Supporting Information for

A Hexaanionic Carboxyphenolate Framework for High Energy Alkali Cation Storage

Vasudeva Rao Bakuru,^a Petru Apostol,^a Darsi Rambabu,^a Shubhadeep Pal,^a Xiaodong Lin,^a Robert Markowski, ^a Tom Goossens,^a Da Tie, ^a Andrii Kachmar, ^a Yan Zhang,^a Géraldine Chanteux, ^a and Alexandru Vlad ^a*

^a Institute of Condensed Matter and Nanosciences, Molecular Chemistry, Materials and Catalysis, Université catholique de Louvain, Louvain-la-Neuve B-1348, Belgium *Email: <u>alexandru.vlad@uclouvain.be</u>

Contents

Experimental section	2
Materials characterization, cell assembly and testing	2
1. Synthesis of Ethyl 2,5-dimethoxybenzoate	4
2. Synthesis of diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate	5
3. Synthesis of diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate	7
4. Synthesis of 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid	9
5. Synthesis of A_6 THBPD materials (A: Li ⁺ , Na ⁺ and K ⁺)	11
6. Air stability test	14
7. Solubility check in aprotic, protic solvent and electrolytes	16
8. Electrochemical performance	18
9. Chemical oxidation of Li_6THBPD using Nitrosonium tetrafluoroborate (NOBF ₄)	22
10. Optimization of Li ₆ THBPD positive electrode material	25
11. Na ₆ THBPD cycling data for two electrons (2e ⁻) limited material utilization	27
12. K ₆ THBPD cycling data for two electrons (2e ⁻) limited material utilization	28
13. Cycling stability of high mass loading electrodes (half-cell)	30

Experimental Section

Chemicals and Reagents

2,5-Dimethoxybenzoic acid (98%), sodium tert-butoxide (NaOtBu, 99.9%), ethanol (EtOH, 99%), sodium sulphate (Na₂SO₄, 99%) dichloromethane (DCM, 100%), tetrahydrofuran (THF, 100%), sodium carbonate (Na₂CO₃, 99%), ethylene carbonate (EC, Battery grade) and ethyl acetate (99.5%) were acquired from Sigma Aldrich. Lithium tert-butoxide (LiOtBu, 99.9%), and anhydrous methanol (MeOH, 99.8%) were procured from Alfa Aesar. Potassium tertbutoxide (KOtBu, >97%) was sourced from TCI Chemicals. Boron tribromide (BBr₃), 1 M solution in dichloromethane and boron trifluoride etherate (48%) were purchased from Thermo Scientific Chemicals. (Bis(trifluoroacetoxy)iodo) benzene (97%) was bought from BLD pharma. Battery-grade diethyl carbonate (DEC) and dimethoxyethane (DME) were used as purchased from DoDochem. Acetonitrile (ACN, 99.9%), ethanol (EtOH, 99%) and hexane were obtained from VWR. Hydrochloric acid (HCl, 37%) was brought from Fischer chemicals. Sodium hydrogen carbonate (NaHCO₃, >99.9%) was bought from Carl Roth GmbH. 1 M LP30 (LiPF_6) in ethylene carbonate/dimethyl carbonate (EC/DMC) in a 1:1 (v/v) ratio (battery-grade) was purchased from Solvionic. Diglyme, NaTFSI and KTFSI salts (battery-grade) were bought from Xiamen TOB new Energy Tech., LTD. Anhydrous solvents were handled within an Arfilled glovebox, with O₂ and H₂O content maintained below 1 ppm. All chemicals and reagents were used as received, unless specifically mentioned.

Materials Characterization

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance II 300/500 spectrometer, operating at 300.1 MHz for ¹H and 75 MHz and 126 MHz for ¹³C. Fourier Transform Infrared (FTIR) spectroscopy was conducted using an Agilent Technologies Cary 630 FTIR operated in ATR mode, covering the wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹ at a resolution of 4 cm⁻¹ and 64 scans for data acquisition. Elemental analysis (CH) was performed using the Thermo ScientificTM FlashSmartTM Elemental Analyzer. X-ray powder diffraction (XRD) patterns were collected on STOE DARMSTADT Transmission diffractometer system using Mo Kα1 radiation with a wavelength of 0.70930 Å. The metal contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Half-Cell Assembly and Testing

The A₆THBPD working electrode (cathode) was typically prepared by mixing 100 mg of A₆THBPD active material (50 wt.%) with 40 wt.% Super-P carbon and 10 wt.% poly(tetrafluoroethylene) (PTFE) dry binder. Other carbon contents and electrode compositions and mass loading have been also tested. The mixing method varied: hand-grinding was used for Li₆THBPD and K₆THBPD, while Na₆THBPD was mixed using ball milling at 5 Hz for 15 minutes. For each coin cell (2032) assembly, approximately 5 mg of the positive electrode composite was placed onto the stainless-steel positive cell case. For Li₆THBPD and K₆THBPD, the composite was directly pressed onto the case using a stainless-steel rod. For Na₆THBPD, the composite was first pressed into a pellet using a 7 mm die set under 1 ton of pressure for 30 seconds before being transferred onto the positive cell case. Two glass fiber separators (19 mm diameter) were placed on top of the positive electrode, and 100 μ L of electrolyte was added to soak the separators. The metal chip or disk (Li, Na, or K), serving as the counter and pseudoreference electrode (anode), was then placed on top of the separator. A stainless steel (316) current collector and spring were placed above the anode, and the cell was sealed with the negative case by applying 0.7 tons of pressure. Galvanostatic charge-discharge tests were conducted at room temperature using Neware, Biologic battery testing systems.

Electrolytes used: Li-half cells: 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate (EC/DMC, LP30, battery-grade, Solvionic). Na-half cells: 3 M NaTFSI in diglyme. K-half cells: 1 M KTFSI in a 1:1 (v/v) mixture of ethylene carbonate and diethyl carbonate (EC/DEC).

Full-Cell Assembly and Testing for Li₆THBPD|Graphite

The cell construction is similar to the half-cell assembly, with the difference being the use of graphite coated on copper foil in place of lithium metal. The electrolyte and Li₆THBPD positive electrode composite, as described in the half-cell assembly, were used. The Li₆THBPD electrode powder was pressed onto a 13 mm aluminum mesh at 1 ton for 20 seconds and placed on the positive side of the coin cell case. The positive electrode had a mass loading of approximately 12 mg/cm² with a negative to positive electrode capacity ratio (N/P) of approximately 1.3. Galvanostatic charge-discharge tests were performed at room temperature using a Neware battery testing system.

1. Synthesis of Ethyl 2,5-dimethoxybenzoate



The synthesis procedure follows a previously reported method.¹ In a 250 mL round-bottom flask, a solution of 2,5-dimethoxybenzoic acid (10.0 g, 54.9 mmol) in ethanol (100 mL), and a catalytic quantity of hydrochloric acid (HCl) was refluxed for 20 hours. After completion, the reaction mixture was cooled to room temperature and neutralized with aqueous sodium carbonate (Na₂CO₃) solution. The resulting mixture was extracted with dichloromethane (150 mL) in three successive cycles and washed twice with water. The organic layer, containing the target product, was dried using sodium sulfate (Na₂SO₄) and concentrated under reduced pressure. The resulting crude dark brown product was subjected to purification using ethyl acetate as the eluent over a short column of silica gel, yielding the final product. The purified product was obtained with a yield of 95%.

2. Synthesis of diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate



Ethyl 2,5-dimethoxybenzoate (11 g, 0.054 mol) was dissolved in dry dichloromethane (DCM) (200 mL) within a 500 mL two-neck round-bottom flask, purged with argon (Ar) for 15 minutes, and cooled to -40 °C using dry ice and acetonitrile (CH₃CN). In a separate round-bottom flask, phenyl iodine bis(trifluoroacetate) (PIFA) (11.2 g, 0.026 mol) was dissolved in dry DCM (50 mL) and purged with argon for 30 minutes. The PIFA solution was subsequently added dropwise to the ethyl 2,5-dimethoxybenzoate solution (at -40 °C) accompanied by the addition of 8.8 mL BF₃·Et₂O solution (48%) to the reaction mixture. The reaction progressed for 3 hours under inert conditions and at -40 °C. Subsequently, the mixture was slowly warmed to room temperature and quenched with aqueous sodium bicarbonate, followed by extraction with dichloromethane. The organic layer was washed with brine, dried, and the solvent removed under low pressure. The final product was obtained through crystallization with hexane and ethyl acetate (10:1).

Diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate was isolated as a white powder with a yield of 51.0% (5.6 g).

¹**H NMR (300 MHz, DMSO**) δ 7.27 (s, 1H), 6.99 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.73 (d, J = 23.0 Hz, 7H), 1.31 (t, J = 7.1 Hz, 3H).

¹³C NMR (**75** MHz, DMSO) δ 166.00, 152.30, 150.60, 131.66, 120.82, 116.58, 113.50, 61.02, 57.59, 57.12, 56.76, 56.61, 14.63.



Figure S1. ¹H NMR spectra of diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate (300 MHz, DMSO-*d*₆).



Figure S2. ¹³C NMR spectra of diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'- dicarboxylate (300 MHz, DMSO-*d*₆).

3. Synthesis of diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate



Diethyl 2,2',5,5'-tetramethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate (5.6g, 0.013 mol, 1 equiv.) was dissolved in anhydrous dichloromethane (250 mL) under nitrogen atmosphere, and reaction mixture cooled to 0 °C. A solution of 1 M boron tribromide (BBr₃) in dichloromethane (4.5 equivalent) was subsequently slowly added at 0 °C, and the reaction proceeded for a duration of 6 hours. Upon completion, the reaction mixture was warmed to room temperature, and 100 ml of methanol was added. The solvents were subsequently removed under reduced pressure, yielding a white powder, followed by washing with dry dichloromethane (95%). The diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate was formed with a yield of 91% (4.4g).

¹**H NMR (300 MHz, DMSO**) δ 9.97 (s, 1H), 9.23 (s, 1H), 7.32 (s, 1H), 6.81 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

¹³C NMR (**75** MHz, DMSO) δ 171.90, 169.09, 153.77, 153.00, 147.45, 147.27, 133.41, 133.21, 119.86, 119.65, 119.49, 118.27, 115.68, 115.26, 112.59, 61.70, 14.52.



Figure S3. ¹H NMR spectra of diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (300 MHz, DMSO-*d*₆).



Figure S4. ¹³C NMR spectra of diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'- dicarboxylate (300 MHz, DMSO-*d*₆).

4. Synthesis of 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid



Diethyl 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (0.012 mol) was first suspended in 50 mL of ethanol. Subsequently, a solution of sodium hydrogen carbonate (25 g) in water (200 mL) was added, and the resulting mixture was stirred at reflux for 6 hours. Afterwards, a concentrated hydrochloric acid (12 M) was added dropwise accompanied by the formation of a yellowish precipitate. The precipitate was washed several times with water and dried at room temperature overnight under vacuum conditions. The 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid was obtained with a yield of 85 % (3.3g).

¹H NMR (300 MHz, DMSO) δ 10.60 (s, 1H), 9.16 (s, 1H), 7.31 (s, 1H), 6.77 (s, 1H).

¹³C NMR (75 MHz, DMSO) δ 171.92, 153.79, 147.28, 133.34, 119.50, 115.67, 112.58.



Figure S5. ¹HNMR spectra of 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid (300 MHz, DMSO-*d*₆).



Figure S6. ¹³C NMR spectra of 2,2',5,5'-tetrahydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid (300 MHz, DMSO-*d*₆).

5. Synthesis of A₆THBPD (A: Li⁺, Na⁺ and K⁺)

A₆THBPD salts were prepared via a solid-state ion exchange reaction. The protocol resumes to mixing (hand grinding) one equivalent (1.14 mmol) of H₆THBPD with six equivalents (6.85 mmol) of Li/Na/K tert-butoxide, for 15 mins, inside an Ar-filed glovebox. The mixed powder was then transferred into a vial and placed in a BUCHI Glass Oven B-585 inside the glove box. The temperature was increased progressively under vacuum as follows: 160 °C for 3 hours, followed by a step at 180 °C for 3 hours, and afterwards maintained at 220 °C for another 6 hours. During this process, the color changed to orange, indicating successful synthesis. All prepared compositions (Li₆THBPD, Na₆THBPD, and K₆THBPD) displayed the same color. The elemental analysis (CH and ICP-OES) data are shown in **Table S1**. Typically, this solid-state mechanochemical method reduces the E-factor (Environmental Factor) under solvent-free conditions. The E-factor, a widely used metric in green chemistry, quantifies the environmental impact of chemical processes by measuring the amount of waste generated per unit mass of product. It is defined as: E-factor = mass of waste / mass of product.

Compound name	Weight (%)	Carbon	Hydrogen	Metal from ICP
Li ₆ THBPD	Theor.	49.19	1.18	12.18 (Li)
	Exp.	47.34	1.47	11.97
Na ₆ THBPD	Theor.	38.38	0.92	31.48 (Na)
	Exp.	37.72	1.17	29.00
K₀THBPD	Theor.	31.44	0.75	43.87 (K)
	Exp.	32.27	1.07	40.83

Table S1. Elemental analysis (CH and ICP-OES) of A₆THBPD materials.



Figure S7. A) X-Ray diffraction patterns of H₆THBPD and A₆THBPD materials. SEM image of B) H₆THBPD, C) Li₆THBPD, D) Na₆THBPD and E) K₆THBPD powders.

The observed decrease in crystallinity from H_6THBPD to Li_6THBPD , along with the amorphous nature of the Na and K forms, may be attributed to the solventless deprotonation process. This reaction, particularly in the presence of larger alkali metal cations (Na⁺ and K⁺), likely disrupts the ordered structure by altering intermolecular interactions, introduces steric effects, and impedes diffusion driven structural reorganization. SEM data also reveals notable variations in particle morphology across the series. H_6THBPD and Na_6THBPD exhibit well-defined, elongated plate-like morphologies with smooth surfaces and some degree of agglomeration, suggesting a layered or anisotropic growth mechanism (**Figures S7B & D**). In contrast, Li_6THBPD presents a more irregular and fragmented structure, indicative of a disordered assembly and increased packing density (**Figure S7C**). For K₆THBPD, densely

packed nanoaggregates with fine spherical features are observed, forming a flower-like or sponge-like morphology (Figure S7E).

6. Air stability test



Figure S8. FTIR analysis of A_6 THBPD salts upon exposure to ambient air for a duration of 24 hours (A, B, and C). D) Color changes after air exposure: Li₆THBPD (dark green), (Na₆THBPD) light green, and K₆THBPD (black), as compared to pristine materials color (displayed in **Figure S7A**). E) Redox potentials of A_6 THBPD (A = Li, Na, K) versus the standard hydrogen electrode (SHE). The dashed line denotes the air stability threshold (2.91 V vs. Li⁺/Li)

We have prioritized the assessment of air stability in alkali cation-carboxyphenolate phase, recognizing the significance of resistance to oxidation in the practical handling and processing conditions of positive electrode materials. The compounds underwent exposure to ambient air for 24 hours, followed by vacuum drying at 120 °C for 5 h (to remove the traces of water). Notably, Li₆THBPD displayed minimal sign of oxidation, corroborating the high redox potential of Li₆THBPD of 2.85 V vs. Li⁺/Li. However, Li₆THBPD phase remains sensitive to moisture, as evidenced by changes observed in the lithium phenolate (C-O-Li) band. In contrast, Na₆THBPD and K₆THBPD both displayed partial oxidation, with quinone carbonyl band evidenced in the infrared spectra analysis. The differing air stability of Na₆THBPD and

K₆THBPD compared to Li₆THBPD can be attributed to both the redox potentials of the materials and the impact of the counter cation on the stability of the THBPD⁶⁻ anionic framework (polarizing power following Li⁺ > Na⁺ > K⁺). As shown in **Figure 2** (in main text), the average discharge redox potentials for Na₆THBPD and K₆THBPD are 2.40 V and 2.50 V vs. Na⁺/Na and K⁺/K, respectively, while Li₆THBPD exhibits an average discharge redox potential of 2.85 V vs. Li⁺/Li, which is close to the O₂ redox potential. Since ambient air stability typically requires a redox potential greater than ~2.91 V vs. Li⁺/Li, the reduced Na₆THBPD and K₆THBPD phases, with lower redox potentials, are more susceptible to air oxidation.

7. Solubility check in aprotic, and protic solvents, as well as electrolytes

The Li₆THBPD material solubility was assessed in different protic and aprotic solvents. As shown in the picture below, Li₆THBPD is insoluble in DMSO, DMF, acetonitrile and THF, but exhibits high solubility in methanol, enabling effective ¹H NMR analysis in the corresponding methanol-d₄ solvent.



Figure S9. Li_6THBPD solubility checks in different solvents. From left to right, the solvents are: DMSO, DMF, ACN, and THF.



Figure S10. Li₆THBPD solubility check in methanol- d_4 and its ¹H-NMR data.



Figure S11. Li₆THBPD solubility check in electrolytes: (from left to right) 1M LiTFSI in EC/DMC, 1M LiTFSI in PYR14FSI, 1M LiTFSI in DOL/DME and 1M LP-30 in EC/DME.

8. Electrochemical performances



Figure S12. Cycling stability of A_6 THBPD positive electrode material with full material utilization (equivalent of four electron - 4e⁻ redox per formula unit). A) Li₆THBPD at 0.1C rate in 1M LiPF₆ - EC/DMC (LP-30) electrolyte; B) Na₆THBPD at 0.1C rate in 3M NaTFSI - diglyme electrolyte; and C) K₆THBPD at 0.1C rate in 1M KTFSI - EC/DEC electrolyte. As discussed earlier and next (**Figure S14**), main degradation mechanism is the dissolution of the fully oxidized phase, with higher solubility noted for Na- and K-versions.



Figure S13. Ex-situ SEM analysis of the Li₆THBPD electrode morphology at different state of charge (SOCs) (0, 50, and 100 %). A) Galvanostatic SOCs profiles obtained at a rate of 0.1C ($4A^+$ exchanged in 10 hours, 313 mA/g) for a Li₆THBPD cell with 1M LiPF₆ in EC/DMC electrolyte; B) SEM of the composite electrode at 0% SOC (pristine, before charging), (C) at 50% SOC (half charged), and (D) at 100% SOC (fully charged).

The pristine electrode (**Figure S13B**) displays an irregular and fragmented composite with a relatively smooth surface, characteristic of the as-synthesized material. At 50% SOC (**Figure S13C**), slight surface roughening and emerging microstructural changes become evident. Upon full charge (**Figure S13D**), the electrode exhibits more pronounced morphological changes, including increased surface roughness and textural variations, which may be associated with the solubilisation of the oxidized phase, or structural transformations occurring during complete lithium extraction.



Figure S14. A & D) Galvanostatic first cycle charge-discharge profiles for the Na₆THBPD and K₆THBPD positive electrode materials, at a rate of 0.1C, and with limited cycling capacity (1 to $4e^{-}$). B & E) The corresponding normalized discharge capacities for each capacity limit. C & F) Visual inspection photographs of separators for the cycled cells.

The capacity fading in the $3e^{-}$ and $4e^{-}$ extraction processes is attributed to the solubility in the electrolyte of the active material, an effect observed in both the Na and K systems (**Figure S14C & F**). However, in the Na system, such solubility effects are not apparent during the initial cycles when extracting $1e^{-}$ or $2e^{-}$, with stable cycling maintained for up to 40 cycles. In contrast to Li and Na, the K system exhibits comparatively lower electrochemical stability, with capacity fading rapidly during the initial cycles. This capacity decline may arise from the inefficiency of the potassium plating/stripping process or instabilities at the potassium metal–electrolyte interface (**Figure S14D–F**).

Organic positive	Redox potential	Attained capacity @	Ref.
electrode material	(V vs. Li ⁺ /Li)	C-rate	
Li ₆ THBPD (4e ⁻)	2.85	313 mAh/g, 0.1C	This work
Li ₆ THBPD (2e ⁻)	2.72	156 mAh/g, 0.1C	This work
Li ₂ -Mn- <i>p</i> -DHT MOF	3.2	58 mAh/g, 0.5C	[2]
Li ₄ - <i>p</i> -DHT	2.55	105 mAh/g, 0.2C	[3]
Li ₄ - <i>p</i> -DHT (nanosheets)	2.6	200 mAh/g, 0.1C	[4]
Li ₄ -o-DHT (a)	2.85	100 mAh/g, 0.2C	[5]
Li ₄ - <i>o</i> -DHT (b)	3.1	75 mAh/g, 0.1C	[6]
Mg(Li ₂)- <i>p</i> -DHT	3.4	95 mAh/g, 0.1C	[7]
Li ₄ - <i>p</i> -DHBDS	3.2	100 mAh/g, 0.05C	[8]
Li ₄ - <i>p</i> -DOBDA	3.35	100 mAh/g, 0.125C	[9]
Li ₂ - <i>p</i> -PDSA	3.15	70 mAh/g, 0.1C	[10]
Li ₄ -PTtSA	2.75	90 mAh/g, 0.2C	[10]
Li ₂ -Co-PTtSA	2.85, 3.40	97 mAh/g, 0.2C	[11]
Li ₂ - <i>p</i> -TESO ₂	3.13	30 mAh/g, 0.2C	[12]

 Table S2. Overview of reported organic Li-containing positive electrode materials.

 Table S3. Overview of reported organic Na/K-containing positive electrode materials.

Organic positive	Redox potential	Attained capacity at C-	Ref
organie positive	Redox potential	Finance capacity at C	iter.
electrode material	(V vs. Na ⁺ /Na or K^+/K)	rate	
Na ₆ THBPD	2.4	244 mAh/g, 0.1C	This work
Na ₄ - <i>p</i> -DHT	2.4	183 mAh/g, 0.1C	[13]
Na ₄ -PTtSA	2.5	95 mAh/g, 0.1C	[14]
Na ₂ -Co-PTtSA	2.75, 3.25	94 mAh/g, 0.2C	[11]
K ₆ THBPD	2.5	200 mAh/g, 0.1C	This work
K ₄ -PTtSA	2.6	80 mAh/g, 0.1C	[14]
K ₂ -Co-PTtSA	2.9, 3.55	83 mAh/g, 0.1C	[11]

9. Chemical oxidation of A₆THBPD using nitrosonium tetrafluoroborate (NOBF₄)

Typically, 0.1mmol of A_6 THBPD was dispersed in acetonitrile, and either 0.2 mmol (2 equivalents for a 2e⁻ reaction) or 0.4 mmol (4 equivalents for a 4e⁻ reaction) of NOBF₄ were added, and the resulting reaction mixture stirred for 24 hours at room temperature under inert atmosphere. After the reaction, the 2e⁻ oxidized product was collected by centrifugation and washed several times with diethyl ether. In contrast, the 4e⁻ oxidized product was found completely soluble in the reaction mixture, and was precipitated by adding diethyl ether and washed several times with ether. Both products (**Figure S15A**) were dried at 150 °C, and the samples were characterized as described next.

The oxidized compounds were analyzed by FTIR, NMR and PXRD (Figures S15B, C). The appearance of the quinone carbonyl ($v_{C=0}$) peak at 1677 cm⁻¹ is noted for both, Li₄THBPD and Li₂THBPD. A shift of characteristic v_{C-OLi} band is observed from 1210 cm⁻¹ to 1194 cm⁻¹, indicating the transformation of v_{C-OLi} to $v_{C-O.}$ The ¹H NMR spectra of Li₆THBPD before and after oxidation reveals that the aromatic ring protons shifted from 7.36 ppm to 7.43 ppm (deshielded) and from 6.85 ppm to 6.75 ppm (shielded) upon oxidation. Li₆THBPD exhibits singlets at δ 7.36 and δ 6.85 ppm, while Li₂THBPD shows singlets at δ 7.43 and δ 6.75 ppm. The downfield shifts in Li₆THBPD suggest electronic changes resulting from oxidation (Figure S16). The powder patterns of the pristine sample suggest an amorphous or poor crystalline structure (Figure S15C). Upon oxidation, the pattern becomes increasingly featureless, indicative of further structural disorder or enhanced amorphization. Notably, while the peak at $2\theta \approx 6.8^{\circ}$ remains apparent, the reflections at $2\theta \approx 11.6^{\circ}$, 12.0° , and 13.0° , observed in the pristine state, are significantly diminished in the oxidized material. Later, we conducted electrochemical tests on the Li₂THBPD composite (50% Li₂THBPD, 40% Super P, and 10% PTFE) between 1.8V to 3.8V at 0.1C rate. The results, presented in Figure S15D, indicate poor cycling performance, attributed to high solubility of Li₂THBPD in the electrolyte also evidenced by coloration of glass fiber separator after ten cycles.



Figure S15. A) Chemical oxidation analysis of Li_6 THBPD products. Associated FTIR spectra (B) and XRD patterns (C) before and after chemical oxidation of Li_6 THBPD. D) Galvanostatic charge-discharge profile of Li_2 THBPD positive material in a 1M LiPF₆ in EC/DMC electrolyte.



Figure S16. ¹HNMR spectra of Li₆THBPD before and after oxidation. Li₆THBPD: ¹H NMR (400 MHz, MeOD) δ 7.36 (s, 1H), 6.85 (s, 1H). Li₂THBPD: ¹H NMR (400 MHz, MeOD) δ 7.43 (s), 6.75 (s).

Solubility test of the oxidized phases: After chemical oxidation, the solubility of three materials (Li₂THBPD, Na₂THBPD, and K₂THBPD) was tested in the respective electrolytes (5 mg per 1 mL of electrolyte). As shown in **Figure S17**, all three compounds were fully dissolved showing a brown coloration of the solution.



Figure S17. Solubility test of oxidized form of A_2 THBPD (A: Li, Na or K) in electrolytes: (from left to right) 1M LiPF₆ in EC/DMC, 3M NaTFSI in diglyme, and 1M KTFSI in EC/DEC. In all experiments, 5 mg of oxidized phase (A₂THBPD) have been found to be fully dissolved per 1 mL of electrolyte.

10. Optimization of Li_6THBPD positive electrode material



Figure S18. Cycling performance for one electron (1e⁻) limited material utilization of Li₆THBPD at 0.1C-rate, in 1M LiPF₆ in EC/DMC electrolyte.



Figure S19. A) Reaction mechanism for the two-electron reversible process of Li₆THBPD. B) Impact of different carbon content in electrodes, from 40wt.% to 10wt.%. C-D) Corresponding cycling performance at 30% and 20% carbon content, limited to $2e^{-}$ capacity at rate of 0.1C, using a 1M LiPF₆ in EC/DMC electrolyte.

The optimized Super-P content facilitates electron transport and mitigates the kinetic limitations of the active material. As illustrated in **Figure S19 (B–D)** and **Figure 4C**, adjusting the active material : Super-P ratio influences both energy density and rate capability. By fine-tuning these components, an optimal electrode composition has been achieved. Electrochemical analysis (**Figure S19B**) indicates that with increasing active material content, the electrodes are still able to deliver full capacity, with nevertheless higher polarization and lower efficiency noted, processes also attributed to the material solubilization. These results highlight the critical role of Super-P in compensating for the low conductivity of the active material. Further increasing the Super-P content to 40% enhances cycling stability and maintains favorable rate performance (**Figure 4C**).

11. Na₆THBPD cycling data for two electron (2e⁻) limited material utilization



Figure S20. Capacity retention for two-electron (2e⁻) limited material utilization of Na₆THBPD positive electrode material at cycling rate of 0.05C, using 3M NaTFSI in diglyme(G2) electrolyte.

12. K₆THBPD cycling data for two electrons (2e⁻) limited material utilization



Figure S21. A) Galvanostatic charge-discharge profile for two-electron ($2e^{-}$) limited active material utilization of K₆THBPD in 1M KTFSI in EC/DEC electrolyte, and B) corresponding cycling performance data.



Figure S22. Representation of redox behavior comparison: (A) The conjugated carboxylate anode reduces to Na-enolates at ~0.5 V vs. Na⁺/Na. (B) Na₆-THBPD undergoes a reversible transformation between Na-phenolate and quinone at 2.40 V vs. Na⁺/Na.

The redox behavior of these two compounds differs in terms of both mechanism and operating potential. In the case of 4,4'-biphenyl dicarboxylate sodium salt,^[15] the electrochemical activity involves the reduction of the carboxylate groups to form sodium enolates, as illustrated in **Figure S22A**. This redox process occurs at approximately 0.5 V vs. Na⁺/Na, which is more consistent with negative electrode (anode) rather than positive electrode (cathode). In contrast, Na₆THBPD undergoes a reversible redox process between Na-phenolate and quinone species, as shown in **Figure S22B**. This transformation occurs at an average potential of 2.40 V vs. Na⁺/Na, indicating its suitability for operation at higher voltages. These differences in redox chemistry and potential profiles underline the distinct electrochemical characteristics of Na₆THBPD compared to 4,4'-biphenyl dicarboxylate sodium salt.



13. Cycling stability of high mass loading electrode (half-cell configuration)

Figure S23. Cycling stability of high mass loading positive electrode (12 mg of Li_6THBPD) at rate of 0.1C followed by at 2C, in 1M LiPF₆ in EC/DMC (1:1 by vol.) electrolyte.

SI References:

[1] M. E. Hoque, R. Bisht, C. Haldar, and B. Chattopadhyay, *J. Am. Chem. Soc.*, 2017, **139**, 7745–7748.

[2] D. Rambabu, A. E. Lakraychi, J. Wang, L. Sieuw, D. Gupta, P. Apostol, G. Chanteux,
T. Goossens, and K. Robeyns, A. Vlad, *J. Am. Chem. Soc.*, 2021, 143, 11641.

[3] S. Renault, S. Gottis, A.-L. Barrès, M. Courty, O. Chauvet, F. Dolhem, and P. Poizot, *Energy Environ. Sci.*, 2013, **6**, 2124-2133.

[4] S. Wang, L. Wang, K. Zhang, Z. Zhu, Z. Tao, and J. Chen, *Nano Lett.*, 2013, **13**, 4404.

[5] S. Gottis, A. L. Barres, F. Dolhem, and P. Poizot, *ACS Appl. Mater. Interfaces.*, 2014, 6, 10870.

[6] L. Bernard, A. Jouhara, E. Quarez, Y. Levieux-Souid, S. Le Caër, P. Tran-Van, S. Renault, P. Poizot, *Inorganics.*, 2022, **10**, 62.

[7] A. Jouhara, N. Dupre, A. C. Gaillot, D. Guyomard, F. Dolhem, and P. Poizot, *Nat. Commun.*, 2018, **9**, 4401.

[8] A. E. Lakraychi, E. Deunf, K. Fahsi, P. Jimenez, J. P. Bonnet, F. Djedaini-Pilard, M. Bécuwe, P. Poizot, and F. Dolhem, *J. Mater. Chem. A.*, 2018, **6**, 19182.

[9] L. Sieuw, A. E. Lakraychi, D. Rambabu, K. Robeyns, A. Jouhara, G. Borodi, C. Morari,P. Poizot, and A. Vlad, *Chem. Mater.*, 2020, **32**, 9996.

[10] J. Wang, A. E. Lakraychi, X. Liu, L. Sieuw, C. Morari, P. Poizot, and A. Vlad, *Nat. Mater.*, 2021, **20**, 665.

[11] J. Wang, X. Guo, P. Apostol, X. Liu, K. Robeyns, L. Gence, C. Morari, J.-F. Gohy, andA. Vlad, *Energy Environ. Sci.*, 2022, **15**, 3923.

[12] Y. Zhang, P. Apostol, X. Guo, X. Liu, D. Rambabu, J. Wang, X. Chen, and A. Vlad, *Mater. Today Chem.*, 2023, **28**, 101379.

[13] S. Wang, L. Wang, Z. Zhu, Z. Hu, Q. Zhao, and J. Chen, *Angew. Chem. Int. Ed.*, 2014, 53, 5892-5896.

[14] J. Wang, X. Liu, H. Jia, P. Apostol, X. Guo, F. Lucaccioni, X. Zhang, Q. Zhu, C. Morari,J. F. Gohy, and A. Vlad, *ACS Energy lett.*, 2022, 7, 668-674.

[15] A. Choi, Y.K. Kim, T.K. Kim, M.S. Kwon, K.T. Lee, and H.R. Moon, J. Mater. Chem. A, 2014, 2, 14986-14993.