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Sodium-difluoro(oxalato)borate (NaDFOB): A new electrolyte salt for Na-ion batteries

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Experiment section

Synthesis of NaDFOB

NaDFOB was synthesized by reacting sodium oxalate ($Na_2C_2O_4$, Sigma-Aldrich, 99.5%) with boron-trifluoride-diethyl-etherate (BF_3·ether, ≥46% BF_3 basis) in acetonitrile (CH_3CN, Sigma-Aldrich, anhydrous, 99.8%). After filtration, the desired product was isolated by removing CH_3CN. Further purification was carried out by washing using tetrahydrofuran (THF, Sigma-Aldrich, anhydrous, ≥99.9%). Dry NaDFOB was obtained after removing THF under vacuum. The authors can be contacted for this compound for further development purpose.

Crystal structure determination

The powder X–ray diffraction(XRD) pattern of $NaC_2O_4BF_2$ was collected incapillary mode (Bruker D8 Advance, Cu Kα_1, Ge monochromator, 0.01° step, 3s dwell, 6–80 2θ°) and indexed in Topas Pro (Bruker AXS; Karlsruhe, Germany). Tetragonal cells such as $I4_1md$, $I4_2d$, $P4_2mc$, and $I222$ were identified as structure solution candidates. Groups were eliminated if they lacked adequate site symmetry to model the structural moiety or gave a poor fit, $P4_2mc$ (weighted profile factor, r_{wp} = 40%) in this case. Molecular subunits were manipulated by density functional theory (DFT) calculations using CASTEP (Accerlys, Inc; San Diego, California, USA). This software package employs a norm-conserving non-local pseudopotential generated by the Kerker scheme, with an energy cut-off of 420 eV. Set parameters: energy charge per atom convergence criterion of 0.00002 eV, root-mean-square displacement of 0.001 Å, and root-mean-square residual force on movable atoms of 0.05 eV/Å. Electron exchange interactions and correlations were modeled following the method developed by Wu and Cohen via a generalized gradient approximation.[S1] The structure was geometry optimized using the Broyden-Fletcher-Goldfarb-Shanno scheme[S2-5], generating atomic coordinates and subsequently, bond geometries. From these, rigid bodies of $[C_2O_4BF_2]^-$ were constructed in Topas and fitted to the X-ray diffraction (XRD) pattern by simulated annealing. Rotational, translational, and torsional degrees of freedom that determine subunit orientation within the unit cell were allowed. Using these results, space groups then underwent Rietveld refinement. Of those structure solutions remaining, $I4_1md$ (r_{wp} = 8.2%) had the best fit; $I4_2d$ (16.7%) and $I222$ (13.8%) were inferior.

The final Reitveld refinement for NaDFOB (Figure S3) had a minor secondary phase, $NaBF_4$. Rigid bodies were retained to maximize available degrees of freedom in the refinement. This allowed the use of an isotropic thermal parameters for the $[C_2O_4BF_2]^-$ subunit, which accounts for thermal motion and (any slight) disorder present in the compound. The goodness of fit for the refinement (Table S1) can be found with the lattice parameters. Atomic positions (Table S2) of ions in the rigid body do not contain estimated standard deviations (ESDs), however, the rotational and translational ESDs associated with the rigid body are reasonable (ESD < 0.1 %). Sodium was allowed to freely undergo refinement. Consequently, ESDs are reported.

Electrolyte and electrode preparation

All tested electrolytes consist of a 1.0 M solution of the salt ($NaClO_4$, $NaPF_6$, or NaDFOB) in propylene carbonate (PC hereafter, Aldrich, anhydrous, 99.7%); 5 vol% fluoroethylene carbonate (FEC, Aldrich, 99 %) added PC (PC + 5 % FEC); binary solvent mixtures (50:50 vol%) of ethylene carbonate (EC, Aldrich, anhydrous, 99.0 %) : PC; EC : dimethyl carbonate (DMC, Aldrich, anhydrous, 99.0 %); and EC : diethyl ether (DEC, Aldrich, anhydrous, 99.0 %).

Electrodes for the electrochemical studies were fabricated by mixing the active materials $Na_{0.44}MnO_2$, Super P carbon black, and polyvinylidenedifluoride (PVDF) in the weight ratio of 80:10:10. N-Methyl-2-pyrrolidone (NMP) was used as the solvent. The mixture was blended well, and then the slurry was coated uniformly on aluminum foil. After heating at 100 °C for 10 h, the coated foil was cut into disks and assembled into CR2032 coin-type cells with different electrolytes (1.0 M NaDFOB, $NaClO_4$, or $NaPF_6$ in PC, PC + 5 % FEC, PC:EC, EC:DEC, or EC:DMC) and a sodium metal disk as counter electrode. The coin cells were assembled in an argon-filled glove box (MBraun, Germany).

Characterization

Elemental analysis of F and B of the as-prepared NaDFOB was carried out on a Dionex Ion Chromatograph ICS-1100 RFIC and inductively coupled plasma (ICP) analyzer, respectively. Fourier transform infrared spectroscopy (FTIR) was conducted on a Shimadzu AIM8000 FT–IR spectrometer. ^{11}B nuclear magnetic resonance (NMR) was performed on a Bruker Avance 400 MHz spectrometer externally referenced to BF_3 at 0.0 ppm. ^{19}F NMR was performed on a VNMRS PS54 500 MHz spectrometer externally referenced to KF at −125.3 ppm.

Melting points of the electrolytes were determined from differential scanning calorimetry (DSC; TA Q100) curves when the samples were heated from −70 °C to 80 °C at the rate of 10 °C min^{-1}. The viscosities of the electrolytes were measured with a parallel-plate rheometer (MCR 301, Anton Paar) at 25 °C. The ionic conductivity of the electrolytes was measured with an Oakton CON 11 standard conductivity meter.

Electrochemical performances

The electrochemical stability window of the electrolytes was evaluated using a sodium metal cube slice as the counter and reference electrode and stainless steel as the working electrode. Cyclic voltammograms (CVs) of cells with electrolytes composed of 1.0 M NaX (X = DFOB, ClO_4, and PF_6) in PC, EC:DEC, and EC:DMC were collected at room temperature at the scan rate of 1 mV·s^{-1}.

Galvanostatic charge-discharge tests were conducted on a Neware battery testing system between 4.0 and 2.0 V (versus Na^+/Na) at room temperature. The $Na_{0.44}MnO_2$/Na half–cells using different electrolytes were charged and discharged with a current of 15, 50, 100, 150, 200, 250, 300, and 15 mA g^{-1} for 6, 21, 21, 21, 21, 21, 21, and 11 cycles, respectively.

Electrochemical impedance spectroscopy (EIS) of the $Na_{0.44}MnO_2$/Na half–cells after 143 cycles was conducted on a Biologic VMP-3 electrochemical work station in the frequency range from 10 mHz to 100 kHz at open circuit potential.

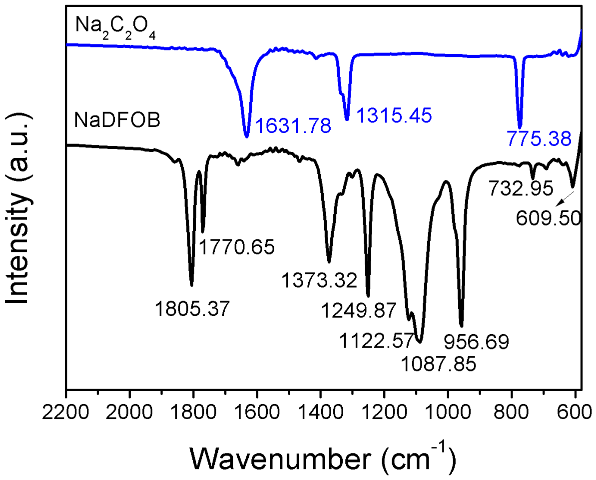

Fig. S1 FTIR spectra of the as-synthesized NaDFOB compared with commercial $Na_2C_2O_4$.

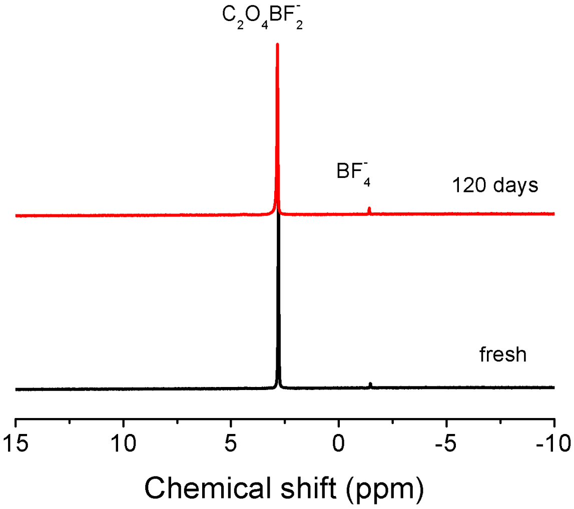

Fig. S2 ^{11}B NMR spectra of the fresh NaDFOB dissolved in CH_3CN and the solution after storage at room temperature for 120 days. Trace amounts of $NaBF_4$ was observed in the solution.

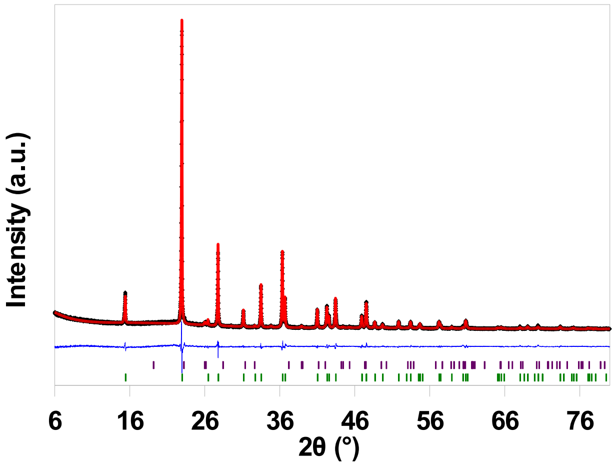

Fig. S3 Rietveld refinement of XRD data for NaDFOB. Red is the calculated, black is the observed, and blue is the difference pattern. The short vertical lines: purple is indexed $NaBF_4$, green is indexed NaDFOB.

Table S1: Lattice and fit parameters for NaDFOB.

Compound	NaDFOB
Space group	$I4_1md$
FW (g/mol)	159.8
Z	4
a	7.7316(1)
b	8.5343(1)
α, β, γ(°)	90
V (Å^3)	510.16(1)
R_{wp} (%)	8.21
R_p(%)	6.53

Table S2: Atomic parameters for NaDFOB. * = U_{eq} value.

Atomic position(s)						
Ion	**Site**	**x**	**y**	**z**	**Occ**	**U_{iso} (Å^2)**
Na	4a	0	0	0.3003(7)	1	0.57(8)
B	4a	0	0	0.6902	1	0.68*
F	8b	0	0.8509	0.5996	1	0.44*
C	8b	0.8908	0	0.9376	1	0.30*
O1	8b	0.8409	0	0.8007	1	0.02*
O2	8b	0.7942	0	0.0638	1	0.20*

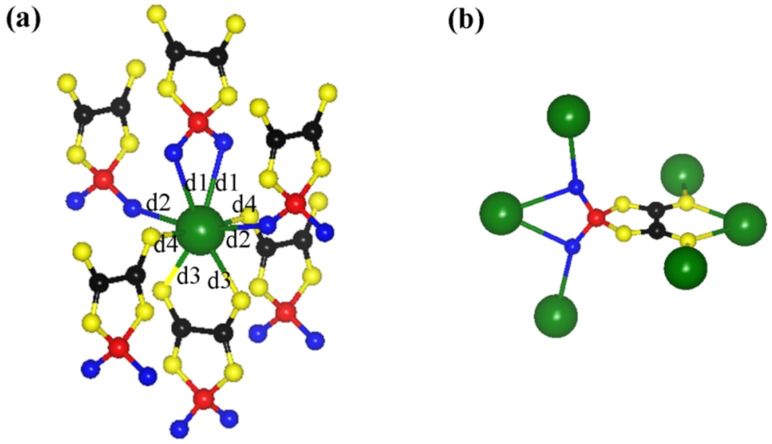

Fig. S4 (a) Na$^+$ cation and (b) DFOB$^-$ anion coordination environments. d1 = 2.802(4) Å, d2 = 2.745(4) Å, d3 = 2.570(1) Å, d4 = 2.277(5) Å. Sodium, oxygen, carbon, boron, and fluorine atoms are represented as green, yellow, black, red, and blue spheres, respectively.

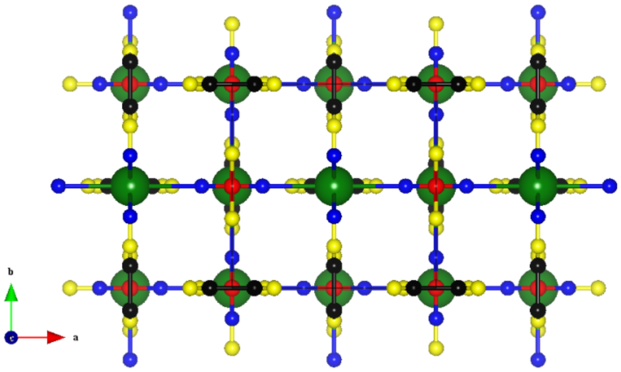

Fig. S5 Crystal structure of NaDFOB. Sodium, oxygen, carbon, boron, and fluorine atoms are represented as green, yellow, black, red, and blue spheres, respectively.

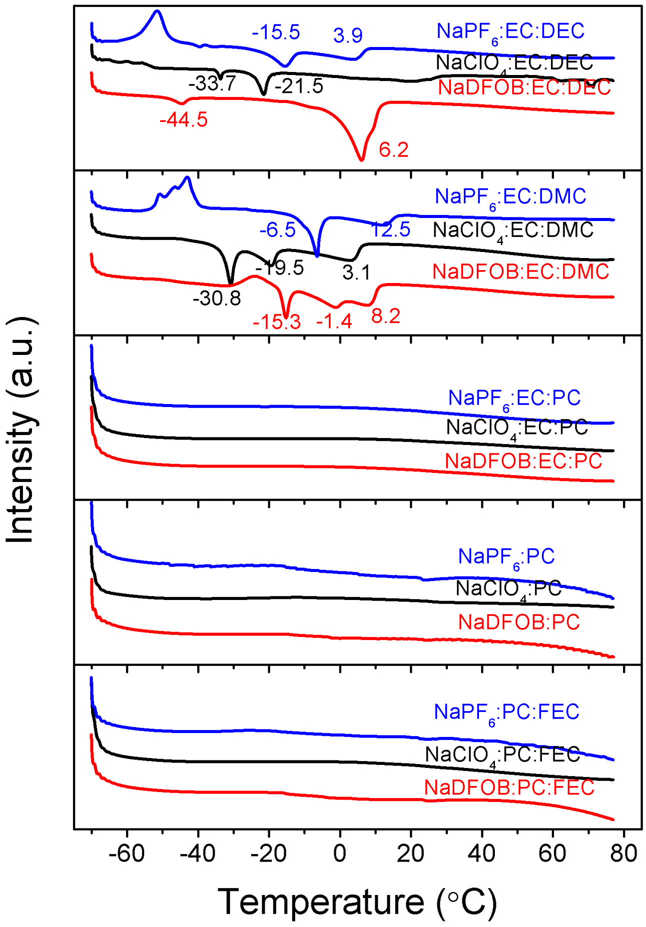

Fig. S6 DSC curves of NaDFOB, $NaClO_4$, and $NaPF_6$ in EC:DEC, EC:DMC, EC:PC, PC, and PC + 5 % FEC, respectively.

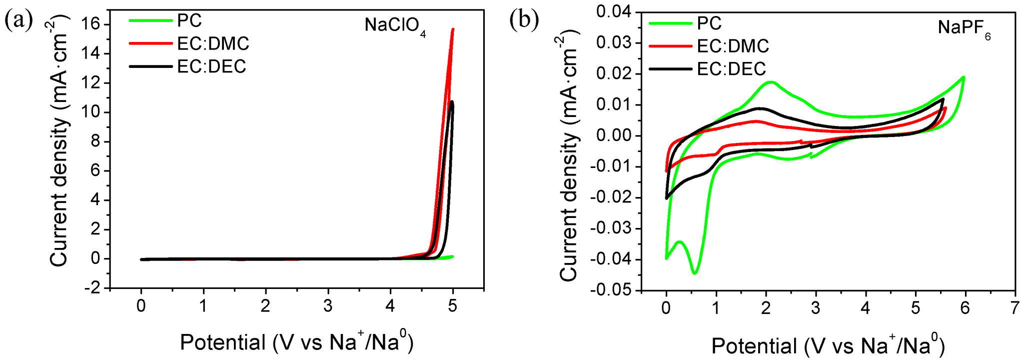

Fig. S7 CV curves of 1.0 M NaX (X =ClO_4 and PF_6) in PC, EC:DMC, and EC:DEC at room temperature at the scan rate of 1 $mV \cdot s^{-1}$.

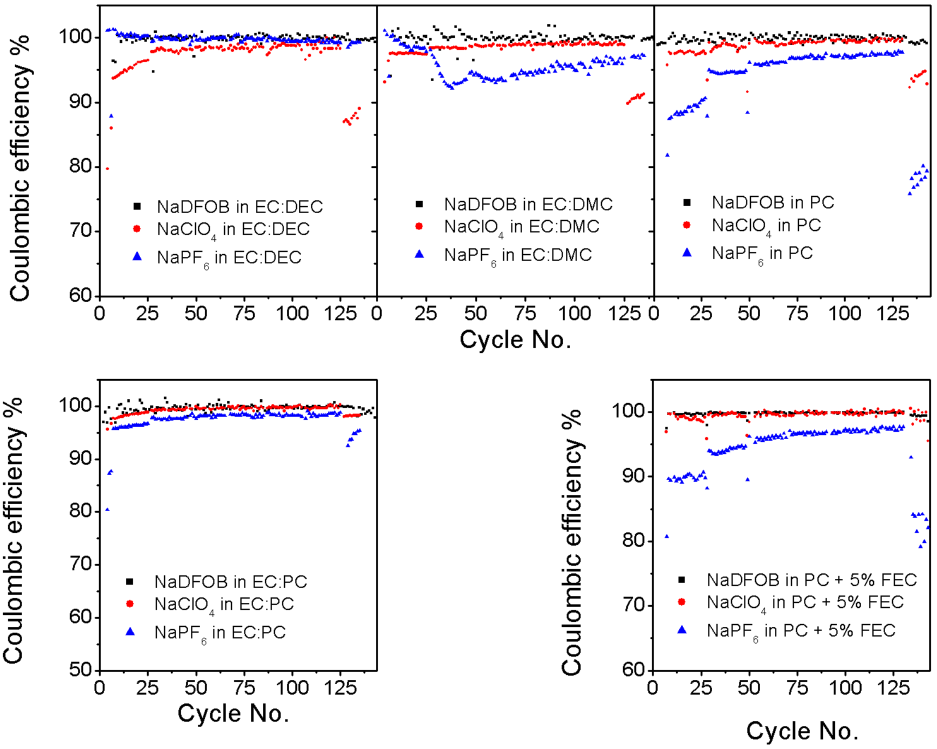

Fig. S8 Coulombic efficiencies of Na/$Na_{0.44}MnO_2$ half cells containing NaX (X = DFOB, ClO_4, PF_6)–based electrolytes.

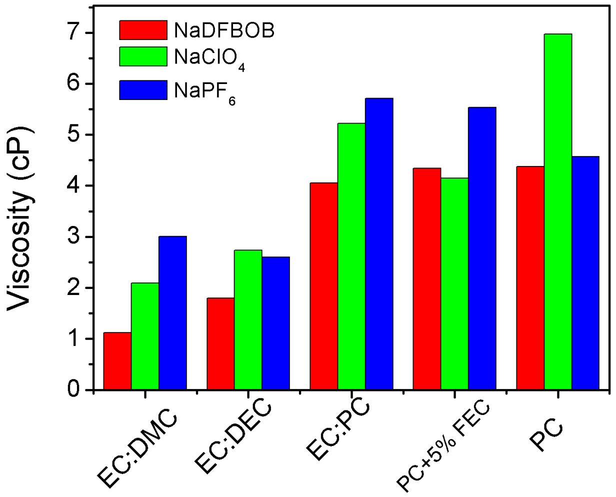

Fig. S9 Viscosity values of 1.0 M NaX (X = ClO_4, PF_6, and DFOB) in EC:DMC, EC:DEC, EC:PC, PC, and PC + 5 % FEC.

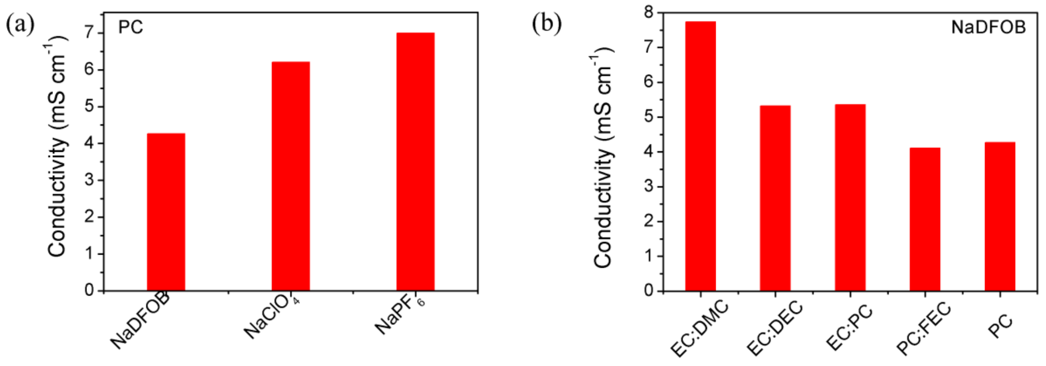

Fig. S10 Conductivity of electrolytes consisting of (a) 1.0 M $NaClO_4$, $NaPF_6$, and NaDFOB in PC, and (b) 1.0 M NaDFOB in EC:DMC, EC:DEC, EC:PC, PC, and PC + 5 % FEC.

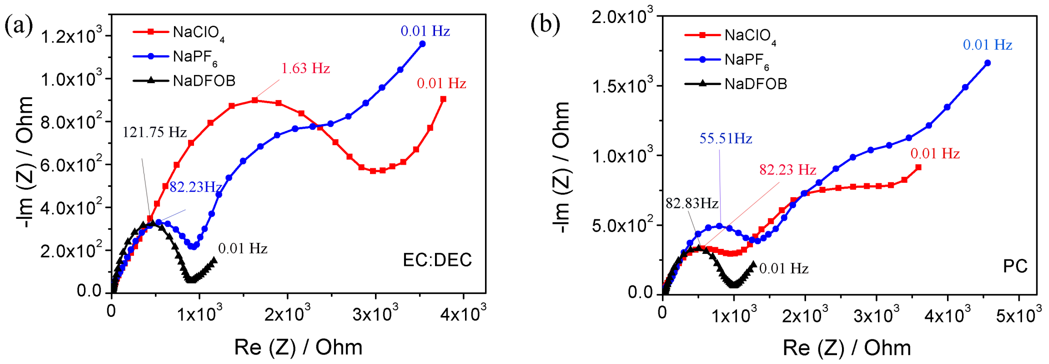

Fig. S11 EIS spectra of $Na/Na_{0.44}MnO_2$ half cells in electrolytes composed of 1.0 M $NaClO_4$, $NaPF_6$, and NaDFOB in (a) EC:DEC and (b) PC at open circuit potential, which were collected after 143 cycles at different rates.

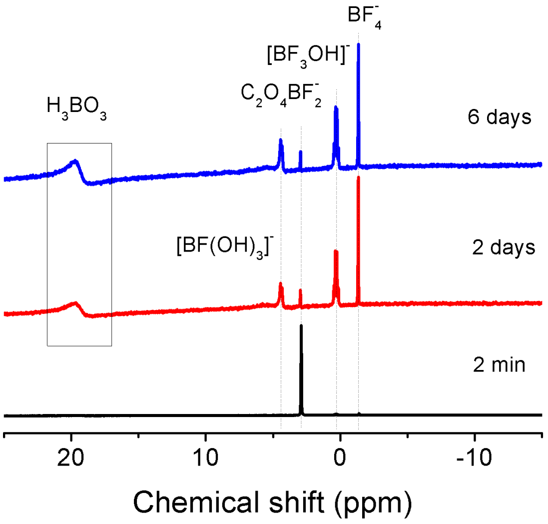

Fig. S12 ^{11}B NMR spectra of NaDFOB after adding deionized water and aging for 2 min, 2 days, and 6 days.

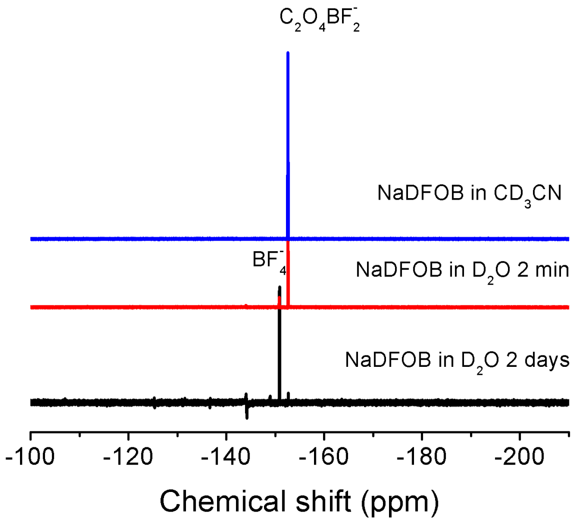

Fig. S13 ^{19}F NMR spectra of NaDFOB dissolved in CD_3CN, D_2O, and the D_2O solution stored at room temperature for 2 days.

References

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