature. After filtering the mixture through a 0.5 μm syringe-tip filter (Millipore, type FH), a saturated aqueous solution (200 mL) was obtained. Then, this aqueous solution was extracted using chloroform (50 mL). The obtained chloroform solution was concentrated by a known amount (5 mL) and the concentration was evaluated by UV-Vis (Shimadzu UV

mini 1240) spectrophotometer. The concentration was calculated according to a pre-calibrated absorbance-concentration curve of known concentrations of 6-PyQX (or 7-Br-DHPZ) in chloroform.

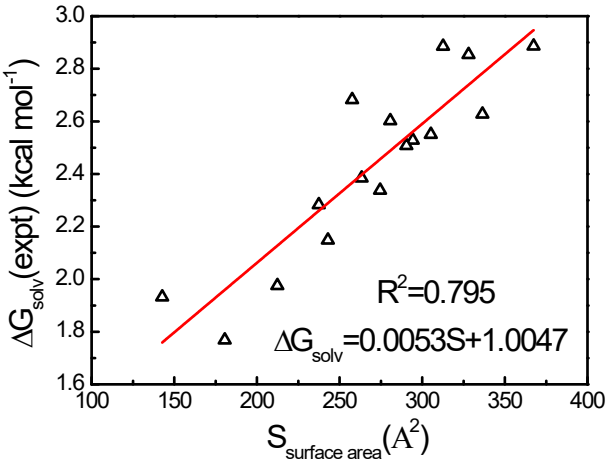

Fig. S1 Dependence of experimental vacuum to water solvation free energies on calculated solvent-accessible surface area (SASA) for various hydrocarbons.

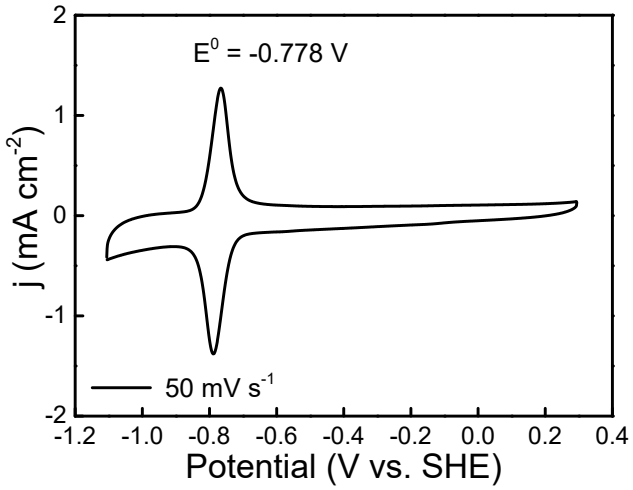

Fig. S2 The CV curve of 1,2:3,4-dibenzophenazine (DBPZ, P14) electrode in a 1 M KOH solution at 50 mV s^{-1}. The standard potential is calculated to be -0.778 V.

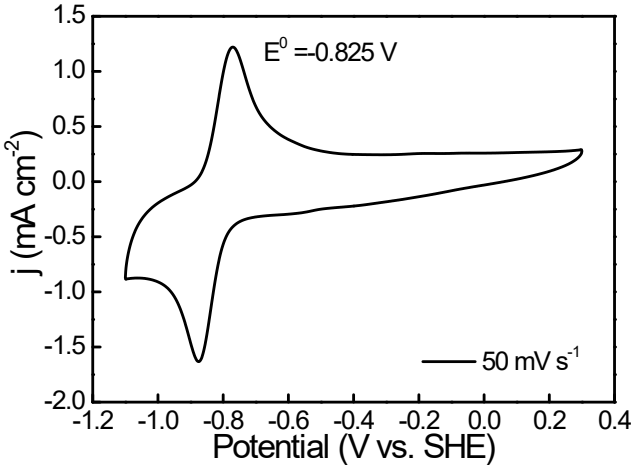

Fig. S3 The CV curve of dibenzo[*a,c*]phenazin-11-amine (DBPZ-11-A, P15) electrode in a 1 M KOH solution at 50 mV s^{-1}. The standard potential is calculated to be -0.825 V.

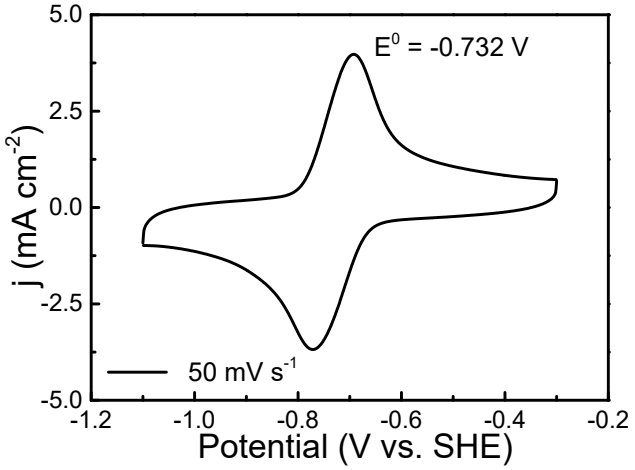

Fig. S4 The CV curve of dipyridophenazine (DPPZ, P16) electrode in a 1 M KOH solution at 50 mV s^{-1}. The standard potential is calculated to be -0.732 V.

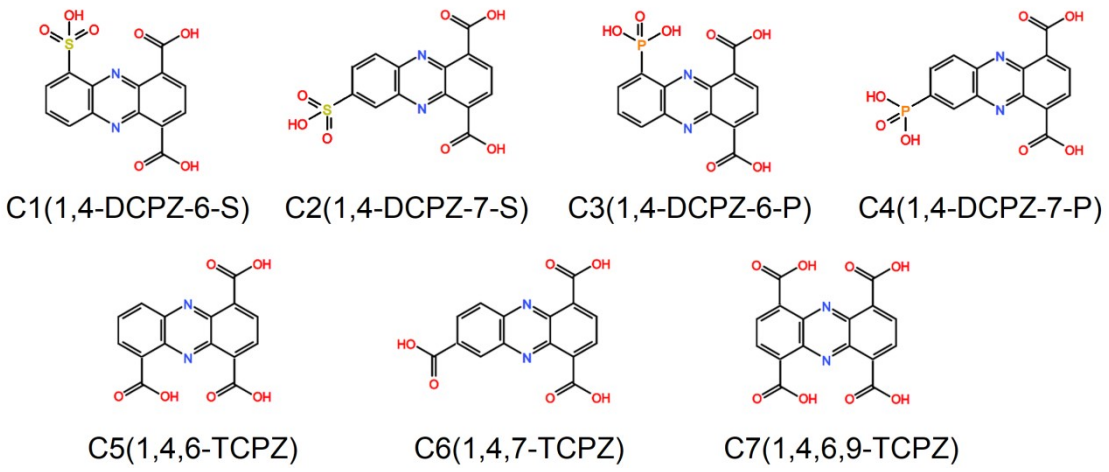

Fig. S5 Proposed phenazine derivative molecules as catholytes.

Table S3 The calculated standard potentials (E^0_{cal}) and solvation free energy (ΔG_{solv}) in water for different DHPZ substitution patterns. 7,8-Dihydroxy-1-phenazinesulfonic acid (7,8-DHPZ-1-S), 7,8-dihydroxy-1-phenazinephosphonic acid (7,8-DHPZ-1-P), 7,8-dihydroxy-2-phenazinephosphonic acid (7,8-DHPZ-2-P), 7,8-dihydroxy-1-phenazinecarboxylic acid (7,8-DHPZ-1-C), 4,7,8-trihydroxy-2-phenazinesulfonic acid (4,7,8-THPZ-2-S), 4,7,8-trihydroxy-2-phenazinephosphonic acid (4,7,8-THPZ-2-P), 4,7,8-trihydroxy-2-phenazinecarboxylic acid (4,7,8-THPZ-2-C), 3,7,8-trihydroxy-2-phenazinesulfonic acid (3,7,8-THPZ-2-S), 3,7,8-trihydroxy-2-phenazinephosphonic acid (3,7,8-THPZ-2-P), 3,7,8-trihydroxy-2-phenazinecarboxylic acid (3,7,8-THPZ-2-C), 1,7,8-trihydroxy-2-phenazinesulfonic acid (1,7,8-THPZ-2-S), 1,7,8-trihydroxy-2-phenazinephosphonic acid (1,7,8-THPZ-2-P), 1,7,8-trihydroxy-2-phenazinecarboxylic acid (1,7,8-THPZ-2-C).

No.	Compound	E^0_{cal} (V)	ΔG_{solv} (kJ mol^{-1})
A1	7,8-DHPZ-1-S	-0.626	-135.0
A2	7,8-DHPZ-1-P	-0.714	-152.9
A3	7,8-DHPZ-2-P	-0.655	-155.9
A4	7,8-DHPZ-1-C	-0.521	-117.3
A5	4,7,8-THPZ-2-S	-0.774	-138.9
A6	4,7,8-THPZ-2-P	-0.787	-163.5
A7	4,7,8-THPZ-2-C	-0.729	-121.2
A8	3,7,8-THPZ-2-S	-0.572	-134.0
A9	3,7,8-THPZ-2-P	-0.643	-157.5
A10	3,7,8-THPZ-2-C	-0.589	-123.1
A11	1,7,8-THPZ-2-S	-0.707	-136.0
A12	1,7,8-THPZ-2-P	-0.767	-153.6
A13	1,7,8-THPZ-2-C	-0.781	-125.5

Table S4 The calculated standard potentials (E^0_{cal}) and solvation free energy (ΔG_{solv}) in water for different DCPZ substitution patterns. 6-Sulfo-phenazine-1,4-dicarboxylic

acid (1,4-DCPZ-6-S), 7-Sulfo-phenazine-1,4-dicarboxylic acid (1,4-DCPZ-7-S), 6-phospho-phenazine-1,4-dicarboxylic acid (1,4-DCPZ-6-P), 7-phospho-phenazine-1,4-dicarboxylic acid (1,4-DCPZ-7-P), phenazine-1,4,6-tricarboxylic acid (1,4,6-TCPZ), phenazine-1,4,7-tricarboxylic acid (1,4,7-TCPZ), phenazine-1,4,6,9-tetracarboxylic acid (1,4,6,9-TCPZ).

No.	Compound	E^0_{cal} (V)	ΔG_{solv}(kJ mol^{-1})
C1	1,4-DCPZ-6-S	-0.304	-168.0
C2	1,4-DCPZ-7-S	-0.274	-160.9
C3	1,4-DCPZ-6-P	-0.389	-183.5
C4	1,4-DCPZ-7-P	-0.234	-175.3
C5	1,4,6-TCPZ	-0.123	-143.0
C6	1,4,7-TCPZ	-0.216	-137.7
C7	1,4,6,9-TCPZ	+0.086	-171.7

References

[S1] A. Hollas,, X. Wei, V. Murugesan, Z. Nie, B. Li, D. Reed, J. Liu, V. Sprenkle and W. Wang, A biomimetic high-capacity phenazine-based anolyte for aqueous organic redox flow batteries, Nat. Energy, 2018, 3, 508-514.

[S2] J.-J. Chen, W. Chen, H. He, D.-B. Li, W.-W. Li, L. Xiong and H.-Q. Yu, Manipulation of microbial extracellular electron transfer by changing molecular structure of phenazine-type redox mediators, Environ. Sci. Technol. 2013, 47, 1033-1039.

[S3] C. Wang, X. Li, B. Yu, Y. Wang, Z. Yang, H. Wang, H. Lin, J. Ma, G. Li, Z. Jin, Molecular design of fused-ring phenazine derivatives for long-cycling alkaline redox flow batteries, ACS Energy Lett. 2020, 5, 411-417.

[S4] L. Miao, L. Liu, K. Zhang, J. Chen, Molecular design strategy for high-redox-potential and poorly soluble n-type phenazine derivatives as cathode materials for lithium batteries, ChemSusChem 2020, 13, 2337-2344.

[S5] C. de la Cruz, A. Molina, N. Patil, E. Ventosa, R. Marcilla and A. Mavrandonakis,

New insights into phenazine-based organic redox flow batteries by using high-throughput DFT modeling, Sustain. Energy Fuels 2020, 4, 5513-5521.

[S6] Z.-J. Yang, H.-B. Hu, X.-H. Zhang and Y.-Q. Xu, Solubility of phenazine-1-carboxylic acid in water, methanol, and ethanol from (278.2 to 328.2) K, J. Chem. Eng. Data 2007, 52, 184-185.

[S7] K. Lin, R. Gómez-Bombarelli, E.S. Beh, L. Tong, Q. Chen, A. Valle, A. Aspuru-Guzik, M.J. Aziz and R.G. Gordon, A redox-flow battery with an alloxazine-based organic electrolyte, Nat. Energy, 2016, 1, 1-8.

[S8] S. Pang, X. Wang, P. Wang and Y. Ji, Biomimetic amino acid functionalized phenazine flow batteries with long lifetime at near-neutral pH, Angew. Chem. Int. Ed., 2020, 1, 5289-5298.

[S9] W. Zhou, W. Liu, M. Qin, Z. Chen, J. Xu, J. Cao and J. Li, Fundamental properties of TEMPO-based catholytes for aqueous redox flow batteries: effects of substituent groups and electrolytes on electrochemical properties, solubilities and battery performance, RSC Adv., 2020, 10, 21839-21844.

[S10] Z. Yang, L. Tong, D.P. Tabor, E.S. Beh, M.-A. Goulet, D. De Porcellinis, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, Alkaline benzoquinone aqueous flow battery for large-scale storage of electrical energy, Adv. Energy Mater., 2018, 8, 1-9.

[S11] J. Cao, M. Tao, H. Chen, J. Xu and Z. Chen, A highly reversible anthraquinone-based anolyte for alkaline aqueous redox flow batteries, J. Power Sources, 2018, 386, 40-46.