Electronic Supplementary Information (ESI)

Covalent Conjugation of 'Hydroxide-Philic' Functional Group Achieving 'Hydroxide-Phobic' TEMPO with Superior Stability in All-Organic Aqueous Redox Flow Battery

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Experimental

Chemicals

All solutions were prepared with deionized Milli-Q water. Sodium hydroxide (NaOH), perchloric acid (HClO₄, 60%), and sodium nitrate (NaNO₃) were purchased from Daejung Chemicals (Siheung, Korea). 4-hydroxy-TEMPO (free radical) and 4,4-bipyridyl were purchased from Alfa Aesar. Chloroacetyl chloride, IRA-900(chloride form), hydrochloric acid (HCl, 37%), and sodium chloride (NaCl) were purchased from Sigma-Aldrich. 1-methylimidazole and 1,3-dibromopropane, trimethylamine were purchased from TCI. Unless otherwise noted, all chemicals were purchased and used without further purification.

Synthesis of MIMAcO-TEMPO



4-hydroxy TEMPO (300 mmol, 51.6 g) was dissolved in dichloromethane (600 mL) at room temperature. Then, the solution was cooled at 0 °C and chloroacetyl chloride (330 mmol, 26.2 mL) was added to the solution dropwise. The mixture was stirred at room temperature for 4 hours. After the reaction had completed, the reaction mixture was extracted with ethyl acetate (300 mL x 3 times), and washed with H₂O (500 mL x 3 times) and brine (300 ml). The combined organic extracts were dried over anhydrous MgSO₄, and then filtered and concentrated *in vacuo*. Purification via silica column chromatography with gradient condition

(Hex 100 ~ Hex:EA=4:1) led to the production of 4-(2-chloroacetoxy)-TEMPO as a red solid (63.2 g, 85% yield). 4-(2-Chloroacetoxy)-TEMPO and 1-methylimidazole were stirred in acetonitrile at 60 °C for 2 days. The reaction mixture was concentrated *in vacuo* and diluted in water (300 mL). The water layer was washed with ethyl acetate (300 mL x 3 times) and concentrated *in vacuo* to yield MIMAcO-TEMPO as a red solid (71.7 g, 85 %yield).

[4-(2-Chloroacetoxy)-TEMPO] ¹H NMR (500 MHz, DMSO-*d*₆) δ 5.03 – 4.89 (m, 1H), 4.30 (s, 2H), 1.90 – 1.78 (m, 2H), 1.42 (t, *J* = 11.7 Hz, 2H), 1.04 (d, *J* = 6.4 Hz, 12H). EI-MS (m/z)= 248, 154, 139, 124, 109.

[MIMAcO-TEMPO] ¹H NMR (500 MHz, DMSO- d_6) δ 9.26 (s, 1H), 7.79 – 7.70 (m, 2H), 5.28 (s, 2H), 5.02 (tt, J = 11.4, 4.2 Hz, 1H), 3.86 (s, 3H), 1.87 (dd, J = 12.2, 4.1 Hz, 2H), 1.48 (t, J = 11.8 Hz, 2H), 1.07 (d, J = 14.1 Hz, 12H). HRMS (FAB+ mode) calculated for C₁₅H₂₅N₃O₃ [M-Cl]⁺: 295.1895. found: 295.1893.

Synthesis of 4-[4-(N-methylimidazolium)-benzyl-oxyl]-2,2,6,6-tetramethyl piperidine-1-oxyl chloride



4-[4-(*N*-methylimidazolium)-benzyl-oxyl]-2,2,6,6-tetramethyl piperidine-1-oxyl chloride was synthesized according to the procedure in the previous literature.¹ In the procedure, α, α' -dichloro-*p*-xylene was used instead of α, α' -dibromo-*p*-xylene.

¹H NMR (500 MHz, DMSO-*d*₆) δ 9.34 (s, 1H), 7.79 (t, *J* = 1.8 Hz, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 5.42 (s, 2H), 4.49 (s, 2H), 3.85 (s, 3H), 3.67 (tt, *J* = 11.0, 4.0 Hz, 1H), 1.92 (ddd, *J* = 11.0, 4.1, 1.7 Hz, 2H), 1.32 (t, *J* = 11.6 Hz, 2H), 1.06 (d, *J* = 28.2 Hz, 13H). LC-MS: [M-C1]⁺=357.1

Synthesis of BTMAP-Vi



1,1'-bis(3-(trimethylammonio)propyl)-[4,4'-bipyridine]-1,1'-diium tetrachloride (BTMAP-Vi) was synthesized according to the procedure in the previous literature.² ¹H NMR (500 MHz, D₂O) δ 9.22 (d, *J* = 7.0 Hz, 2H), 8.70 – 8.58 (m, 2H), 4.94 – 4.84 (m, 2H), 3.67 – 3.55 (m, 2H), 3.21 (s, 9H), 2.75 – 2.64 (m, 2H).

Computational Details

All DFT calculations were performed using the ORCA 5.0.1 quantum chemistry package, at the PBE0/6-31+G(d,p) level of theory for both structural optimization and Gibbs free energy calculation.³⁻⁸ To account for the solvated environment, the conductor-like polarizable continuum model (CPCM) was used with a dielectric constant set to that of water.⁹ Unrestricted Hartree-Fock (UHF) calculations were performed for each of the systems to obtain singlet and triplet state energy. Structural optimization was carried out using the BFGS algorithm, and the default convergence criterion was implemented in ORCA (energy change tolerance 5.0e-06 Eh, maximum gradient 3.0e-04 Eh/bohr, RMS gradient tolerance 4.0e-04 Eh/bohr, Maximum displacement 4.0e-03 bohr, RMS displacement 2.0-03 bohr).

Permeability Studies

An H-type cell was used to measure the permeability of MIMAcO-TEMPO and 4-OH-

TEMPO. 50 mL of 0.2 M TEMPO derivative and 0.2 M NaCl solution were placed into the concentrate and dilute chambers, respectively. An anion exchange membrane (Selemion[®] AMVN) with active interfacial area of 3.12 cm² was located between the concentrate and dilute chambers. Concentration gradients around the membrane were minimized by continuously stirring each chamber throughout the test period. To quantify the TEMPO derivatives permeating from the concentrate chamber to the dilute chamber, 4 ml of solution was sampled from the dilute chamber; then, its TEMPO concentration was measured using a UV-Vis. spectrophotometer (Mega-800, Scinco). The permeability can be calculated from the concentration of TEMPO derivatives in the dilute chamber as a function of test time:

$$P = -\frac{V\delta}{2At} \ln\left(1 - \frac{2C_d}{C_0}\right)$$

where P is permeability of each TEMPO derivative through the membrane, C_0 is the initial TEMPO concentration (0.2 M) in the concentrate chamber, C_d is the TEMPO concentration in the dilute chamber, V is the volume of solution in each chamber (50 mL), A and δ are the surface area (3.12 cm²) and thickness (100 µm) of the membrane, and t stands for the test time.

Electrochemical Measurements

Cyclic Voltammetry (CV) was carried out in a home-made three-electrode system using a potentiostat (VSP, BioLogic). Graphite bipolar plates (Morgan) were used as working and counter electrodes, each adjacent to copper current collectors. By covering the graphite electrode with a PVC gasket with a hole in it, the active surface area of the working electrode was kept constant at 0.187 cm². Ag/AgCl (3M NaCl) was used as the reference electrode. CV data were obtained at scan rates in a range of 2 - 100 mV/s. For electrochemical impedance spectra (EIS) analysis, an AC voltage of 10 mV amplitude with 100 mHz – 1 MHz frequency

range was applied. EIS data was recorded at open circuit voltage in a 50 mM TEMPO derivative and 1.0 M NaCl solution. Glassy carbon was used as working electrode to clearly indicate differences in charge-transfer behavior. Its active surface area was kept constant at 0.196 cm². Linear sweep voltammetry (LSV) was conducted on a glassy carbon rotating disk electrode at rotating speeds from 100 to 2500 rpm in 0.5 M NaCl solutions containing either 1 mM MIMAcO-TEMPO or the same concentration of 4-OH-TEMPO. For the LSV analysis, the potential was scanned from 0.3 to 1.2 V at 5 mV/s. The limiting currents (*i.e.* the mass transport-limited current) were obtained at 1.0 V and plotted over the square root of the rotating speed. The data were fitted to yield a straight Levich plot, with the slope (*i_L*) defined by the Levich equation (equation 1).¹⁰

$$i_L = 0.620 FAC_0 D^{2/3} \omega^{1/2} v^{-1/6} \tag{1}$$

where n = 1 is the electron number for electro-oxidation of TEMPO, F = 96485 C mol⁻¹ is the Faraday's constant, A is the electrode area, C_0 and D are the bulk concentration and diffusion coefficient of TEMPO, w is the angular rotation rate of the electrode, and v is the kinematic viscosity, which are estimated to 0.0383 and 0.0426 cm²/s for 4-OH-TEMPO and MIMAcO-TEMPO, respectively. The kinetic currents (i_k) were obtained at the different electrode potentials from the Koutecký–Levich equation described as equation 2, where i is the measured current.

$$1/i = \frac{1}{i_k} + \frac{1}{(0.620FAC_0 D^{2/3} \omega^{1/2} v^{-1/6})}$$
(2)

Then, $\log i_k$ vs. $|E-E^0|$ plot was constructed from the equation 3 and shown in Figure 3b of the revised manuscript.¹¹

$$\log i_k = \log i_0 + \alpha F(|E - E^{0'}|)/2.303RT$$
(3)

Where i_0 is the exchange current, *R* is the gas constant, and *T* is the absolute temperature. From the *y*-intercept of the plot in Figure 3b, i_0 was estimated, which is defined as follows.

$$i_0 = FAC_0 k_0 \tag{4}$$

Where, k_0 is the electron transfer rate constant for electro-oxidation of 4-OH-TEMPO and MIMAcO-TEMPO. To analyze the electrochemical behavior on an ultramicroelectrode (UME), a platinum UME with a radius of 5 µm was applied as a working electrode. Electrochemical measurements were conducted in a home-built Faraday cage at room temperature. Voltammetric simulations were performed using DigiElch Professional v6.F software (ElchSoft.com).

Characterizations

UV-Vis. spectra were measured with a spectrometer (Mega-800, Scinco) using a cuvette cell with 1.0 cm width. UV-Vis. absorption profile was obtained in a wavelength range of 300 nm ~ 600 nm. The sampling interval was set at 1 nm. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a JEOL (500 MHz) spectrometer and Bruker AVANCE NEO Nanobay (9.4 T) spectrometer using the solvent peak as an internal reference (DMSO-d6 or D2O). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (J) are reported in Hertz (Hz). GC-MS(EI) analysis was conducted on a GC-MSD system (HP6890 Gas Chromatography, HP5973 Mass Selective Detector, Agilent Technologies). LC-MS(ESI) analysis was conducted on an HP1100 HPLC System (Agilent6130 Single quadrupole LC/MS, Diode Array Detector, Ion source: ESI, Mass range: m/z 2~3,000.).

Flow Battery Tests

AORFB single flow cells consisting of felt electrodes, graphite bipolar plates, copper current

collectors, polytetrafluoroethylene flow frames, and a sheet of anion exchange membrane (Selemion® AMVN, 100 um thickness) were assembled for the charge-discharge test. A piece of carbon felt (XF-30A, Toyobo, 4.3 mm thickness), with surface area of 35 cm², was used as the negative and positive electrodes. Carbon felts were mounted in polytetrafluoroethylene flow frames with a thickness of 3 mm and fixed at a compression ratio of about 30%. Graphite bipolar plates (Sigracell TF6, SGL Carbon, 0.6 mm thickness) served to electrically connect the felt electrode and the copper current collector, preventing the current collector from being corroded by the electrolyte. The membrane was soaked in 3 M NaCl solution for at least 24 hours prior to cell assembly. The single cell was connected to the external electrolyte reservoir by Tygon tubes (Tygon® Chemical, Masterflex). Electrolytes were circulated at a constant flow rate of 100 mL/min using a peristaltic pump (Masterflex pump, Cole-Parmer). 40 ml of TEMPO catholyte was combined with an excess volume of BTMAP-Vi (80 mL ~ 135 mL) to exclude the effect of anolyte-derived capacity loss. The molar ratio of TEMPO to BTMAP-Vi was adjusted to approximately 1:2 (Table S5). Furthermore, to minimize the effect of SoC imbalance between the catholyte and anolyte, half the volume of the catholyte (20 ml) was replaced with discharged TEMPO solution after the 1st charge process. While the catholyte was charged and discharged in the SoC range of $0 \sim 100\%$, the analyte SoC changed in a range of 25% ~ 75%. All electrolytes were prepared in an Ar filled glovebox, using N₂-purged DI water as solvent to eliminate the dissolved oxygen in the electrolytes. Charge-discharge performances of AORFBs were tested using a Maccor Series 400 battery test system in the Ar filled glovebox. The rate performance was tested at current densities of 20 to 100 mA/cm² with an increment of 20 mA/cm². For the cycling test, the AORFB cells were operated within a voltage cut-off of 0.8-1.4 V at current density of 40 mA/cm².



Figure S1. UV-Vis spectra of (a) 4-OH-TEMPO· and (b) 4-OH-TEMO⁺ dissolved in 0.2 M NaCl solution under argon atmosphere at room temperature. The initial concentration of 4-OH-TEMPO·/ 4-OH-TEMO⁺ was 0.1 M. The absorbance intensity decreased with degradation time because the solution color gradually changed from yellow to colorless on the degradation progress.



Figure S2. UV-Vis spectra obtained for (a) 4-OH-TEMPO· and (b) 4-OH-TEMPO⁺ with different concentrations ranging from 6.25 mM to 100 mM. To calculate calibration curves for 4-OH-TEMPO·(c) and 4-OH-TEMPO⁺(d), the absorbance at wavelengths of 429 nm and 476 nm was plotted as a function of the TEMPO concentration.



Figure S3. UV-Vis spectra for 4-OH-TEMPO· and 4-OH-TEMO⁺ dissolved in 0.2 M NaCl solution 2 hours after treatment with different amounts of HCl or NaOH. The initial concentration of 4-OH-TEMPO·/ 4-OH-TEMO⁺ was 0.1 M.



Figure S4. ¹H NMR spectra of 0.1 M 4-OH TEMPO· 2 hours after treatment with 5 ~ 40 mM HCl or NaOH solution, recorded in DMSO- d_6 . Samples were reduced by phenyl hydrazine prior to characterization. The peak at 4.9 ppm is assigned to the proton of hydroxyl group (-OH), and gradually disappeared in acid solution and was not observed in basic conditions. This is probably because H⁺/D⁺ exchange between 4-OH-TEMPO and D₂O, which may be generated from DMSO- d_6 in the presence of acid/base catalyst.



Figure S5. GC-MS(EI) spectra of 4-OH-TEMPO[.] 2 hours after treatment with HCl or NaOH solution.



Figure S6. ¹H NMR spectra of 0.1 M 4-OH-TEMPO⁺ 2 hours after treatment with $5 \sim 40 \text{ mM}$ HCl or NaOH solution, recorded in DMSO- d_6 . Samples were reduced by phenyl hydrazine prior to characterization. Peaks (a) are from ring opened compound and peaks (b) are from 4oxo-TEMPO.

0.1 M Charged 4-OH TEMPO in 40 mM NaOH after 2 h



Figure S7. GC-MS(EI) spectra of 4-OH-TEMPO⁺ 2 hours after treatment with 40 mM NaOH solutions.



Figure S8. GC-MS(EI) spectra of 4-OH-TEMPO⁺ 2 hours after treatment with $0 \sim 40$ mM NaOH solutions.



Figure S9. ¹H NMR spectrum of 4-(2-chloroacetoxy)-TEMPO recorded in DMSO- d_6 . Sample was reduced by phenyl hydrazine prior to characterization. Peaks in the region from 6.5 to 7.5 ppm belong to phenyl hydrazine.



Figure S10. GC-MS(EI) spectrum of 4-(2-chloroacetoxy)-TEMPO



Figure S11. ¹H NMR spectrum of MIMAcO-TEMPO recorded in DMSO- d_6 . Sample was reduced by phenyl hydrazine prior to characterization. Peaks in region from 6.5 to 7.5 ppm belong to phenyl hydrazine.



Figure S12. HRMS (FAB+) spectrum of MIMAcO-TEMPO. Calculated: 295.1895. Found: 295.1893.



Figure S13. Optimized molecular structures of three OH⁻-TEMPO adducts with different reaction sites (Site-I, II, and III) in MIMAcO-TEMPO(a-c) and 4-OH-TEMPO(d-e).



Figure S14. CVs measured in 1.0 M NaCl solutions containing 0.1 M 4-OH-TEMPO at different scan rates (solid lines), and corresponding best-fit simulation results (dotted circles).



Figure S15. (a) CV curves of 0.1M MIMAcO-TEMPO in 1.0M NaCl solution at various scan rates. (b) Plots of peak current density versus square root of scan rate for MIMAcO-TEMPO⁺/MIMAcO-TEMPO⁺ redox reaction.



Figure S16. (a) Linear sweep voltammograms of 1 mM MIMAcO-TEMPO in 0.5 M NaCL solution at scan rate of 5 mV/s on glassy carbon electrode rotating at different speeds from 100 to 2500 rpm. (b) Levich plot of limiting currents versus square root of rotation rates. (c) Koutecky-Levich plot at different overpotentials ($|E-E^{0'}|$). The y-intercept denotes the kinetic current (i_k), which is independent of the mass transfer rate (at $\omega^{-1/2} \rightarrow 0$). E and E0' indicate the applied potential and formal potential, respectively.



Figure S17. (a) Linear sweep voltammograms of 1 mM 4-OH-TEMPO in 0.5 M NaCL solution at scan rate of 5 mV/s on glassy carbon electrode rotating at different speeds from 100 to 2500 rpm. (b) Levich plot of limiting currents versus square root of rotation rates. (c) Koutecky-Levich plot at different overpotentials ($|E-E^{0'}|$). The y-intercept denotes the kinetic current (i_k), which is independent of the mass transfer rate (at $\omega^{-1/2} \rightarrow 0$). E and E0' indicate the applied potential and formal potential, respectively.



Figure S18. Cyclic voltammograms for (a) MIMAcO-TEMPO⁺ and (b) 4-OH-TEMPO⁺ over 10,000 cycles at scan rate of 100 mV/s. (c) Variation of cathodic peak current as a function of cycle.



Figure S19. UV-vis spectra variation for (a) MIMAcO-TEMPO⁺ and (b) 4-OH-TEMPO⁺ during storage under Ar atmosphere at room temperature.



Figure S20. UV-vis spectra variation for (a) MIMAcO-TEMPO⁺ and (b) 4-OH-TEMPO⁺ 2 hours after adding different amounts of NaOH.



Figure S21. The CVs associated with PtO_x/Pt redox reaction in 0.5 M NaNO₃ on Pt UME from the aqueous solutions at different pH conditions (3.9, 5.2, and 6.4), where pH was adjusted with HClO₄.



Figure S22. Successive CVs associated with electrode-oxidation of (a) 5 mM 4-OH-TEMPO or (b) identical concentration of MIMAcO-TEMPO on Pt UME with radius of 5 μ m where the electrochemical window was set to be from 0.03 to 1.03 V; all aqueous solutions contained 0.5 M NaNO₃ and pH was adjusted to 6.4.



Figure S23. The CVs of 1^{st} (black) and 5^{th} (red) cycle associated with electrode-oxidation of 3 mM Fe(CN)₆⁴⁻ on Pt UME where the electrochemical window was set to be from 0.03 to 1.03 V; the aqueous solution contained 0.5 M NaNO₃ and pH was adjusted to 6.4.



Figure S24. (a) Schematic of H-type cell for measuring cross-over rate of TEMPO-derivatives through AMVN anion exchange membrane. UV-vis spectra for concentration variation of (b) MIMAcO-TEMPO and (c) 4-OH-TEMPO in dilute chamber of H-type cell. 0.2 M TEMPO-derivative solution and 0.2 M NaCl solution were placed in concentrate and dilute chambers, respectively. The concentration variation of TEMPO-derivatives in the dilute chamber was monitored by UV-vis spectrometer.



Figure S25. Variation in CE and VE for MIMAcO-TEMPO/BTMAP-Vi and 4-OH-TEMPO/BTMAP-Vi AORFBs at different current densities.



Figure S26. (a) Galvanostatic charge-discharge profiles of 0.1 M MIMAcO-TEMPO at 40 mA/cm², using two different anion exchange membranes of AMVN and DSVN and (b) their corresponding efficiency results.



Figure S27. Representative charge-discharge curve of MIMAcO-TEMPO at 2nd, 250th, 500th, 750th, and 1000th cycles during long-term operation. AORFBs were tested for 0.1M MIMAcO and 1.0M NaCl catholyte, and were paired with 0.1M BTMAP-Vi and 1.0M NaCl anolyte.



Figure S28. UV-Vis spectra of (a) MIMAcO-TEMPO and (b) 4-OH-TEMPO in catholyte at 1st, 300th, and 1000th cycles during long-term operation.



Figure S29. 1H NMR spectrum of 0.1 M MIMAcO-TEMPO after cycles recorded in DMSO- d_6 . Sample was reduced by phenyl hydrazine prior to characterization. Peaks in region from 6.5 to 7.5 ppm belong to phenyl hydrazine.



Figure S30. 1H NMR spectra of 0.1 M 4-OH-TEMPO after cycles, recorded in DMSO- $d_{6.}$ Sample was reduced by phenyl hydrazine prior to characterization. Peaks in region from 6.5 to 7.5 ppm belong to phenyl hydrazine.



Figure S31. GC-MS(EI) spectrum of 0.1 M 4-OH-TEMPO (a) before galvanocycling and after (b) 300 cycles and (c) 1,000 cycles.



Figure S32. Galvanostatic cycling of MIMAcO-TEMPO and 4-OH-TEMPO at $100mA/cm^2$ for 1000 cycles. Discharge capacity, CE, and VE were plotted every 10 cycles.



Figure S33. Galvanostatic cycling of 4-OH-TEMPO, MIMAcO-TEMPO, and TEMPO-1 at $40mA/cm^2$ for 1000 cycles. (a) Discharge capacity, (b) CE, and (c) VE were plotted every 10 cycles.



Figure S34. CE, VE, and capacity utilization for MIMAcO-TEMPO/BTMAP-Vi AORFBs at different concentrations of MIMAcO-TEMPO.



Figure S35. I-V polarization and power density of 2.5 M MIMAcO-TEMPO/BTMAP-Vi AORFB at SoC-100%.

Table S1. pH of TEMPO derivatives*

entry	name	structure	pН
1	4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-OH-TEMPO)		7.13
2	4-[4-(N-methylimidazolium)-benzyl- oxyl]-2,2,6,6-tetramethyl piperidine-1- oxyl chloride (TEMPO-1)		6.58
3	4-[2-(N-methyl imidazolium) acetoxy]- 2,2,6,6-tetramethylpiperidine-1-oxyl chloride (MIMAcO-TEMPO)		3.19
4	1-butyl-3-methylimidazolium chloride		6.87
5	3-(2-methoxy-2-oxoethyl)-1-methyl-1 <i>H</i> - imidazol-3-ium chloride		2.81

 * pH of a solution was measured 1 hour after dissolving 0.1 M solute in DI water (pH of blank DI water is 7.03)

Table S2. Gibbs free energy changes (ΔG) for each OH⁻-TEMPO adduct formation reaction with three different reaction sites (Sites I, II, and III) on both reduced and oxidized forms of 4-OH-TEMPO and MIMAcO-TEMPO, and [(OH⁻ \rightarrow MIMAcO)-TEMPO⁺]: $\Delta G = G_{adduct} - G_{OH-} - G_{TEMPO}$, where G_{adduct} , G_{OH-} and G_{TEMPO} are Gibbs free energy of adduct for each formation reaction, OH⁻, and corresponding TEMPO species. *for ΔG by interaction of OH⁻ with MIMAcO functional group of MIMAcO-TEMPO⁺ to form [(OH⁻ \rightarrow MIMAcO)-TEMPO⁺]; this adduct is more stabilized in its triplet state, while the other possible adducts prefer their singlet states.

$\Delta G \left[eV \right]$	TEMPO (nitroxyl radical o	MIMAcO functional group		
	Site-I	Site-II	Site-III	
4-OH-TEMPO•	0.300	0.327	_	
4-OH-TEMPO ⁺	0.176	-0.736	_	
MIMAcO-TEMPO•	3.109	2.387	-0.055	
MIMAcO-TEMPO+	-0.124	-0.829	-1.194	
[(OH-→MIMAcO)- TEMPO ⁺]	0.299	0.975	_	

	4-ОН-ТЕМРО	MIMAcO-TEMPO
E ⁰ [V vs. Ag/AgCl]	0.60	0.64
K ⁰ [cm/s]	7.11×10^{-3}	1.34×10^{-2}
α	0.48	0.48
D [cm ² /s]	8.29×10^{-6}	6.35×10^{-6}
R [ohm]	17	19
RC constant [µsec]	9.8	12.1
C [F]	5.76×10^{-7}	6.38×10^{-7}

Table S3. Parameters for voltammetric simulations of 4-OH-TEMPO and MIMAcO-TEMPO, shown in Figure 3a and Figure S14.

Catholyte	Anolyte	Cell Voltage [V]	Concentration [M] (Catholyte/ Anolyte)	Current Density [mA/cm ²]	No. of Cycles	Capacity Fade Rate [%/Cycle]	Ref.
Λ_ΟΗ_ΤΕΜΡΟ	MV	1.25	0.1 / 0.1	40	100	N.A.	[12]
4-011-1 EM1 0	IVI V	1.23	0.5 / 0.5	60	100	>0.11	[12]
	$(NPr)_{o}V$	1.35	0.25 / 0.25	20	~550	N.A.	
N ₂ -TEMPO			0.1 / 0.1	20	400	N.A	[13]
	()2		0.5 / 0.5	60	400	N.A	[15]
			1.0 / 1.0	60	400	0.025	
			0.05 / 0.05	30	400	0.06	[14]
4–CO ₂ Na–TEMPO	(SPr) ₂ V	1.19	0.4 / 0.4	30	50	0.20	
			1.0 / 1.0	30	20	1.65	
TEMPO-SO ₃ K	(NPr) ₂ VBr	1.13, 1.49	0.5 / 0.25	20	1200	2.33	[15]
NMe TEMPO	$(NPr)_2TTZ]$	1.44	0.2 / 0.1	40	300	0.03	[16]
N ^{TT} -IEMPO			0.5 / 0.25	60	50	0.06	
	[PyrPV]Cl ₄	1.57	0.2 / 0.1	40	500	0.04	[17]
Pyr-TEMPO			0.5 / 0.25	40	1000	0.05	
•			1.0 / 0.5	40	250	0.2	
	BTMAP – Vi	1.19	0.1 / 0.1	40	1000	0.007	[18]
TMAP-TEMPO			0.5 / 0.5	100	200	0.025	
			1.5 / 1.5	100	250	0.015	
$(TPARP_{M})(T)$		1 200	0.1 / 0.1	60	2000	0.0022	[10]
(11 HD1 y)013	BIMAP – VI	1.299	1.5 / 1.2	60	100	0.02	[19]
TMAA ANU TEMDO	(NPr) V	1.22	0.1 / 0.1	50	1500	0.0033	[20]
ΙΜΑΑζΝΠ-ΙΕΜΡΟ	$(1017)_2$		0.5 / 0.5	50	1000	0.014	
N ^{Me} -TEMPO	$(NPr)_2V$	1.38	0.5 / 0.5	60	500	0.005	[21]
№ ^{Ме} -ТЕМРО	MV	1.45	0.5 / 0.5	60	500	0.018	[21]
MIMAcO-TEMPO	BTMAP – Vi	1.18	0.1 / 0.1	40	1000	0.0117	This Wor k

Table S4. Battery performance comparison of AORFBs using TEMPO-based molecules as catholyte.

Concentration of	Electrolyte composition (electrolyte volume)			
MIMAcO-TEMPO [M]	Catholyte	Anolyte		
0.1	0.1M MIMAcO-TEMPO + 1.0M NaCl (40ml)	0.1M BTMAP-Vi + 1.0M NaCl (80ml)		
0.5	0.5M MIMAcO-TEMPO + 1.0M NaCl (40ml)	0.4M BTMAP-Vi + 1.0M NaCl (100ml)		
1.0	1.0M MIMAcO-TEMPO + 1.0M NaCl (40ml)	0.7M BTMAP-Vi + 1.0M NaCl (115ml)		
2.0	2.0M MIMAcO-TEMPO + 0.5M NaCl (40ml)	1.2M BTMAP-Vi + 0.5M NaCl (135ml)		
2.5	2.5M MIMAcO-TEMPO (40ml)	1.2M BTMAP-Vi + 0.5M NaCl (135ml)		

Table S5. Detailed composition of anolyte and catholyte in MIMAcO-TEMPO/BTMAP-ViAORFB for concentration-dependent charge-discharge test.

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