Supplemental Information

Molecular Polarity Regulation of Polybromide Complexes for High-Performance Low-Temperature Zinc-Bromine Flow Batteries

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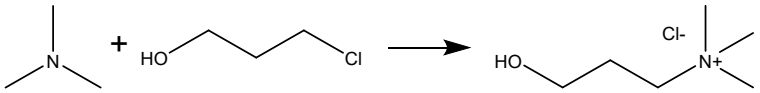
Supplemental Experimental Procedures

Materials

Zinc bromide ($ZnBr_2$, Israel Chemicals), choline chloride (N[1,1,1,2OH]Cl, Shanghai Macklin Biochemical Co., Ltd., China), trimethylamine 30 wt.% in the water (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 3-chloro-1-propanol (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 4-chloro-1-butanol (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 5-chloro-1-pentanol (Shanghai Aladdin Biochemical Technology Co., Ltd., China), N,N-dimethylethanolamine (Shanghai Macklin Biochemical Co., Ltd., China), bromoethane (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 1-bromopropane (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 1-bromobutane (Shanghai Aladdin Biochemical Technology Co., Ltd., China), N,N-diethylmethylamine (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 2-bromoethanol (Shanghai Aladdin Biochemical Technology Co., Ltd., China), 2-(diethylamino)ethanol (Shanghai Aladdin Biochemical Technology Co., Ltd., China), ether (Liaoning Quan Rui Reagent Co., Ltd., China), acetonitrile (Shanghai Aladdin Biochemical Technology Co., Ltd., China), potassium chloride (KCl, Liaoning Quan Rui Reagent Co., Ltd., China), potassium bromide (KBr, Shanghai Aladdin Biochemical Technology Co., Ltd., China), carbon felt (Liaoyang J-Carbon Materials Co., Ltd., China), membrane (Daramic® HP Polypore (Shanghai) Membrane Products Co., Ltd, China).

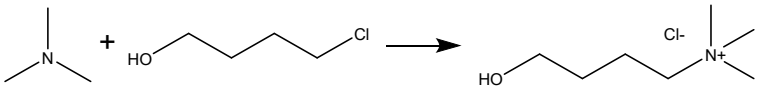
Preparation of the choline derivatives

3-Hydroxyethyltrimethylammonium chloride (N[1,1,1,3OH]Cl)



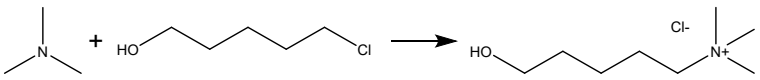
A mixture of 197 g trimethylamine 30 wt.% and 94 g 3-chloro-1-propanol was stirred at room temperature over 48 hours. The most of water in the reaction product was removed by a rotary evaporator (IKA RV10 DS096). The concentrated product was then placed in a drying chamber to acquire yellowish solid product which was washed with ether to remove residue reactant. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

4-Hydroxybutyltrimethylammonium chloride (N[1,1,1,4OH]Cl)



A mixture of 197 g trimethylamine 30 wt.% and 127 g 4-chloro-1-butanol was stirred at room temperature over 48 hours. The most of water in the reaction product was removed by a rotary evaporator, and residue water was removed in a drying chamber to acquire yellow solid product. The solid product was put into appropriate amount of acetonitrile. The mixture was refluxed at 80 °C to supersaturate, and was slowly cooled and recrystallized to obtain pure N[1,1,1,4OH]Cl.

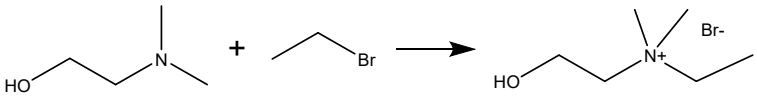
5-Hydroxypentyltrimethylammonium chloride (N[1,1,1,5OH]Cl)



A mixture of 197 g trimethylamine 30 wt.% and 136 g 5-chloro-1-pentanol was stirred at room temperature over 48 hours. The most of water in the reaction product was removed by a rotary evaporator. The concentrated product was then placed in a drying chamber to acquire yellow solid

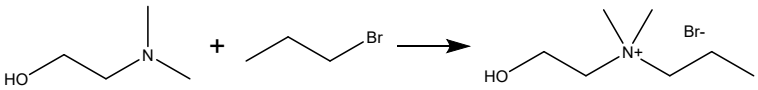
product which was washed with ether to remove residue reactant. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

Ethyl-(2-hydroxyethyl)-dimethylammonium bromide (N[1,1,2,2OH]Br)



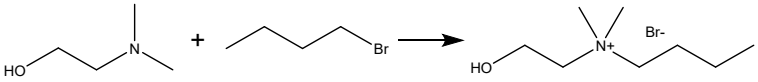
89 g N,N-dimethylethanolamine was added dopy by dopy into a mixture of 200 mL acetonitrile and 109 g bromoethane and stirred at room temperature over 48 hours, and a white solid precipitate was obtained. The precipitate was washed with ether to remove residue reactant and acetonitrile. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

N-propyl-(2-hydroxyethyl)-dimethylammonium bromide (N[1,1,3,2OH]Br)



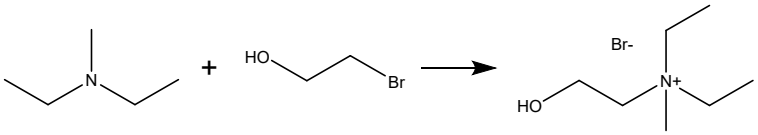
89 g N,N-dimethylethanolamine was added dopy by dopy into a mixture of 200 mL acetonitrile and 123 g 1-bromopropane and stirred at room temperature over 48 hours, and a white solid precipitate was obtained. The precipitate was washed with ether to remove residue reactant and acetonitrile. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

N-butyl-(2-hydroxyethyl)-dimethylammonium bromide (N[1,1,4,2OH]Br)



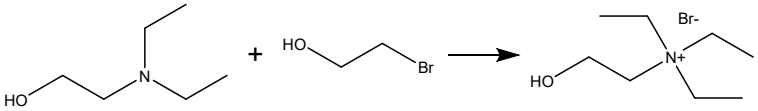
89 g N,N-dimethylethanolamine was added dopy by dopy into a mixture of 200 mL acetonitrile and 137 g 1-bromobutane and stirred at room temperature over 48 hours, and a white solid precipitate was obtained. The precipitate was washed with ether to remove residue reactant and acetonitrile. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

Diethyl-(2-hydroxyethyl)-methylammonium bromide (N[1,2,2,2OH]Br)



87 g N,N-diethylmethylamine was added dopy by dopy into a mixture of 200 mL acetonitrile and 125 g 2-bromoethanol and stirred at room temperature over 48 hours. After the reaction, 300 mL of ether was added to the mixture and stirred to obtain a yellowish solid precipitate. The precipitate was washed with ether to remove residue reactant and acetonitrile. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

Triethyl-(2-hydroxyethyl)-ammonium bromide (N[2,2,2,2OH]Br)



117 g 2-(diethylamino)ethanol was added dopy by dopy into a mixture of 200 mL acetonitrile and 125 g 2-bromoethanol and stirred at room temperature over 48 hours, and a white solid precipitate was obtained. The precipitate was washed with ether to remove residue reactant and acetonitrile. Finally, the pure product was obtained after drying in a vacuum oven at 60 °C for 10 hours.

All synthesized choline derivative structures were analyzed by ^{1}H NMR (Bruker AVANCE III 400 MHz).

Preparation of different polybromide complex

The polybromide complex phase was separated from the bottom of the cathode reservoir after charging for 1 hour at 40 mA cm^{-2} in a ZBFB with 50 mL flowing catholyte and anolyte, respectively. The electrolyte composition was listed in Table S28.

Characterization of polybromide complexes

The digital photos of the polybromide phase were taken after putting it into a low-temperature chamber (LS-225) at different temperatures for over 24 hours.

The changes of phases on 8 kinds of polybromide complexes (except N[1,1,1,5OH]$^+$) were charactered by Differential Scanning Calorimetry (DSC, NETZSCH STA 449 F3) with the temperature change rate of 10 °C min^{-1}. Raman spectroscopy (Bruker SENTERRA) with the 532 nm excitation laser was used to analyze the structure of the polybromide phases. The concentration of bromine on the aqueous phase was detected by UV spectrum (TU-1901) after Iodine-starch test.

Batteries Tests

ZBFBs were assembled with flowing anolyte and nonflow catholyte. The composition of catholyte and anolyte was the same. The anolyte volume was 40 mL. And the cathode electrolyte was impregnated in the carbon felt and sealed in the cathode cavity. Batteries were tested by ARBIN (LBT, America) and NEWARE (CT-4008T-5V12A) charge-discharge systems. 40 mA cm^{-2} and 20 mAh cm^{-2} were set as the battery operating conditions. Specifically, the low-temperature batteries were put into the constant temperature chamber (GDW-050C) for 12 hours with running pump before tests.

Theoretical calculations

Density Functional Theory (DFT) calculations were implemented to optimize the structure and vibration frequency of quaternary ammonium cations and polybromide complexes to obtain the most thermodynamically stable state. The calculations were performed in the Gaussian packages[1] under B3LYP[2] functional with 6-311g(d) basis set, and dispersion correction was implemented. The electronic properties were analyzed by Multifwn after optimization.

Based on the results of single point energies with B3LYP/def2-TZVP, the Molecular polarity index (MPI) was calculated by Multifwn package based on the following formula:

$$MPI = \frac{1}{A}\iint_S |V(r)|\mathit{dS}\#(1)$$

Where *V(r)* refers to the electrostatic potential at *r*, and *A* represents the surface area of molecular.

The solvation free energy (ΔG_{solv}) of polybromide complex was calculated by extended easy solvation estimation (xESE) based on the following formula:[3]

$$\Delta G_{solv} = E_{solv} + \Delta G_{corr}\#(2)$$

where E_{solv} refers to the energy about the general PCM formalism. ΔG_{corr} is thermal correction to Gibbs Free Energy.

The average local ionization energies (ALIE) of O atom on the different cations and polybromide complexes were calculated by Multifwn based on the equation follow:

$$ALIE = \sum_i \frac{\rho_i(r) \cdot |\varepsilon_i|}{\rho(r)} \#(3)$$

Where $\rho_i(r)$ represents the electron density of the *i* molecular orbital at *r*, $|\varepsilon_i|$ was the absolute value of the energy of the *i* molecular orbital, and $\rho(r)$ refers to the total energy of electron density at *r*.

The polybromide complex cluster configurations and their energies were also calculated by DFT. Firstly, 100 initial configurations were randomly generated using the Genmer module in Molclus software, and the energies of them were calculated by semi-empirical quantum chemistry at PM6-D3H4 precision level. Next, the Boltzmann distributions of the configurations were calculated at 298 K according to the energies, and removed the configurations whose probability of Boltzmann distributions was less than 0.01%. The structure and vibrational frequency of the rest cluster configurations were calculated under B3LYP functional with 6-311g(d) basis set. After that the energies of them were calculated under M062x/def2tzvp lever. And the Boltzmann distributions were calculated again to obtain the probabilities of different configurations. Molecular structures with cation-cation HB (C-C HB) configurations were drawn in Table S1-S27.

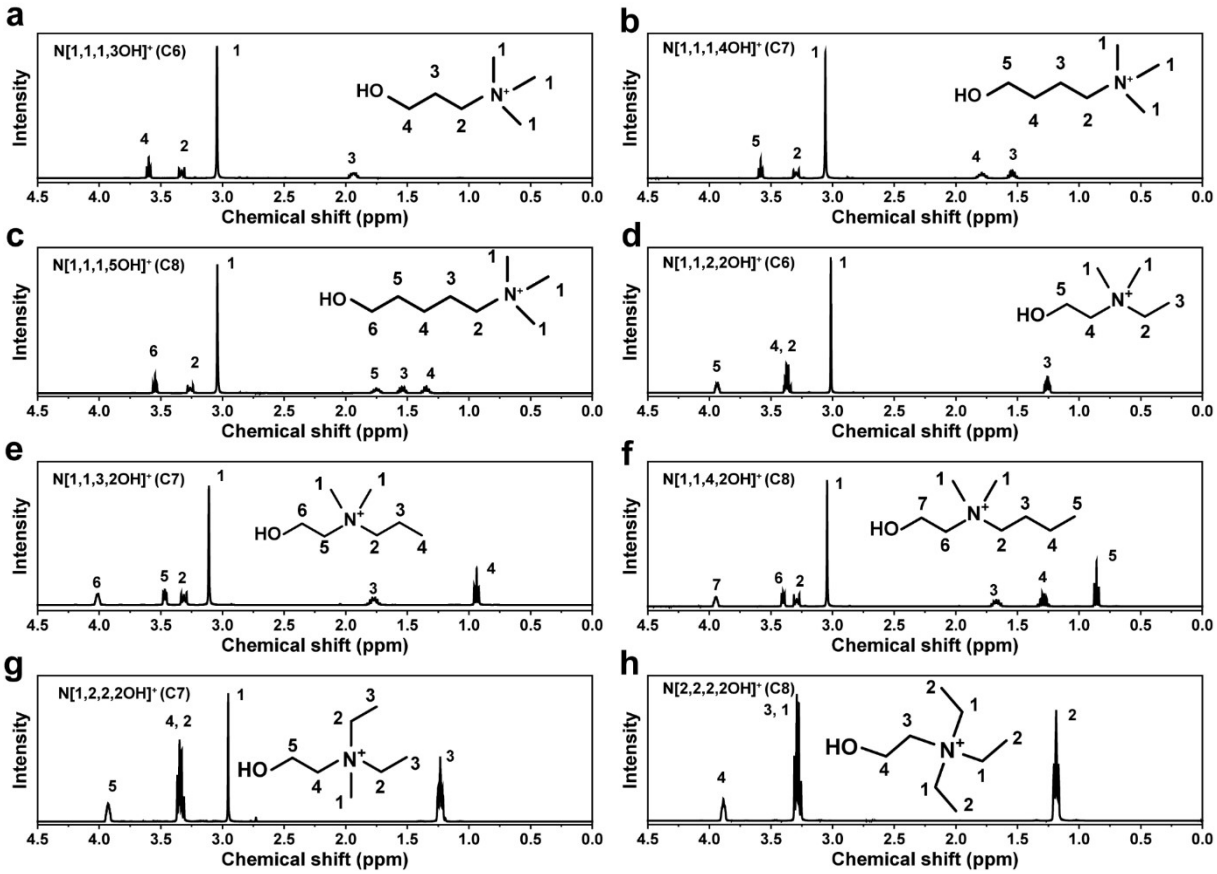


Fig. S1. ^{1}H NMR spectra of choline derivatives.

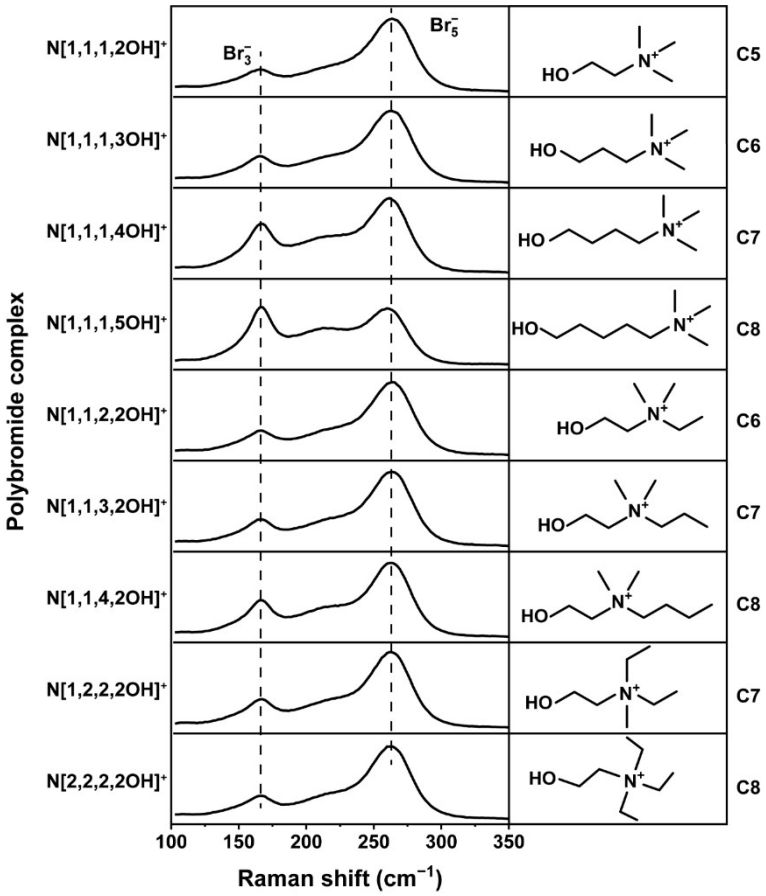


Fig. S2. The Raman spectra of the polybromide complexes with different choline derivatives.

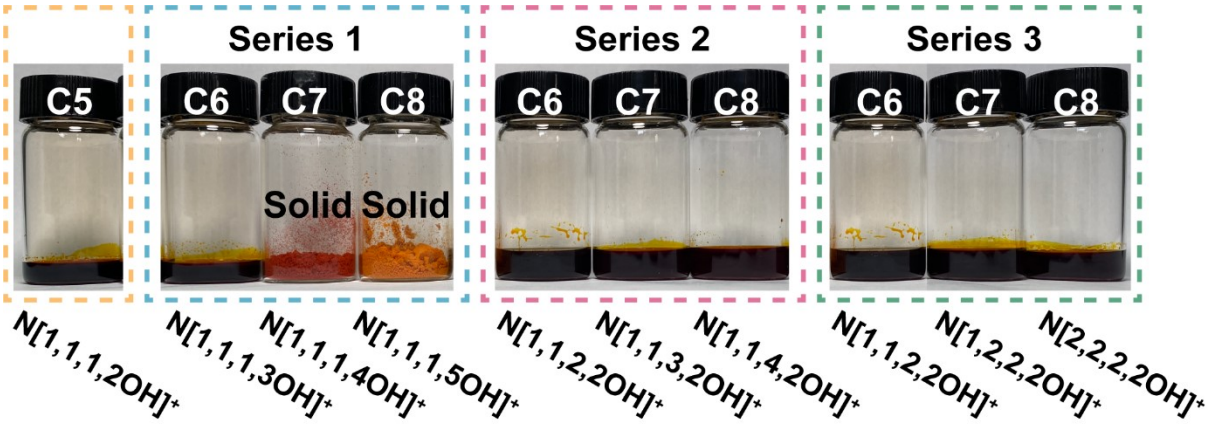


Fig. S3. The digital photos of polybromide complex phase with different choline derivatives at RT.

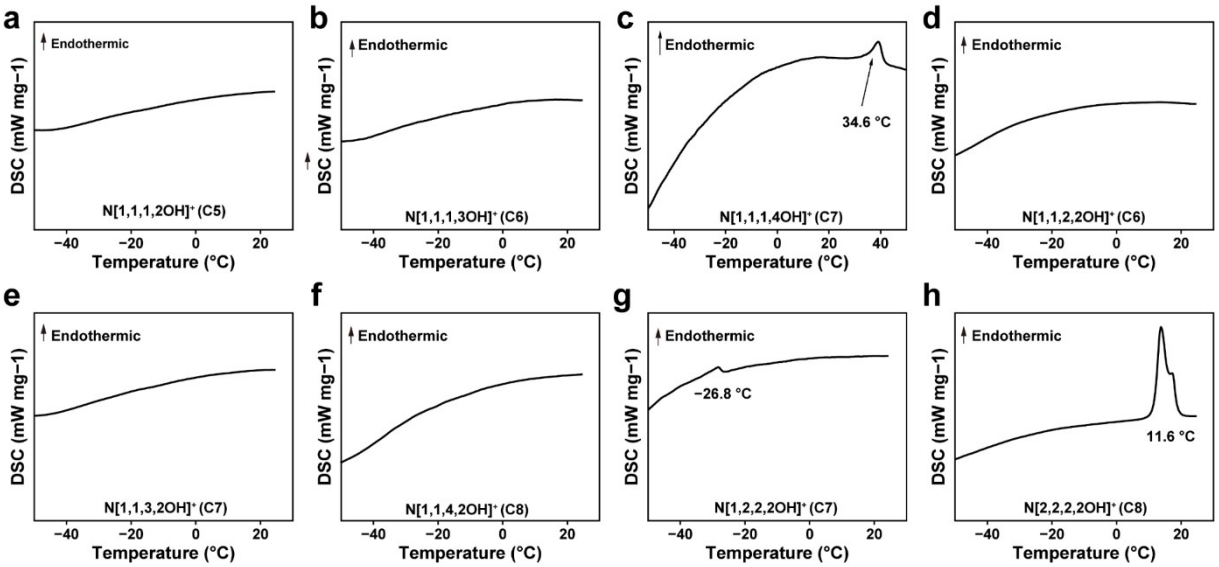


Fig. S4. DSC curves of the polybromide complexes with various choline derivatives ($N[1,1,1,5OH]^+$-polybromide complexes were missing because it would decompose in the high temperature and damage the DSC instrument).

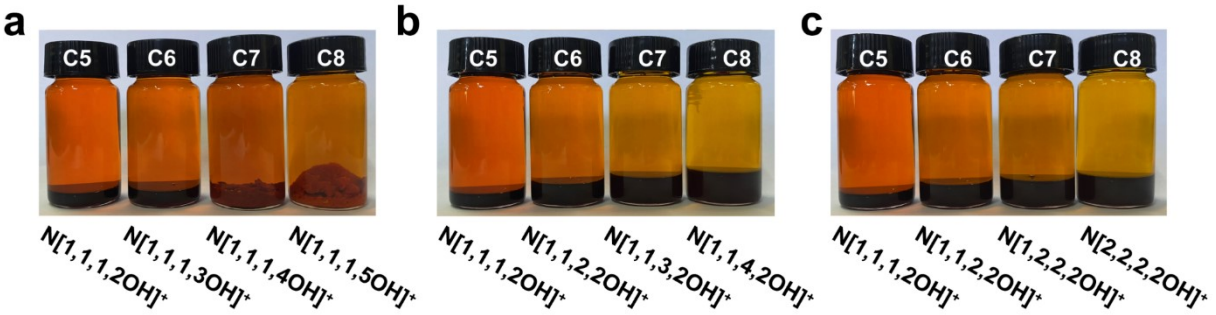


Fig. S5. Digital photo of the catholytes with different choline derivatives. (a) Series 1. (b) Series 2. (c) Series 3.

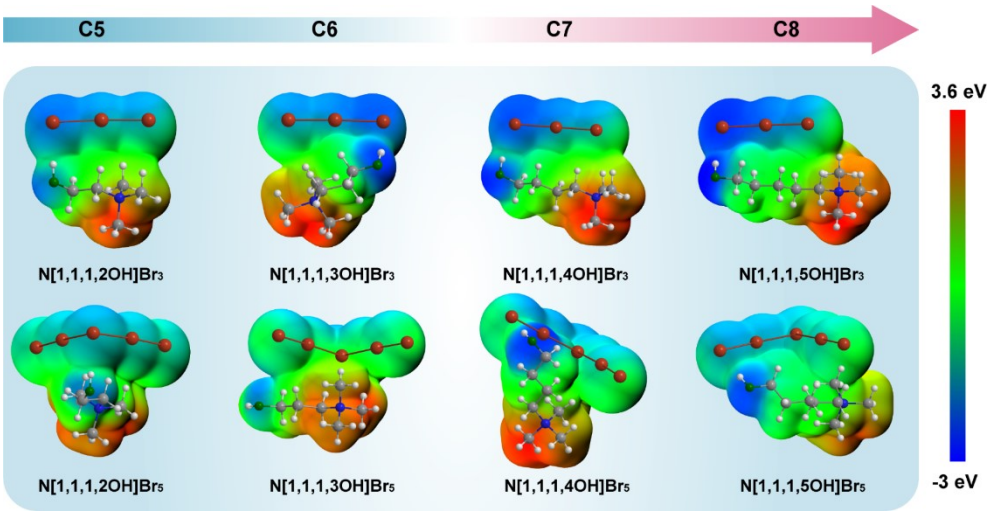


Fig. S6. ESP mapping of polybromide complexes with Series 1.

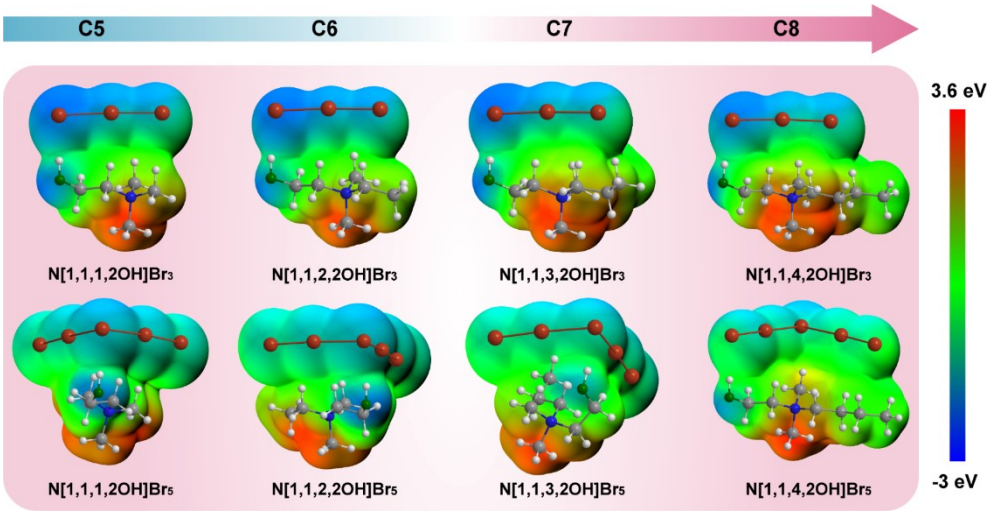


Fig. S7. ESP mapping of polybromide complexes with Series 2.

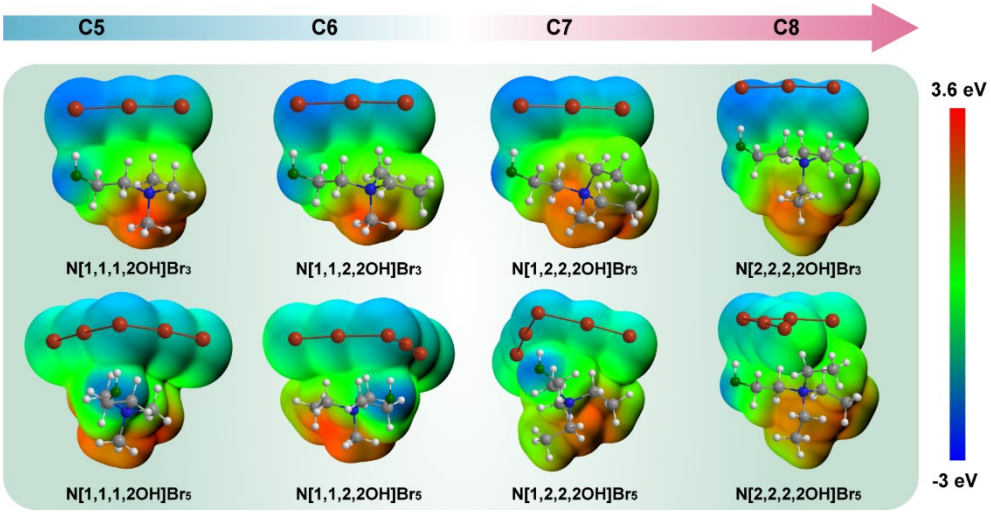


Fig. S8. ESP mapping of polybromide complexes with Series 3.

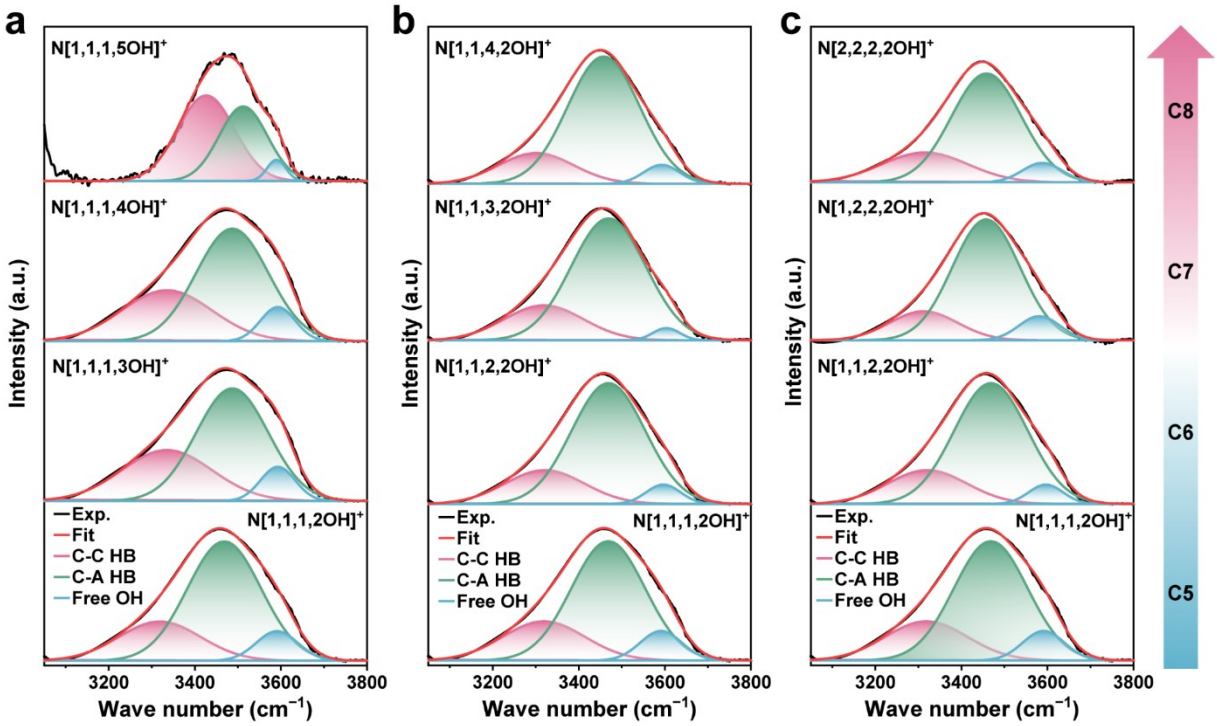


Fig. S9. IR spectrums of different polybromide complex

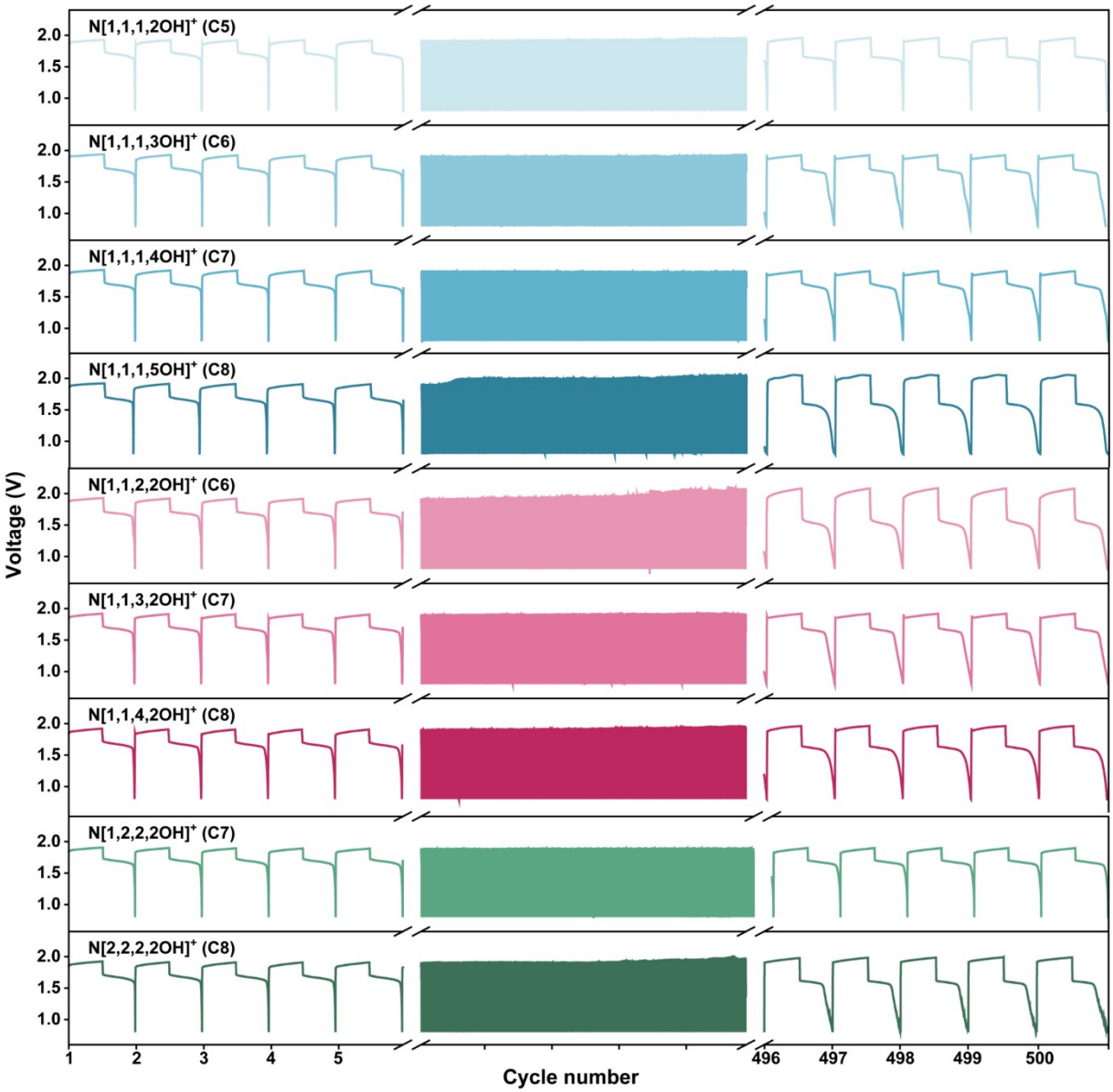


Fig. S10. The charge-discharge curves of ZBFBs with different choline derivatives at RT.

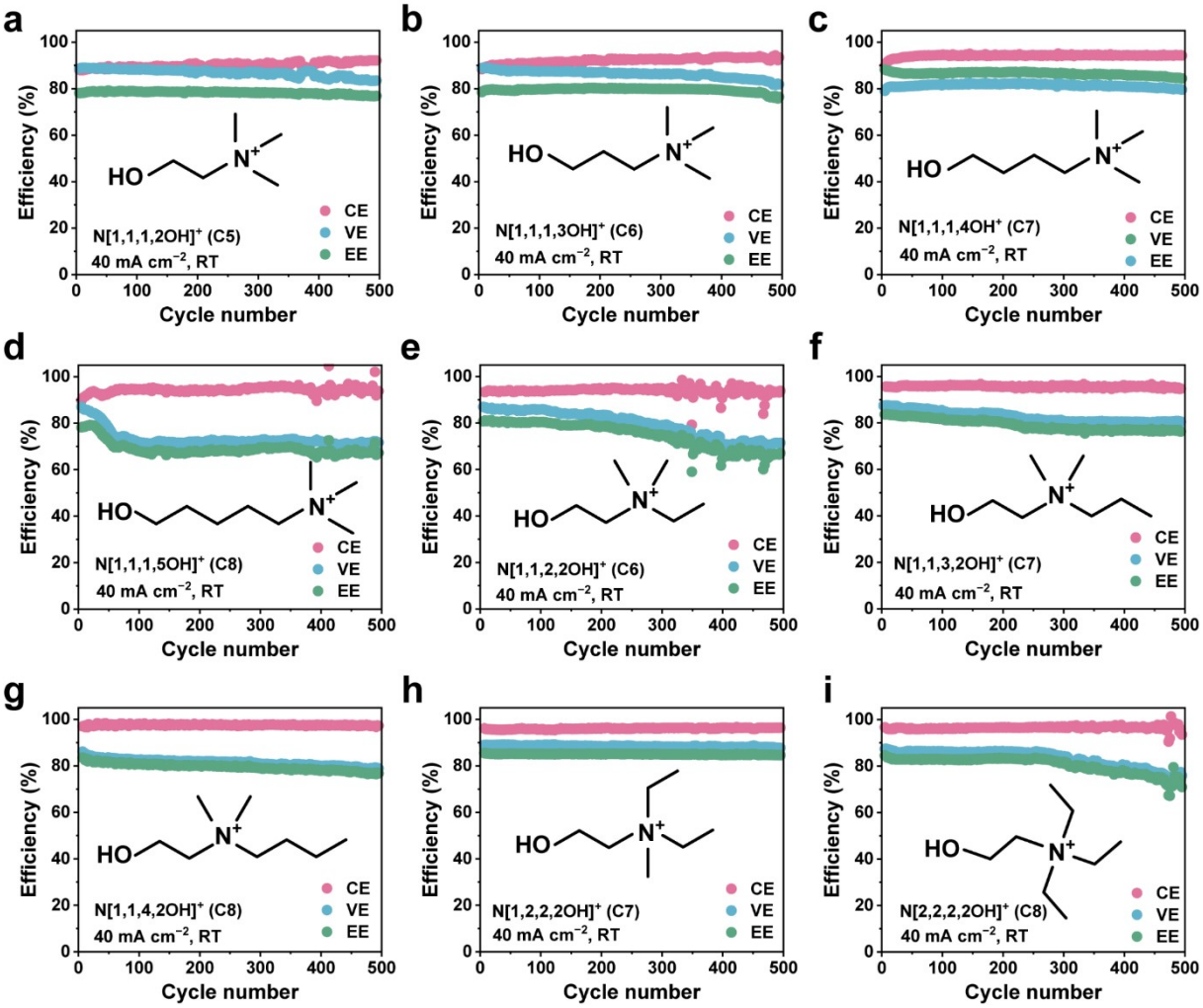


Fig. S11. The cycling performance of ZBFBs with different choline derivatives at RT.

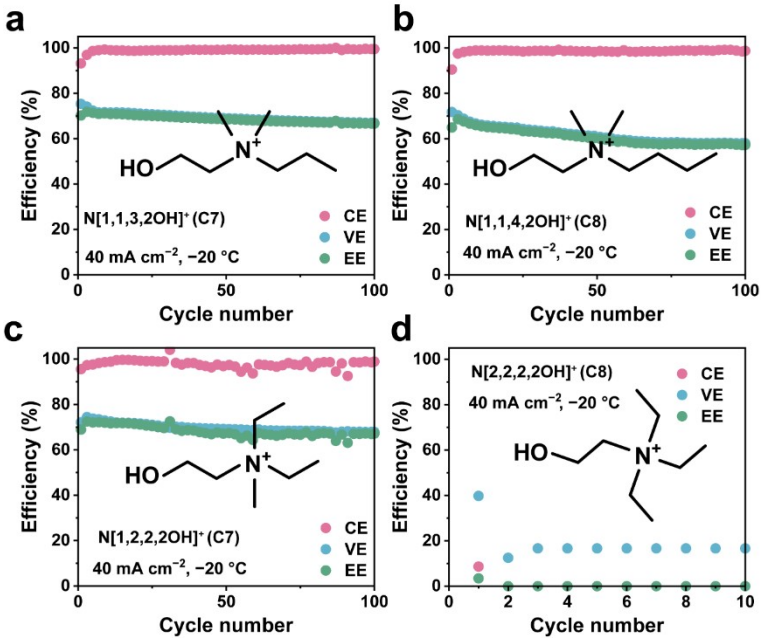


Fig. S12. The cycling performance of ZBFBs with (a) $N[1,1,3,2OH]^+$, (b) $N[1,1,4,2OH]^+$, (c) $N[1,2,2,2OH]^+$ and (d) $N[2,2,2,2OH]^+$ at −20 °C.

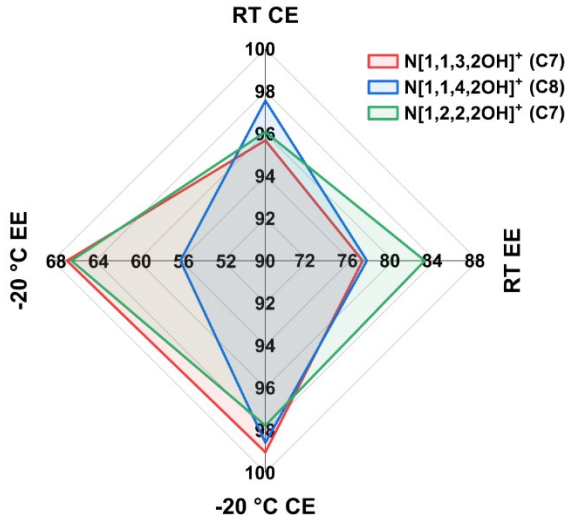


Fig. S13. Performance comparison of ZBFBs with $N[1,1,3,2OH]^+$, $N[1,1,4,2OH]^+$ and $N[1,2,2,2OH]^+$, respectively, at different temperatures.

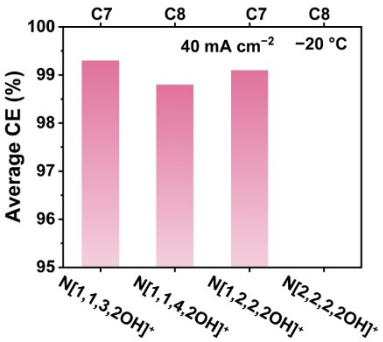
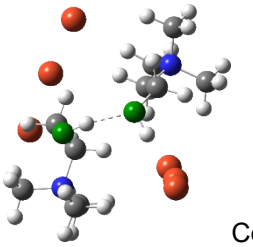


Fig. S14. At −20 °C, the average CE of ZBFBs with $N[1,1,3,2OH]^+$, $N[1,1,4,2OH]^+$, $N[1,2,2,2OH]^+$ and $N[2,2,2,2OH]^+$, respectively.

Table S1. The results of DFT calculations of N[1,1,1,2OH]Br_3-N[1,1,1,2OH]Br_3.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0	91.265	NaN	
2	1.90	3.688	NaN	
3	2.19	2.248	1.915	
4	2.33	1.778	NaN	
5	2.67	1.012	NaN	
6	5.98	0.004	NaN	
7	6.22	0.003	NaN	
8	6.51	0.002	NaN	
9	7.05	0.001	NaN	
Total probability of C-C HB: 2.248%				



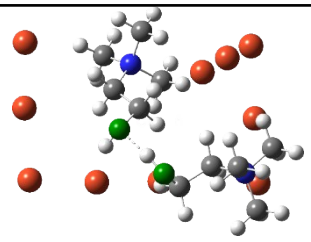
Configuration 1

Table S2. The results of DFT calculations of N[1,1,1,2OH]Br_3-N[1,1,1,2OH]Br_5.

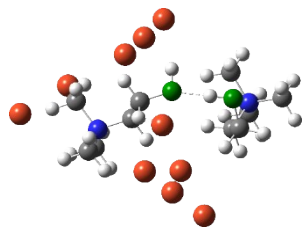
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	99.785	NaN	
2	3.91	0.136	NaN	
3	4.23	0.079	NaN	
Total probability of C-C HB: 0%				

Table S3. The results of DFT calculations of N[1,1,1,2OH]Br_5-N[1,1,1,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	98.852	NaN	
2	2.87	0.78	NaN	
3	3.35	0.348	NaN	
4	5.67	0.007	NaN	
5	6.00	0.004	NaN	
6	6.16	0.003	1.887	
7	6.17	0.003	1.835	
8	6.30	0.002	NaN	
Total probability of C-C HB: 0.006%				



Configuration 6



Configuration 7

Table S4. The results of DFT calculations of N[1,1,1,3OH]Br_3-N[1,1,1,3OH]Br_3.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	99.699	NaN	
2	3.52	0.264	NaN	
3	4.68	0.037	NaN	
Total probability of C-C HB: 0%				

Table S5. The results of DFT calculations of N[1,1,1,3OH]Br_3-N[1,1,1,3OH]Br_5.

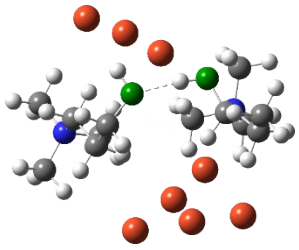
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	91.213	NaN	
2	1.63	5.866	NaN	
3	2.53	1.277	NaN	
4	2.62	1.098	NaN	
5	3.48	0.256	1.801	 Configuration 5
6	3.78	0.154	NaN	
7	4.24	0.071	NaN	
8	4.50	0.046	NaN	
9	5.17	0.015	NaN	
10	5.87	0.005	NaN	
Total probability of C-C HB: 0.256%				

Table S6. The results of DFT calculations of N[1,1,1,3OH]Br_5-N[1,1,1,3OH]Br_5.

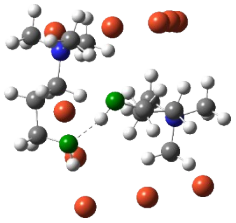
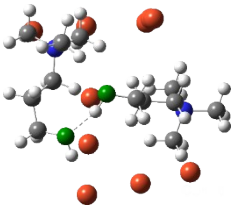
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	42.801	NaN	
2	0.01	42.169	NaN	
3	0.83	10.504	1.823	 Configuration 3
4	2.16	1.117	NaN	
5	2.17	1.103	NaN	
6	2.25	0.96	1.838	 Configuration 6
7	2.50	0.628	NaN	
8	3.08	0.238	NaN	
9	3.28	0.167	NaN	
10	3.58	0.102	NaN	
11	3.92	0.057	NaN	
12	3.94	0.056	NaN	
13	3.94	0.055	NaN	
14	4.16	0.038	NaN	
15	5.58	0.003	NaN	
16	6.08	0.001	NaN	
Total probability of C-C HB: 11.464%				

Table S7. The results of DFT calculations of N[1,1,1,4OH]Br_3-N[1,1,1,4OH]Br_3.

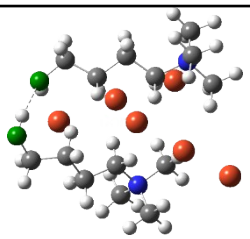
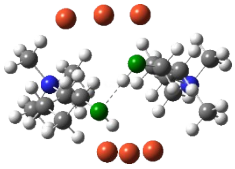
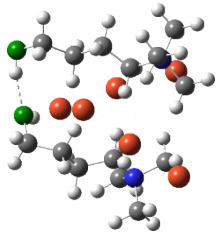
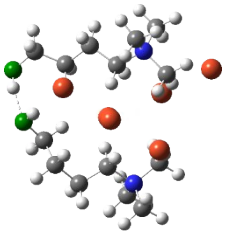
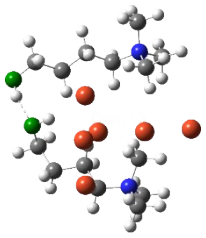
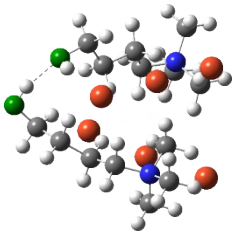
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	69.28	NaN	
2	0.76	19.131	NaN	
3	1.43	6.238	1.977	 Configuration 3
4	1.99	2.411	NaN	
5	2.27	1.498	NaN	
6	2.74	0.684	1.914	
7	3.05	0.402	1.861	
8	3.30	0.264	1.930	 Configuration 6
9	4.03	0.077	NaN	
10	5.58	0.006	NaN	
11	5.79	0.004	NaN	
12	6.08	0.002	NaN	
13	6.12	0.002	1.853	
14	6.50	0.001	1.958	 Configuration 7
				 Configuration 8
		Total probability of C-C HB: 7.591%		 Configuration 13
				 Configuration 14

Table S8. The results of DFT calculations of N[1,1,1,4OH]Br_3-N[1,1,1,4OH]Br_5.

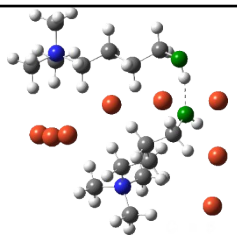
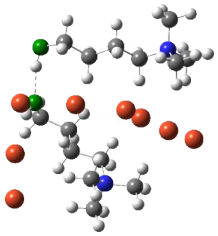
Configuration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	71.514	NaN	 Configuration 5
2	0.78	19.075	NaN	
3	1.27	8.36	NaN	
4	3.03	0.427	NaN	
5	3.30	0.275	1.794	
6	3.30	0.274	1.795	
7	4.22	0.057	NaN	 Configuration 6
8	5.45	0.007	NaN	
9	5.60	0.006	NaN	
10	5.84	0.004	NaN	
11	6.78	0.001	NaN	
Total probability of C-C HB: 0.549%				

Table S9. The results of DFT calculations of N[1,1,1,4OH]Br_5-N[1,1,1,4OH]Br_5.

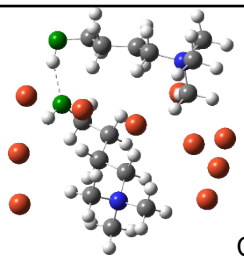
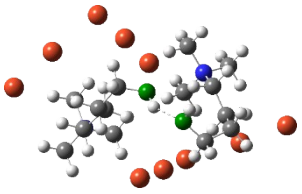
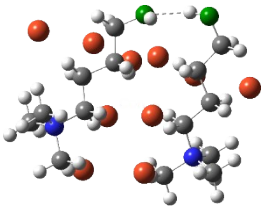
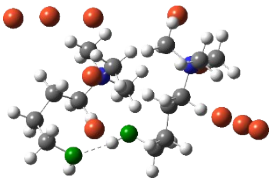
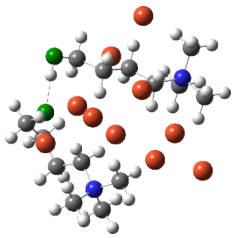
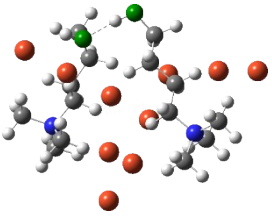
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	80.84	NaN	 Configuration 5
2	1.53	6.109	NaN	
3	1.53	6.086	NaN	
4	1.91	3.193	NaN	
5	2.33	1.583	1.886	
6	2.79	0.727	NaN	
7	2.86	0.652	1.894	 Configuration 7
8	3.24	0.342	1.998	
9	3.44	0.244	NaN	
10	4.22	0.065	1.892	 Configuration 8
11	4.30	0.057	1.805	
12	4.30	0.057	1.805	 Configuration 10
13	4.45	0.044	NaN	
		Total probability of C-C HB: 2.937%		 Configuration 11
				 Configuration 12

Table S10. The results of DFT calculations of N[1,1,1,5OH]Br_3-N[1,1,1,5OH]Br_3.

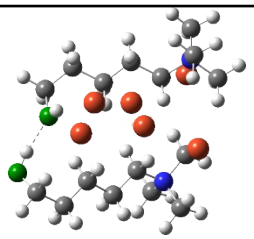
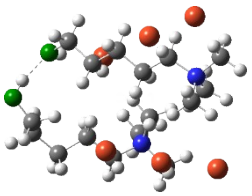
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	56.903	NaN	 Configuration 2
2	0.17	42.929	1.806	
3	4.02	0.065	NaN	
4	4.43	0.032	NaN	
5	4.50	0.029	NaN	
6	4.55	0.026	1.851	
7	5.24	0.008	NaN	
8	5.47	0.006	NaN	
9	6.20	0.002	NaN	
Total probability of C-C HB: 42.955%				 Configuration 6

Table S11. The results of DFT calculations of N[1,1,1,5OH]Br_3-N[1,1,1,5OH]Br_5.

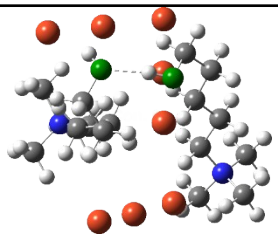
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	49.431	NaN	 Configuration 2
2	0.39	25.537	1.851	
3	0.41	24.678	NaN	
4	2.93	0.351	NaN	
5	5.67	0.003	NaN	
Total probability of C-C HB: 25.537%				

Table S12. The results of DFT calculations of N[1,1,1,5OH]Br_5-N[1,1,1,5OH]Br_5.

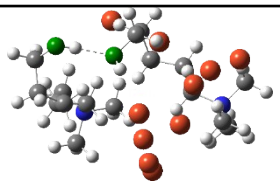
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	63.1	NaN	
2	0.46	29.192	1.839	
3	1.25	7.691	NaN	
4	4.87	0.017	NaN	
				Configuration 2
		Total probability of C-C HB: 29.192%		

Table S13. The results of DFT calculations of N[1,1,2,2OH]Br_3-N[1,1,2,2OH]Br_3.

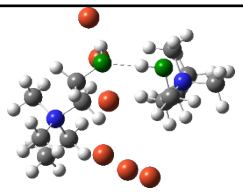
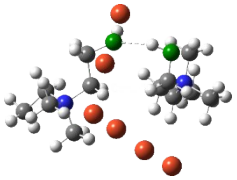
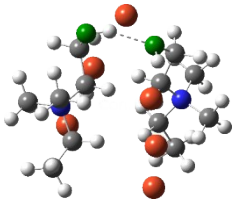
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	72.28	NaN	
2	0.98	13.896	NaN	
3	0.98	13.817	NaN	
4	5.94	0.003	1.857	
5	6.22	0.002	2.039	Configuration 4
6	6.76	0.001	NaN	
7	6.98	0.001	1.952	
				Configuration 5
		Total probability of C-C HB: 0.006%		
				Configuration 7

Table S14. The results of DFT calculations of N[1,1,2,2OH]Br_3-N[1,1,2,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	87.63	NaN	
2	1.21	11.32	NaN	
3	3.13	0.444	NaN	
4	3.19	0.402	NaN	
5	3.64	0.187	NaN	
6	5.31	0.011	NaN	
7	5.75	0.005	NaN	
Total probability of C-C HB: 0%				

Table S15. The results of DFT calculations of N[1,1,2,2OH]Br_5-N[1,1,2,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	99.131	NaN	
2	2.81	0.865	NaN	
3	6.08	0.003	NaN	
Total probability of C-C HB: 0%				

Table S16. The results of DFT calculations of N[1,1,3,2OH]Br_3-N[1,1,3,2OH]Br_3.

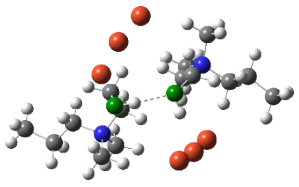
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	99.604	NaN	
2	6.44	0.002	NaN	
3	3.29	0.387	NaN	
4	5.70	0.006	NaN	
5	9.82	0.001	1.966	 Configuration 5
Total probability of C-C HB: 0.001%				

Table S17. The results of DFT calculations of N[1,1,3,2OH]Br_3-N[1,1,3,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	98.09	NaN	
2	2.52	1.401	NaN	
3	3.44	0.295	NaN	
4	3.76	0.173	NaN	
5	4.62	0.04	NaN	
6	7.06	0.001	NaN	
Total probability of C-C HB: 0%				

Table S18. The results of DFT calculations of N[1,1,3,2OH]Br_5-N[1,1,3,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	41.626	NaN	
2	0.04	38.994	NaN	
3	0.65	13.783	NaN	
4	1.65	2.557	NaN	
5	1.96	1.511	NaN	
6	2.36	0.773	NaN	
7	2.43	0.69	NaN	
8	3.81	0.067	NaN	
Total probability of C-C HB: 0%				

Table S19. The results of DFT calculations of N[1,1,4,2OH]Br_3-N[1,1,4,2OH]Br_3.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	97.279	NaN	
2	2.53	1.358	NaN	
3	2.53	1.352	NaN	
4	5.76	0.006	1.966	
5	6.06	0.004	NaN	
6	6.67	0.001	NaN	Configuration 4
Total probability of C-C HB: 0.006%				

Table S20. The results of DFT calculations of N[1,1,4,2OH]Br_3-N[1,1,4,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	42.004	NaN	
2	0.01	41.316	NaN	
3	0.57	16.116	NaN	
4	2.89	0.319	NaN	
5	3.59	0.099	NaN	
6	3.64	0.09	NaN	
7	4.31	0.029	NaN	
8	4.38	0.026	NaN	
9	6.09	0.001	NaN	
Total probability of C-C HB: 0%				

Table S21. The results of DFT calculations of N[1,1,4,2OH]Br_5-N[1,1,4,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	79.305	NaN	
2	0.80	20.514	NaN	
3	3.60	0.181	NaN	
Total probability of C-C HB: 0%				

Table S22. The results of DFT calculations of N[1,2,2,2OH]Br_3-N[1,2,2,2OH]Br_3.

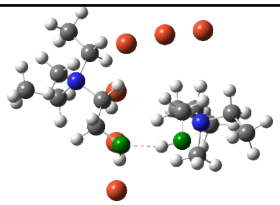
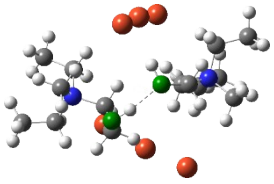
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	99.946	NaN	 Configuration 2
2	4.91	0.025	1.916	
3	6.36	0.002	1.886	
4	6.51	0.002	NaN	
Total probability of C-C HB: 0.027%				 Configuration 3

Table S23. The results of DFT calculations of N[1,2,2,2OH]Br_3-N[1,2,2,2OH]Br_5.

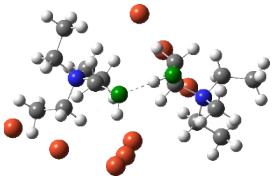
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	90.825	NaN	
2	1.76	4.62	NaN	
3	2.09	2.667	NaN	
4	2.32	1.809	NaN	
5	4.21	0.075	1.908	 Configuration 5
6	6.09	0.003	NaN	
7	6.69	0.001	NaN	
Total probability of C-C HB: 0.075%				

Table S24. The results of DFT calculations of N[1,2,2,2OH]Br_5-N[1,2,2,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	73.051	NaN	
2	1.03	12.857	NaN	
3	1.14	10.707	NaN	
4	1.82	3.385	NaN	
Total probability of C-C HB: 0%				

Table S25. The results of DFT calculations of N[2,2,2,2OH]Br_3-N2,2,2,2OH]Br_3.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	36.538	NaN	
2	0.00	36.53	NaN	
3	0.19	26.37	NaN	
4	2.47	0.561	NaN	
5	6.48	0.001	NaN	
Total probability of C-C HB: 0%				

Table S26. The results of DFT calculations of N[2,2,2,2OH]Br_3-N[2,2,2,2OH]Br_5.

Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	68.778	NaN	
2	0.98	13.237	NaN	
3	1.03	12.118	NaN	
4	1.89	2.85	NaN	
5	2.16	1.81	NaN	
6	2.44	1.123	NaN	
7	4.03	0.077	NaN	
8	5.47	0.007	NaN	
Total probability of C-C HB: 0%				

Table S27. The results of DFT calculations of N[2,2,2,2OH]Br_5-N[2,2,2,2OH]Br_5.

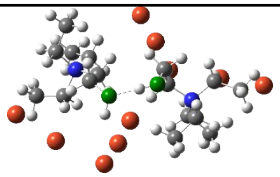
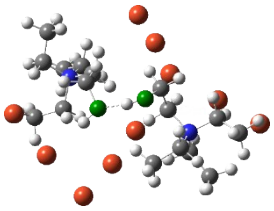
Config-uration	$\Delta E_{rel.}$ (kcal mol^{-1})	The probability of the Boltzmann distribution (%)	C-C HB length (Å)	Structure of the configuration with C-C HB
1	0.00	80.798	NaN	
2	0.96	15.906	NaN	
3	2.00	2.76	1.805	
4	3.08	0.45	NaN	
5	4.19	0.068	1.854	Configuration 3
6	4.98	0.018	NaN	
Total probability of C-C HB: 2.828%				Configuration 5

Table S28. Composition of electrolytes with different choline-based complexing agents.

Electrolyte composition	Abbreviation
2 M $ZnBr_2$ + 2.4 M KCl + 0.6 M KBr + 0.6 M N[1,1,1,2OH]Cl	N[1,1,1,2OH]-electrolyte
2 M $ZnBr_2$ + 2.4 M KCl + 0.6 M KBr + 0.6 M N[1,1,1,3OH]Cl	N[1,1,1,3OH]-electrolyte
2 M $ZnBr_2$ + 2.4 M KCl + 0.6 M KBr + 0.6 M N[1,1,1,4OH]Cl	N[1,1,1,4OH]-electrolyte
2 M $ZnBr_2$ + 2.4 M KCl + 0.6 M KBr + 0.6 M N[1,1,1,5OH]Cl	N[1,1,1,5OH]-electrolyte
2 M $ZnBr_2$ + 3 M KCl + 0.6 M N[1,1,2,2OH]Br	N[1,1,2,2OH]-electrolyte
2 M $ZnBr_2$ + 3 M KCl + 0.6 M N[1,1,3,2OH]Br	N[1,1,3,2OH]-electrolyte
2 M $ZnBr_2$ + 3 M KCl + 0.6 M N[1,1,4,2OH]Br	N[1,1,4,2OH]-electrolyte
2 M $ZnBr_2$ + 3 M KCl + 0.6 M N[1,2,2,2OH]Br	N[1,2,2,2OH]-electrolyte
2 M $ZnBr_2$ + 3 M KCl + 0.6 M N[2,2,2,2OH]Br	N[2,2,2,2OH]-electrolyte

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