Redox-Active, Porous Pyrene Tetraone Dendritic Polymers as Cathode Material for Li Ion Batteries

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-Supporting Information-

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1 Experimental Section

1.1 General Remarks

All reagents and solvents were purchased from Fisher Scientific, Alfa Aesar, Sigma-Aldrich, TCI or VWR and were used without further purification unless otherwise noted. For thin-layer chromatography, silica gel 60 F254 plates from Merck were used and examined under UV irradiation (λ = 254 and 365 nm). Flash column chromatography was performed on silica gel from Sigma-Aldrich (particle size 0.04-0.063 mm) with petroleum ether (PE) and dichloromethane as the eluents. Melting points (not corrected) were measured by using a Büchi Melting Point B-545 instrument. IR spectra were recorded on a Ge ATR crystal by using a Bruker Lumos spectrometer. NMR spectra were recorded by using Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million [ppm] relative to trace CHCl₃ in the corresponding deuterated solvent. Elemental Analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Absorption spectra were recorded on a Jasco UV-VIS V-730. Emission spectra were recorded on a Jasco FP-8300. Electrochemical data were obtained in a solution of TBAPF (tetra-n-butyl ammonium hexafluorophoshate) (0.05 M) in CH₂Cl₂ that contained 1 mM of the investigated compound, as indicated. Ferrocene (1 mM) was used as an internal standard. Cyclic voltammograms were obtained at a scan rate of 0.1 Vs⁻¹ with a Pt working electrode (0.78 mm²), a Pt counter electrode, and an Ag reference electrode. Powder X-ray diffractograms were obtained with a Rigaku Smartlab X-Ray Diffractometer with a HyPix-3000 detector, measured in a glass capillary ($\emptyset = 0.5$ mm) as sample container. Thermal gravimetric analyses were measured on a Mettler-Toledo TGA/DSC1 instrument with a TGA/DSC-Sensor 1100 equipped with a MX1 balance (Mettler-Toledo) and a GC100 gas control box for nitrogen supply. TGA samples were measured in 70 µL Al₂O₃ crucibles. All measurements were carried out under a flow of nitrogen (20 mL/min) with a heating rate of 10 K/min. Materials for XPS characterization were transferred to the ultrahigh vacuum chamber of the XPS system (Thermo Scientific ESCALAB 250Xi). The XPS measurements were performed using a XR6 monochromated AI K_a source (hv = 1486.6 eV) and a pass energy of 20 eV. Scanning electron micrographs were acquired using a Crossbeam 540 field emission scanning electron microscope (Carl Zeiss Microscopy, Germany). Gas sorption measurements were carried out by nitrogen (Air Liquide 5.0, 99.999%, non-ideality factor: 6.580.10⁻⁶ torr⁻¹) adsorption and desorption analysis at 77.35 K with autosorb computer-controlled surface analyzers (AUTOSORB-iQ2 or AUTOSORB-iQ3, Quantachrome) using the Vector DoseTM analysis method. Materials were dried 12 h at T = 120 °C at the activation station of the AUTOSORB-iQ2 or AUTOSORB-iQ3 instruments (Quantachrome) in the corresponding sample tubes and were measured directly after the activation. The Brunauer-Emmett-Teller (BET) surface areas were calculated assuming a cross sectional area of 0.162 nm² for the nitrogen molecules in the pressure range $p/p_0 = 0.01-0.1$. Rouquerol plots were created to assure using the right pressure range for the BET equations, here only the relative pressure values with a positive slope in the Rouquerol plot were taken into account.^[S1] The quenched soliddensity functional theory (QSDFT model) and isotherm data were used to calculate the pore size distribution.^[S2]

1.2 Synthetic Procedures

Model compounds **1** and $2^{[S3]}$ and borylated pyrene tetraketal $3^{[S4]}$ were prepared according to literature-known procedures.



Scheme S1. Molecular structures of model compounds 1 and 2.

General procedure for the synthesis of **D-PTK (GP1):** A screw capped vial (8 mL or 20 mL) was charged with borylated pyrenetetraketal $\mathbf{3}^{[S2]}$ (3 equiv.) and 1,3,5-tribromobenzene **8** (2 equiv.). THF and aqueous K₂CO₃ solution (1 M) (1:1) were added subsequently under argon atmosphere and the mixture was degassed with argon for 30 seconds. While stirring tris(dibenzylideneacetone)dipalladium(0) and tri*tert*-butylphosphonium tetrafluoro-borate were added. The vial was capped and heated to 80 °C for 14-19 h while stirring vigorously. After cooling to rt the mixture was filtered over a polyamide microfilter and purified as described below.

batch	diboronic ester 4 [mg]	tribromide 8 [mg]	Pd₂(dba)₃ [mg] ([mol-%])	H′BuPBF₄ [mg]	THF/K₂CO₃ (1:1) [mL]	time [h]	yield [%]
D-PT-1	69	21	9 (10)	12	0.2	19	82
D-PTK-2	1035	318	82 (6)	104	3.0	14	~100*
D-PTK-3	201	61	5 (2)	7	0.6	18	61
			- (-)	-			

Table S1. Amounts of reagents and solvents, reaction times and yields of the syntheses of PPTAs **1-3**.

* solvent/water residues

General procedure for the synthesis of **D-PTO** (**GP2**): A screw capped vial (8 mL) was charged with the **D-PTK** and trifluoroacetic acid/water (9:1). The deep red suspension was stirred at room temperature for 24-72 h and filtered off. The solid was washed with water and ethanol, stirred for one hour in 1 M sulfuric acid, filtered and purified as described below.

batch	Prepared from	D-PTK [mg]	TFA/ H ₂ O (9:1) [mL]	1 M H₂SO₄ [mL]	time [h]	yield [%]
D-PTO-1	D-PTK-1	48	1.0	0.5	72	92
D-PTO-2a	D-PTK-2	709	15	10	24	79
D-PTO-3	D-PTK-3	120	2.5	1.0	62	99

Table S2. Amounts of reagents and solvents, reaction times and yields of the syntheses of D-PTOs 1-3.

D-PTK-1 was prepared according to **GP1** using the amounts and reaction time given in Tab. S1. The crude product was washed successively with CH_2Cl_2 (50 mL), EtOH (50 mL) and Et_2O (50 mL). After drying under reduced pressure over $CaCl_2$ the product was obtained as grey powder (59 mg, 82%). **m.p.** > 410 °C. **IR** (ATR): \tilde{v} [cm⁻¹] = 3423 (w), 2961 (w), 2876 (w), 1707 (vw), 1635 (w), 1597 (w), 1450 (w), 1389 (vw), 1362 (vw), 1327 (w), 1286 (w), 1263 (m), 1180 (m), 1095 (vs), 1014 (s), 980 (m), 926 (w), 901 (m), 874 (w), 814 (vw), 795 (vw), 754 (m), 729 (w), 700 (w), 642 (w), 623 (vw). **Elemental analysis calc. for C₄₂H₃₃O₁₂•7H₂O** [%]: C: 58.94, H: 5.54. Found: C: 58.69, H: 4.78.

D-PTK-2 was prepared according to **GP1** using the amounts and reaction time given in Tab. S1. The crude product was washed successively with water (100 mL), EtOH (150 mL) and Et₂O (200 mL). After drying under reduced pressure, the product was obtained as grey powder (888 mg, >100%; solvent/water residues). **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3473 (w), 2974 (w), 2951 (w), 2875 (w), 1615 (w), 1452 (w), 1405 (w), 1386 (w), 1374 (m), 1331 (w), 1289 (m), 1263 (m), 1249 (m), 1182 (m), 1143 (w), 1117 (m), 1094 (vs), 1024 (m), 1013 (s), 980 (m), 959 (m), 917 (w), 906 (m), 899 (m), 889 (w), 873 (w), 852 (m), 754 (m), 730 (w), 690 (m), 644 (w). **Elemental analysis calc. for C₄₂H₃₃O₁₂•C₄H₁₀O•4H₂O [%]: C: 63.08, H: 5.87. Found: C: 63.48, H: 5.89.**

D-PTK 3: **D-PTK 3** was prepared according to **GP1** using the amounts and reaction time given in Tab. S1. The crude product was washed successively with water (50 mL), conc. NH₃ (10 mL), EtOH (50 mL), CH₂Cl₂ (50 mL) and Et₂O (50 mL). After drying at a Kugelrohrofen the product was obtained as light grey powder (127 mg, 61%). **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3531 (w), 2962 (w), 2874 (w), 2727 (vw), 1597 (w), 1450 (w), 1389 (vw), 1325 (w), 1286 (w), 1263 (m), 1180 (m), 1095 (vs), 1014 (s), 980 (m), 964 (m), 926 (m), 901 (m), 872 (m), 816 (vw), 810 (vw), 795 (vw), 754 (m), 729 (vw), 704 (vw), 642 (w). **Elemental analysis calc. for C₄₂H₃₃O₁₂•3H₂O [%]: C: 64.36, H: 5.02. Found: C: 65.45, H: 5.08.**

D-PTO-1: D-PTK-1 (48 mg) was reacted according to **GP2** using the amounts and reaction time given in Tab. S2. The crude product was washed with water (50 mL), EtOH (50 mL) and Et₂O (50 mL). After drying at a Kugelrohrofen (100 °C) the product was obtained as red powder (28 mg, 92%). **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3445 (w), 3069 (vw), 2970 (vw), 1682(vs), 1597(m), 1543 (w), 1493 (vw), 1433 (m), 1311 (m), 1259 (s), 1188 (w), 1155 (w), 1095 (m), 1057 (w), 1016 (w), 970 (vw), 918

(w), 876(m), 835 (w), 796 (vw), 760 (vw), 734 (vw), 715 (m), 700 (w), 638 (w). Elemental analysis calc. for $C_{30}H_9O_6\bullet 5H_2O$ [%]: C: 64.87, H: 3.45. Found: C: 65.29, H: 3.51.

D-PTO-2a: D-PTK-2 (709 mg) was reacted according to **GP2** using the amounts and reaction time given in Tab. S2. The crude product was washed with water (150 mL), EtOH (100 mL) and Et₂O (100 mL). After drying at a Kugelrohrofen (100 °C) the product was obtained as red powder (356 mg, 79%). **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3433 (w), 3070 (vw), 1682 (vs), 1599 (m), 1543 (w), 1495 (vw), 1433 (m), 1402 (w), 1313 (m), 1261 (m), 1190 (w), 1155 (vw), 1095 (m), 1049 (w), 1014 (w), 968 (vw), 920 (w), 877 (w), 854 (vw), 831 (vw), 795 (vw), 715 (m), 702 (w), 638 (w). **Elemental analysis calc. for C₃₀H₉O₆•4H₂O [%]: C: 67.04, H: 3.19. Found: C: 67.38, H: 3.60. Elemental composition (XPS**) [%]: C: 77.03, O: 19.66, H: 1.84, B: 1.47.

D-PTO-2b: D-PTO-2a (102 mg) was extracted via a Soxhlet apparatus with MeOH (14 h), THF (7 h), CH_2Cl_2 (15 h) and Et_2O (2 h). The insoluble residue was dried under reduced pressure over CaCl₂. **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3472 (w), 3069 (vw), 2970 (vw), 2874 (vw), 1682 (vs), 1599 (w), 1547 (w), 1493 (vw), 1433 (m), 1313 (m), 1261 (m), 1190 (w), 1153 (vw), 1097 (m), 1049 (w), 1014 (w), 968 (vw), 920 (w), 877 (w), 854 (vw), 833 (vw), 796 (vw), 781 (vw), 733 (w), 715 (m), 702 (w), 638 (w). **Elemental analysis calc. for C₃₀H₉O₆•4H₂O [%]: C: 67.04, H: 3.19. Found: C: 67.07, H: 4.11. Elemental composition (XPS**) [%]: C: 81.46, O: 17.90, H: 0.64.

D-PTO-3: **D-PTK 2** (709 mg) was reacted according to **GP2** using the amounts and reaction time given in Tab. S2. The crude product was washed with water (50 mL), EtOH (50 mL) and Et₂O (50 mL). After drying at a Kugelrohrofen (100 °C) the product was obtained as red powder (356 mg, 79%). **m.p.** > 410 °C. **FT-IR** (ATR): \tilde{v} [cm⁻¹] = 3404 (w), 1682 (vs), 1599 (m), 1547 (w), 1433 (s), 1313 (m), 1261 (m), 1192 (w), 1095 (m), 1051 (w), 1016 (w), 991 (vw), 968 (vw), 920 (w), 877 (w), 854 (vw), 833 (w), 796 (vw), 733 (w), 715 (m), 638 (w). **Elemental analysis calc. for C₃₀H₉O₆•3H₂O [%]: C: 69.37, H: 2.91. Found: C: 68.70, H: 3.21.**



Figure S2. ¹³C CP MAS NMR spectrum (10000 Hz) of D-PTO 2a.

3 FT-IR Spectra



Figure S3. FT-IR spectra (ATR) of tetraketal 1 and D-PTK 1-3 (from top to bottom).



Figure S4. FT-IR spectra (ATR) of tetraone 2 and D-PTOs 1-3 (from top to bottom).

4 X-Ray Photoemission Spectroscopy



Figure S5. XPS spectra measured on **D-PTO 1**. Please note that the features in the B1s spectrum originate from Br3p and not from B.

Element	Atomic %
Br species 1	0.43
Br species 2	0.28
C species 1	70.49
C species 2	9.29
C species 3	3.29
O species 1	14.21
O species 2	0.98
Pd species 1	0.11
Pd species 2	0.28

Table S3. Elemental composition of D-PTO 1.



Figure S6. XPS spectra measured on D-PTO 2a.

Table S4. Elemental con	nposition o [.]	f D-P1	O 2a .
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Element	Atomic %
C species 1	61.92
C species 2	12.73
C species 3	3.82
O species 1	17.02
O species 2	3.01
B species 1	1.49



Figure S7. XPS spectra measured on D-PTO 2b.

Element	Atomic %
C species 1	63.61
C species 2	13.53
C species 3	4.85
O species 1	15.84
O species 2	2.18



Figure S8. XPS spectra measured on D-PTO 3.

Table S6. Elemental composition of D-PTO 3.

Element	Atomic %
C species 1	53.72
C species 2	13.8
C species 3	10.22
O species 1	0.27
O species 2	21.99

Table S5. Elemental composition of D-PTO 2b.



Figure S9. TGA curves of D-PTOs 1, 2b and 3 measured under N₂ atmosphere with 10 K min⁻¹.



6 Powder X-Ray Diffraction

Figure S10. PXRD spectra of D-PTOs 1-3.



Figure S11. a-d) Rouquerol plots of D-PTOs 1-3 (BET area highlighted in red). e-h) t-Plots of D-PTOs 1-3.

8 Electrode Fabrication and Battery Setup

The electrochemical measurements to study the materials properties with respect to their application in LIBs were performed by means of Swagelok-type half-cells with lithium metal foil (Alfa Aesar) as counter electrode.^[S5] 1M LiTFSI in dioxolane-dimethoxyethane DOL/DME (1:1) was used as the liquid electrolyte, 200 µL per cell. Cyclic voltammetry and galvanostatic cycling measurements were performed at 25 °C using a VMP3 multichannel potentiostat (Bio-LogicSAS). For the electrode preparation, as-prepared **D-PTO** samples were mixed with carbon black (Super C65, Timcal) and polyvinylidene fluoride (PVDF, Sigma-Aldrich, 99%) binder at a weight ratio of 35:60:5 (40:50:10 in the case of **D-PTO-3** electrode used for the CV), and further soaked in anhydrous 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich, 99%). The slurry was stirred for 24 h and then casted onto a circular Aluminum mesh current collector (approx. 10 mm in diameter) with a mass loading of about 3.3-5.1 mg cm⁻², the wet electrodes were dried for 20 h under vacuum at 80 °C, pressed and weighed. The resulting electrodes were dried again in a vacuum oven at 80 °C for 2 h before transferred to an Ar atmosphere glove box.

Ultrasonic treatment has been applied in the aim to achieved better dispersion of **D**-**PTO**. Although the particle size has been effectively reduced, the influence on cycling stability turned out to be detrimental. The specific capacity showed a higher initial value but experienced fast decay upon cycling, which can be attributed to the structural degradation induced by oscillation and heating during ultrasonic treatment, hence the electrodes were prepared with normal procedure described before.

The morphological characteristics of the **D-PTO** based electrodes have been studied via SEM (Fig. S8). The particles possess amorphous surfaces and a certain degree of agglomeration. Due to the insoluble nature of **D-PTO** in organic solvents, the materials could not be fully dispersed during stirring process and thus was embedded in the carbon network as small particles in the resulting electrodes (Fig. S8c,d).



Figure S12. Morphological characteristics of D-PTO 2b at a) 1 μ m; b) 10 μ m scales and D-PTO 2b based electrode at c) 1 μ m; b) 10 μ m scales.



Figure S13. Behavior evolution of **D-PTO 2a** based electrode from subsequent cycles in different potential ranges: a) 2.5-3.5V, 1~6th cycle; b) 1.5-4.0V, 7~8th cycle; c) 2.5-3.5V, 9~10th cycle.

9 References

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