# Effect of *N*-substitution in Naphthalenedimides on the Electrochemical Performance of Organic Rechargeable Batteries

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# Electronic Supplementary Information

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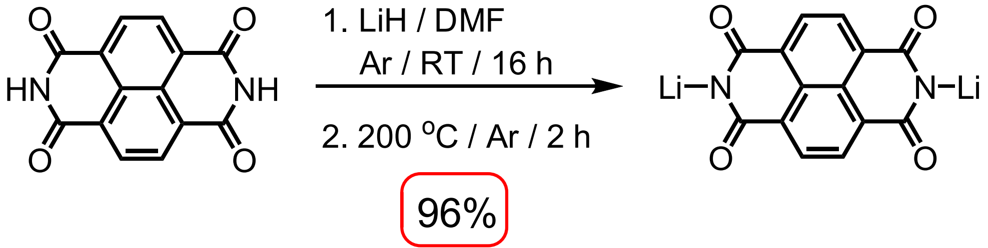
## Section A. Materials / General Methods / Instrumentation

Starting materials and reagents were purchased from Aldrich or Fisher and used as received. 1,4,5,8-naphthalenetetracarboxylicdimide[S1] (NDH) and *N*,*N*′-dimethyl-1,4,5,8-naphthalene-carboxylicdimide[S2] (NDMe) were prepared following procedures reported in the literature. All reactions were performed under an argon atmosphere and in dry solvents unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-$F_{254}$ (Merck 5554). Flash chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance 300 and 400 MHz spectrometers at ambient temperature. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 ppm, $(CD_3)_2SO$: δ 2.50 ppm). MALDI-TOF mass spectra were measured on a Bruker autoflex III mass spectrometer. Termogravimetric analysis (TGA) experiment was carried out by using Setaram 92-18 TG/DTA analyzer at a heating rate of $5^{o}C \cdot min^{-1}$ (up to 350$^{o}$C) under argon atmosphere. Elemental analysis (EA) experiment was carried out by using Thermo Scientific Flash 2000 Series element analyzer. All of electrochemical measurements were carried out by using 2032 coin cells fabricated in an argon filled glove box. Working electrode was prepared of mixing naphthalenedimide derivatives with carbon black and PVDF binder in a ratio of 60:30:10 using NMP (*N*-methylpyrrolidone) as a solvent. As prepared slurry of the working electrode was coated on an Al-foil and dried under vacuum oven at 70 $^{o}$C overnight. Metallic lithium foil was used as a counter/reference electrode. The microporous membrane (Celgard 2400) was used as seperator and 1 M solution of Lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI) in 1,3-Dioxolane/1,2-Dimethoxyethane was used as an electrolyte. Cyclic voltammetry and galvanostat tests were carried out by Biologic VSP.

## Section B. Synthetic Protocols



NDH

NDLi

**Scheme S1.** Synthesis of NDLi.

*Synthesis of Naphthalenedimide dilithium salt*[S3] *(NDLi):* Lithium hydride (5,69 mmol, 45.2 mg) was added in one portion to a solution of naphthalenediimide (NDH) (2.18 mmol, 581 mg ) in 10 mL of anhydrous DMF under Ar atmosphere. The reaction mixture was stirred at room temperature for 16 h and then the solvent was removed under reduced pressure to yield NDLi·2DMF as a pale brown solid. Removal of coordinating DMF solvent molecules was achieved by heating the sample at 200°C (Note: Higher temperatures resulted in the degradation of the product.) for 2 h in a horizontal tubular oven under inert atmosphere. NDLi (580 mg) was obtained as dark brown solid in 96% yield. $^{1}$H NMR (400 MHz, $(CD_3)_2SO$, 298K): δ = 8.18 (s, 4H) ppm. $^{13}$C NMR (75 MHz, $(CD_3)_2SO$, 298K): δ = 173.3, 129.1, 128.6, 127.8 ppm. MS (MALDI–TOF) calcd for $m/z$ = 333.065 $[M + Na + MeOH]^+$, found $m/z$ = 333.024. Elemental Analysis (Found: C, 60.4; H, 1.2; N, 10.3. $C_{14}H_4Li_2N_2O_4$ requires C, 60.5; H, 1.5; N, 10.1%).

## Section C. $^1$H NMR Spectroscopic Characterization

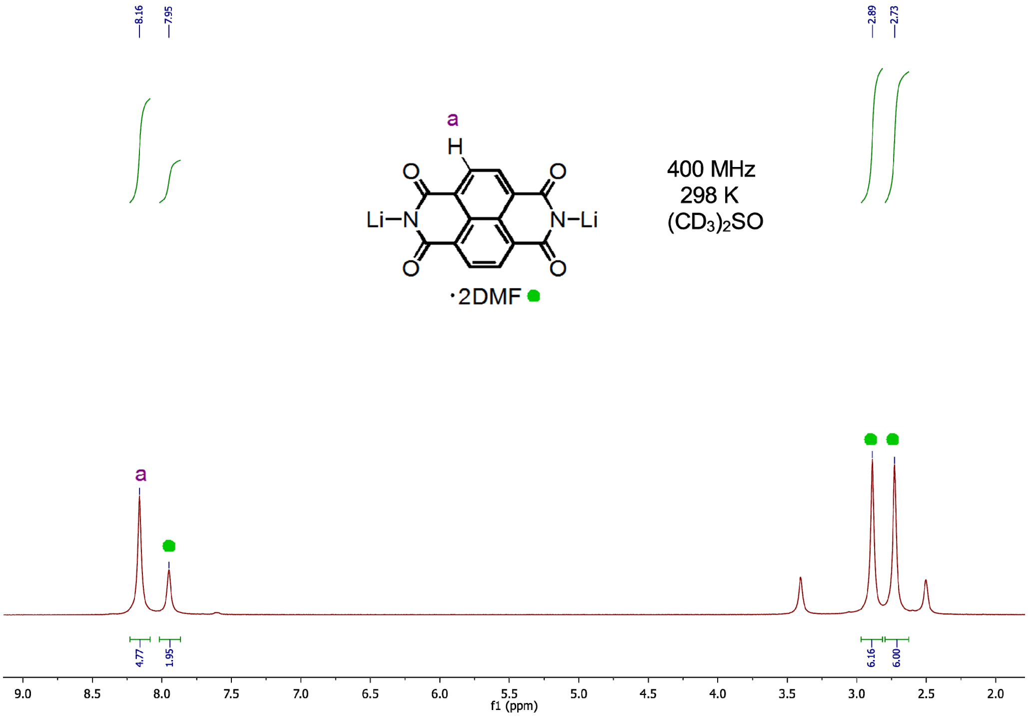
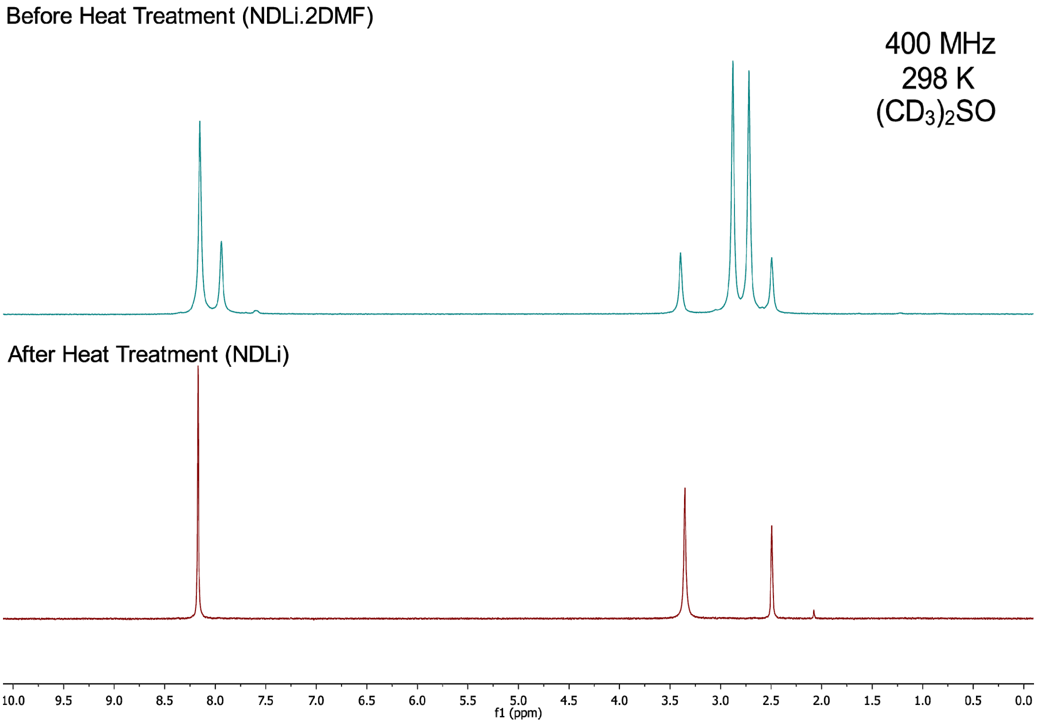


**Figure S1:** $^1$H NMR spectrum of NDLi·2DMF in $(CD_3)_2SO$ at 298 K.


Before Heat Treatment (NDLi.2DMF)

After Heat Treatment (NDLi)

**Figure S2:** $^1$H NMR spectra of NDLi before and after heat treatment. This experiment demonstrates that the DMF solvent molecules were completely removed after heat treatment.

## Section D. TGA experiment

TGA experiment was carried out at a heating rate of 5 °C/min up to 350°C.

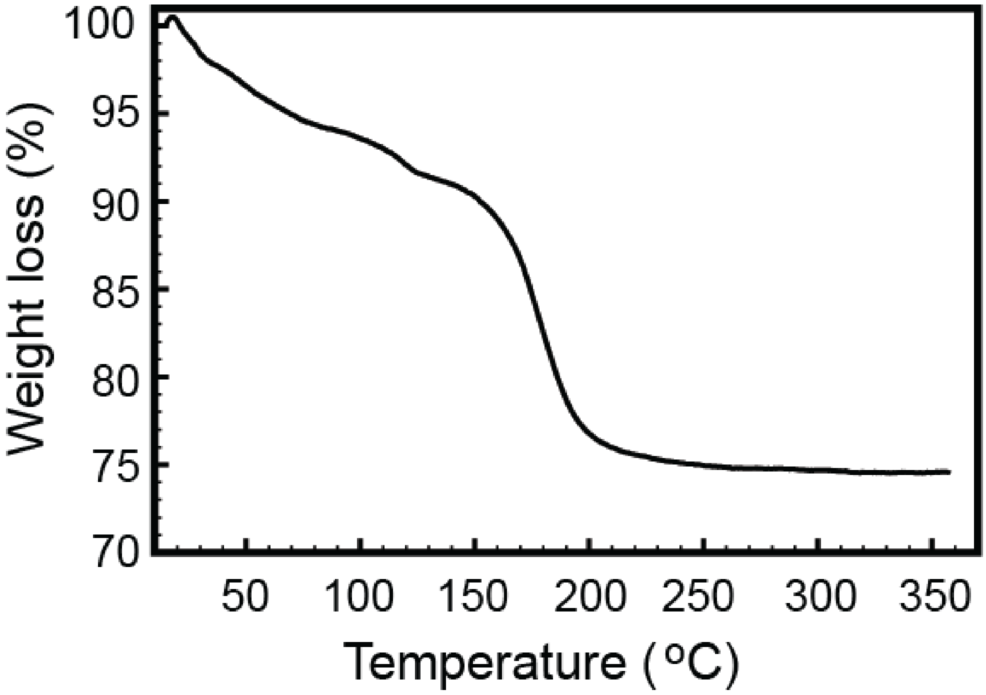


**Figure S3.** Thermal analysis of NDLi.2DMF. The weight loss around 150 °C indicates the presence of $H_2O$ molecules in the sample, and the following weight loss corresponds to the removal of coordinating DMF solvent molecules.

## Section E. References

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S3. S. Renault, J. Geng, F. Dolhem, and P. Poizot, *Chem. Commun.*, 2011, **47**, 2414–2416.