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FULL PAPER

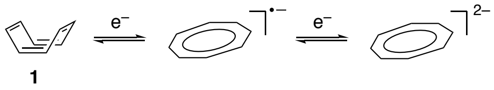
# Evaluation of cyclooctatetraene-based aliphatic polymers as battery materials: Synthesis, electrochemical and thermal characterization, supported by DFT-calculations

Martin E. Speer,[a] Christopher Sterzenbach,[b] and Birgit Esser*[a]

**Abstract:** Organic electrode materials for rechargeable batteries are becoming a viable alternative for existing technologies. In particular, redox polymers have shown great performances. While many cathode-active derivatives are known, the development of their anode-active counterparts, required for the design of full-organic batteries, lacks behind. Here we present our investigation on the suitability of cyclooctatetraene (COT)-based aliphatic polymers as anode-active battery materials, inspired by the known reversible reduction chemistry of COT at low electrochemical potential. We found that both synthesized polystyrene derivatives, side-group functionalized with COT, showed limited electrochemical reversibility of the reduction processes, while reductions proceeded reversibly in model compounds for these polymers. Differential scanning calorimetry measurements and density-functional theory calculations showed that this incomplete reversibility was due to cross-linking reactions occurring between COT units in the polymers. For a future design of COT-based redox polymers we propose to employ a molecular design that prevents these cross-linking reactions.

## Introduction

The development of organic electrode materials for batteries is a growing field of research.[1–6] In order to find suitable organic materials, new monomeric and polymeric compounds have to be identified, which show an electrochemically highly reversible redox chemistry.[7] While the majority of organic electrode materials developed is of p-type and can be reversibly oxidized at potentials of up to 4.1 V *vs.* Li/Li$^+$,[6,8] making them suitable as battery cathode materials, fewer examples for n-type and potential anode-materials exist.[9,10] These, however, are necessary to build full-organic batteries. Cyclooctatetraene (COT, **1**) could be ideally suited as n-type, redox-active unit. Its redox chemistry has interested chemists for almost 60 years.[11–13] Upon two-electron reduction, COT is transformed to a 10 π-aromatic, planar and stable dianion (Scheme 1). This reduction can be performed chemically[13] as well as electrochemically.[14] The electrochemical reversibility of this process has rendered COT of interest to the design of molecular actuators,[15] due to the conformational change from tub-shape to planar upon reduction, and for the storage of electrons in battery applications.[16–18] In order to be employed as electrode-active battery material, the incorporation of the COT unit into a polymeric architecture is required to provide insolubility in solvents commonly used for battery electrolytes.[6] While molecules containing several COT units have been reported before,[17,19–22] to the best of our knowledge, there is no account of polymers incorporating COT units in the side group.



Scheme 1. Two-step reduction of cyclooctatetraene (**1**) to its dianion.

We herein describe the synthesis and electrochemical characterization of the two aliphatic polymers **P1** and **P2**, which are side-group functionalized with COT, as well as their electrochemical characterization. The thermal properties of these polymers were investigated, supported by DFT calculations, showing cross-linking reactions in the solid state. We furthermore report on the synthesis and electrochemical investigation of the four COT model compounds **2**-**5**, whose electrochemical properties guided the design of the polymers mentioned above.

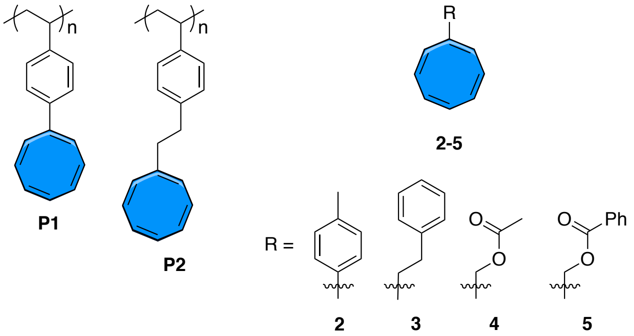


Figure 1. Cyclooctatetraene-based polymers **P1** and **P2** and model compounds **2**-**5** investigated in this study.

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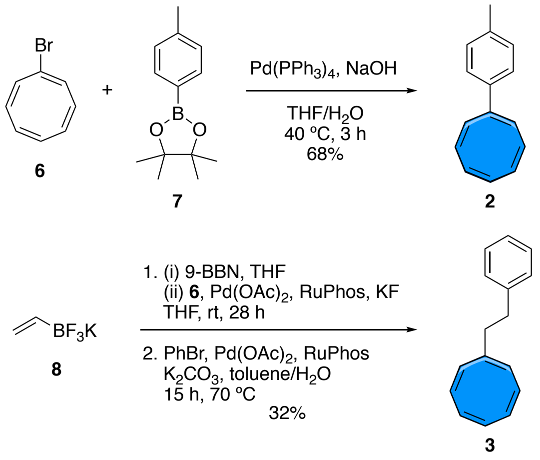
## Results and Discussion

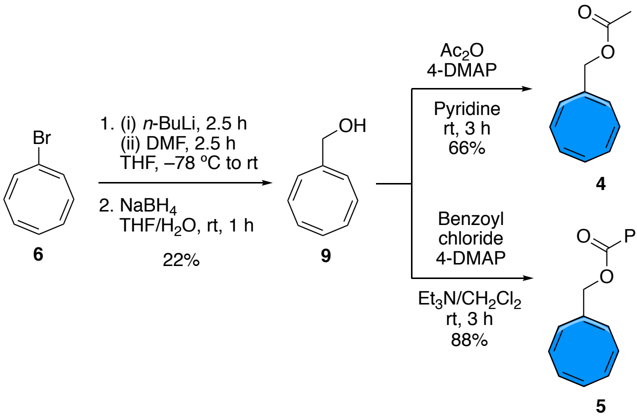
A variety of different aliphatic polymer backbones are available, which could be used to incorporate COT as a side group. Initially, the direct free-radical polymerization of vinyl-COT was attempted, however, did not lead to any polymerized material. Hence model compounds **2**–**5** were synthesized in order to identify a suitable polymer backbone, which would allow for a reversible reduction of the COT unit. **2** and **3** represent models for polystyrene derivatives, in which the COT unit is directly attached to the styrene unit (**2**) or separated by an ethyl linker (**3**). **4** is a model compound for an acrylate polymer, and **5** for a polystyrene derivative, in which the COT unit is attached via an ester group.



Scheme 2. Synthesis of model compounds **2** and **3**.

Model compounds **2**–**5** were synthesized starting from bromo-COT (**6**).[23] A Suzuki-Miyaura coupling with *p*-tolyl boronic ester **7**[24] afforded model compound **2** in 68% yield (Scheme 2). For the synthesis of **3** a procedure by Molander *et al.*[25] was employed. Potassium vinyltrifluoroborate (**8**) was hydroborated with 9-BBN *in situ*, yielding a 1,2-dibora intermediate. This was then subjected to two sequential Suzuki-Miyaura couplings with bromo-COT (**6**) followed by bromobenzene to afford model compound **3** in 32% overall yield. For the synthesis of model compounds **4** and **5**, the bromo functionality in **6** was replaced by an aldehyde group, which was subsequently reduced to alcohol **9** (Scheme 3). **9** was then transformed to esters **4** and **5** through reaction with acetic anhydride and benzoyl chloride, respectively, employing standard protocols.

Cyclic voltammetry measurements in solution were performed on model compounds **2**–**5** to provide information on the reversibility of the reduction process of the COT unit. Depending on the solvent, derivative **2** showed one or two chemically reversible reduction waves of the COT moiety (Figure 2). While in DMF the two one-electron reductions leading to the COT radical anion and dianion appeared at separate half-wave potentials of $E_{1/2}$ = −2.17 and −2.30 V *vs.* Fc/Fc$^+$, in THF only one two-electron reduction wave was visible at a half-wave potential of −2.33 V *vs.* Fc/Fc$^+$. A similar solvent dependence of the electrochemical behaviour of COT has been observed before.[26–28]



Scheme 3. Synthesis of model compounds **4** and **5**.

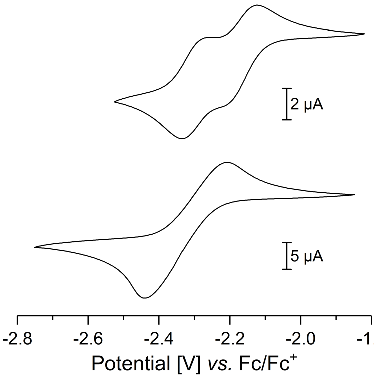


Figure 2. Cyclic voltammograms of **2** in DMF (top) and THF (bottom) (1 mM, scan rate 100 mV s$^{-1}$, with 0.1 M *n*-$Bu_4NPF_6$, glassy carbon electrode).

The reductions of model compound **3** with an ethyl linker were slightly less reversible, as shown in Figure 3. In DMF two separate reduction waves appeared at half-wave potentials of $E_{1/2}$ = −2.26 and −2.42 V *vs.* Fc/Fc$^+$. In THF both reductions took place at the same half-wave potential of $E_{1/2}$ = −2.41 V *vs.* Fc/Fc$^+$, however, in the anodic scan direction a shoulder is visible at about −2.44 V *vs.* Fc/Fc$^+$, indicating that re-oxidation to the radical anion and neutral COT took place at two separate potentials. Compared to model compound **2**, the reductions of **3** are shifted to more negative potentials by ca. 0.1 V. This is likely due to electronic conjugation between the *p*-tolyl and COT groups in **2**, which is absent in **3**.

In compounds **4** and **5** the reductions were irreversible, likely due to the redox activity of the ester functionalities (see SI).[29] Hence, the highest reversibility of the COT reductions was found for model compounds **2** and **3**, and for this reason a poly(styrene) backbone was chosen for the COT polymers with a direct connection to the COT unit (**P1**) or connected via an ethyl linker (**P2**).

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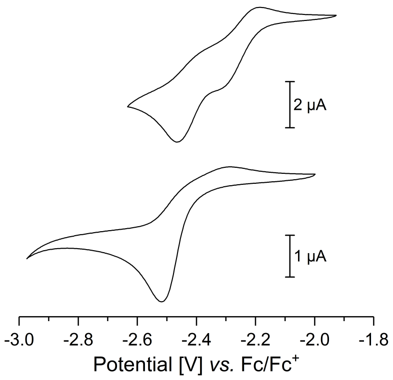
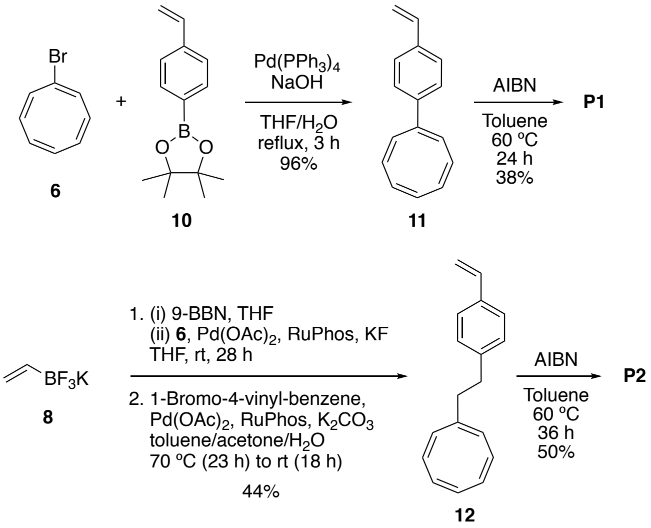


Figure 3. Cyclic voltammograms of **3** in DMF (top) and THF (bottom) (1 mM, scan rate 100 mV s$^{-1}$, with 0.1 M $n$-$Bu_4NPF_6$, glassy carbon electrode).

The synthesis of polymers **P1** and **P2** proceeded from bromo-COT (**6**), as shown in Scheme 4. Suzuki-Miyaura coupling of **6** with styrene boronic ester **10** provided monomer **11** in 96% yield. Monomer **12** was synthesized employing the procedure mentioned above by Molander *et al.*:[25] **6** and 1-bromo-4-vinylbenzene were sequentially coupled to the 1,2-dibora intermediate generated by hydroboration of vinyltrifluoroborate (**8**) with 9-BBN. This provided monomer **12** in 44% yield. The free-radical polymerizations of **11** led to polymer **P1** with a molecular weight of $M_n$ = 10,900 g mol$^{-1}$ and a PDI of 1.90, while **P2** was obtained from **12** with a molecular weight of $M_n$ = 37,000 g mol$^{-1}$ and a PDI of 2.90.



Scheme 4. Synthesis of polymers **P1** and **P2**.

In order to evaluate the reversibility of the reduction processes in COT-polymers **P1** and **P2**, cyclic voltammetry measurements were performed. In DMF **P1** showed two reduction waves in close proximity with cathodic peak potentials of $E_{pc}$ = −2.25 V and −2.34 V *vs.* Fc/Fc$^+$, but reoxidation occurred with incomplete reversibility. In THF **P1** showed one reduction wave for both electron transfers, as was observed for model compound **2**, with a cathodic peak potential of $E_{pc}$ = −2.38 V *vs.* Fc/Fc$^+$. For **P2** the reduction occurred at a cathodic peak potential of $E_{pc}$ = −2.64 V *vs.* Fc/Fc$^+$ in THF (Figure 5).

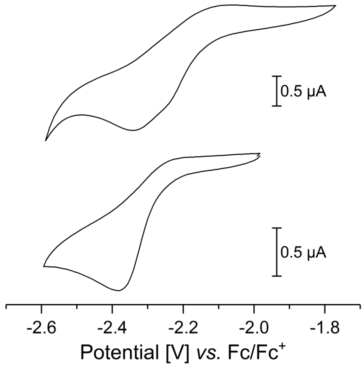


Figure 4. Cyclic voltammograms of **P1** in DMF (top) and THF (bottom) (1 mM, scan rate 100 mV s$^{-1}$, with 0.1 M $n$-$Bu_4NPF_6$, glassy carbon electrode).

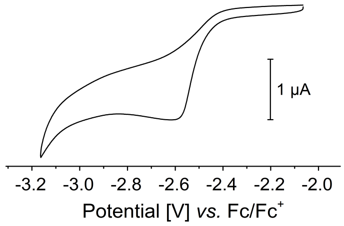


Figure 5. Cyclic voltammogram of **P2** in THF (1 mM, scan rate 20 mV s$^{-1}$, with 0.1 M $n$-$Bu_4NPF_6$, glassy carbon electrode).

We assume that the incomplete reversibility of the reduction processes in **P1** and **P2** was partly due to inter- and intramolecular dimerization processes between COT units. These were observed when the thermal properties of **P1** and **P2** were investigated. While thermal gravimetric analysis (TGA) indicated a high thermal stability and no decomposition below 435 ºC for **P1** and 402 ºC for **P2** (see SI), the DSC measurements showed the occurrence of strongly exothermic reactions upon heating above 200 ºC (Figure 6). To gain information on the enthalpy change during this reaction, the DSC curves were evaluated using the method by Borchardt and Daniels.[30] This single scan method allows for a fast determination of the activation energy of an *n*th order reaction, proceeding from the general rate equation (for further details see SI). For **P1** the exothermic reaction occurred with an activation enthalpy of $\Delta H^{\ddagger}$ = 22.7 kcal mol$^{-1}$ (per COT subunit) in a reaction order of $n$ = 1.3 and with a total enthalpy change of $\Delta H$ = −21.4 kcal mol$^{-1}$ (per COT subunit). For **P2** the activation enthalpy amounted to $\Delta H^{\ddagger}$ = 48.8 kcal mol$^{-1}$ per COT subunit (reaction order of $n$ = 2) and the total enthalpy change to $\Delta H$ = −27.7 kcal mol$^{-1}$ (for details see SI).

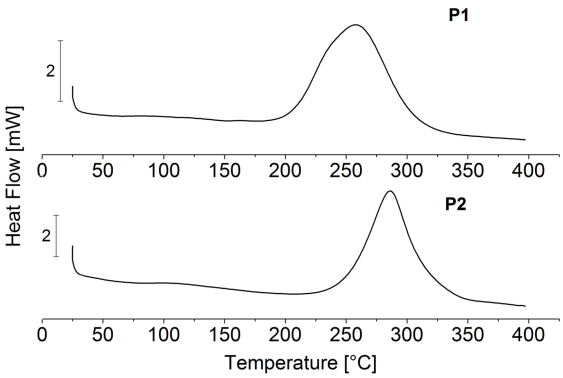
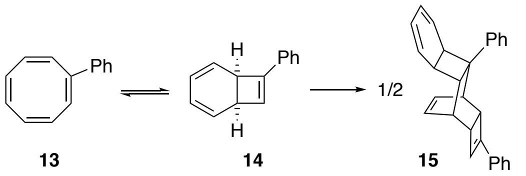


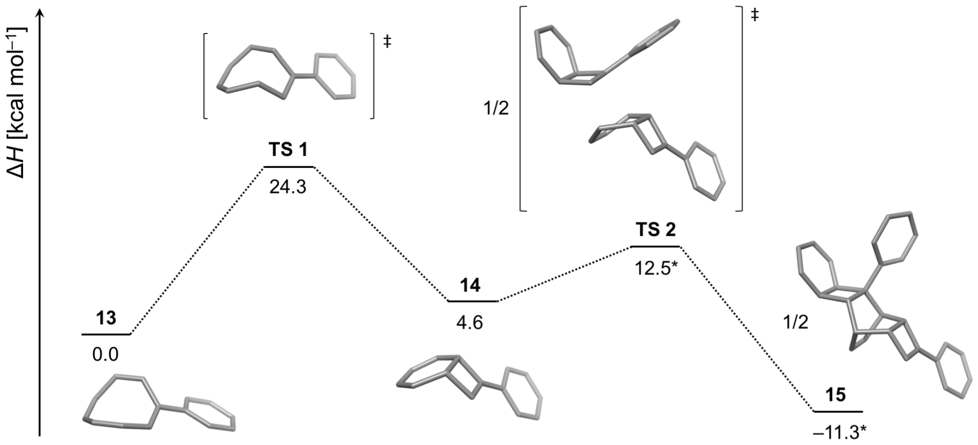
Figure 6. Differential scanning calorimetry (DSC) heating curves of **P1** (top) and **P2** (bottom) (Heating rate 10 K min$^{-1}$, $N_2$). The DSC measurements show the occurrence of strongly exothermic reactions at 258 °C (**P1**) and 286 °C (**P2**). No glass transition appeared during heating.

COT is known to undergo dimerization processes upon heating in the bulk state or even upon standing at room temperature.[11] The initial reaction of this process is either a valence tautomerization of the COT units to bicyclo[4.2.0]-octa-2,4,7-triene through disrotatory ring closure (see Scheme 5), which can act both as diene and dienophile in a [4+2]-cycloaddition, or a direct [4+2]-cycloaddition between two COT units.[11,12] Both the initial adducts can undergo further rearrangement or bond-forming processes leading to a number of dimeric products that have been well characterized.[11,31,32] In order to investigate whether the experimental values from the DSC measurements correspond to cycloaddition reactions between COT units in **P1** and **P2**, density functional theory (DFT) calculations were performed (for details see Experimental Section and SI) using phenyl-COT (**13**) as a model compound for **P1** and methyl-COT (**16**) for **P2**. **13** can undergo valence tautomerization to a bicyclo[4.2.0]-octa-2,4,7-triene, of which four constitutional isomers were optimized with **14** being the most stable one (Scheme 5). The activation enthalpy for the valence tautomerization of **13** to **14** was calculated to be $\Delta H^{\ddagger}$ = 24.3 kcal mol$^{-1}$ (PW6B95-D3/def2-QZVP(COSMO-RS, benzene)//TPSS-D3/def2-TZVP, see also Figure 7). This corresponds well with the activation enthalpy experimentally determined by Huisgen for the rearrangement of **13** to **14** of $\Delta H^{\ddagger}$ = 25 kcal mol$^{-1}$,[33,34] and with the experimental value of activation enthalpy obtained from the DSC heating curve of **P1** of $\Delta H^{\ddagger}$ = 22.7 kcal mol$^{-1}$ per COT subunit.



Scheme 5. Valence tautomerization of phenyl-COT (**13**) as a model compound for **P1** to the bicyclo[4.2.0]-octa-2,4,7-triene **14** and [4+2]-cycloaddition to **15**.

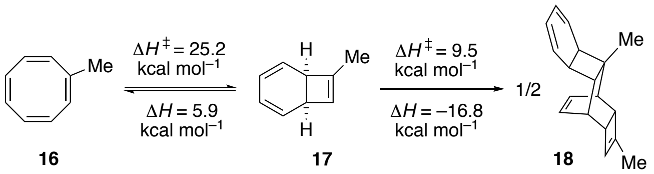
Once **14** is formed it can undergo dimerization in form of a [4+2]-cycloaddition. The structures of eight different dimers were optimized, of which **15** was the most stable. With $\Delta H^{\ddagger}$ = 7.9 kcal mol$^{-1}$ (PW6B95-D3/def2-QZVP(COSMO-RS, benzene)//TPSS-D3/def2-TZVP) the activation enthalpy for the dimerization of **14** to **15** is significantly lower than that for the valence tautomerization of **13** to **14**. The reaction enthalpy for the whole process **13** → **15** was calculated to be $\Delta H$ = −13.6 kcal mol$^{-1}$ (normalized to one molecule of **13**), while the experimental reaction enthalpy obtained from the DSC heating curve of **P1** amounted to $\Delta H$ = −21.4 kcal mol$^{-1}$ per COT subunit. This deviation can be rationalized by assuming that the dimerization products of the COT units in **P1** can undergo further exothermic reactions.



* Enthalpies are normalized to one molecule of **13**

Figure 7. Calculated reaction path for the valence tautomerization of **13** to **14** followed by dimerization through [4+2]-cycloaddition to **15** (PW6B95-D3/def2-QZVP(COSMO-RS, benzene)//TPSS-D3/def2-TZVP).

Methyl-COT (**16**) served as a model compound for **P2** (Scheme 6). The calculated activation enthalpy for the valence tautomerization of **16** to **17** amounts to $\Delta H^{\ddagger} = 25.2$ kcal mol$^{-1}$ (PW6B95-D3/def2-QZVP(COSMO-RS, benzene)//TPSS-D3/def2-TZVP), which is close to that calculated for the phenyl derivative **13**. With $\Delta H^{\ddagger} = 48.8$ kcal mol$^{-1}$ per COT subunit the experimental value from the DSC curve of **P2**, however, deviates significantly. The reason for this is not clear. The reaction enthalpy for the whole process **16** → **18** was calculated to be $\Delta H = -10.9$ kcal mol$^{-1}$ (normalized to one molecule of **16**), while the experimental reaction enthalpy obtained from the DSC heating curve of **P2** amounted to $\Delta H = -27.7$ kcal mol$^{-1}$ per COT subunit. Again, this deviation is likely due to the fact that the COT units in **P2** can undergo further exothermic reactions once structures such as **18** are formed.



Scheme 6. Valence tautomerization of methyl-COT (**16**) as a model compound for **P1** to bicyclo[4.2.0]-octa-2,4,7-triene **17** and [4+2]-cycloaddition to **18** including calculated activation and reaction enthalpies (PW6B95-D3/def2-QZVP(COSMO-RS, benzene)//TPSS-D3/def2-TZVP).

These dimerization reactions of COT units in **P1** and **P2** were likely responsible for the lower observed electrochemical reversibility of the reduction processes compared to model compounds **2** and **3**. Furthermore, the resulting cross-linking between polymer chains in **P1** and **P2** already occurred at room temperature, since these polymers turned insoluble in organic solvents after storing them for several days on the bench.

## Conclusions

In conclusion we have reported on the synthesis of two novel aliphatic polymers **P1** and **P2**, side-group-functionalized with cyclooctatetraene (COT) units, and on four model compounds **2**-**5**. Electrochemical investigations showed the reduction processes of the COT units to occur with high reversibility in model compounds **2** and **3**, while electrochemical reversibility was slightly reduced in the structurally similar polymers **P1** and **P2**. This was ascribed to thermal dimerization and cross-linking reactions between COT units in **P1** and **P2**, which were investigated using differential scanning calorimetry (DSC) and density functional theory (DFT) calculations. Hence, due to the limited electrochemical reversibility of the reduction processes in **P1** and **P2**, these COT-polymers are not suitable for an application as electrode-active battery material. In a more advanced design of COT redox polymers, such cross-linking processes will have to be prevented to achieve high electrochemical reversibility of the redox processes, e.g. by adding more space between COT subunits along the polymer chain.

## Experimental Section

Chemicals were obtained from commercial suppliers and used without further purification. Experiments with water- or oxygen-sensitive substances were carried out under an argon atmosphere using glassware dried by heating under vacuum and standard Schlenk-techniques. Anhydrous solvents (THF, toluene, $CH_2Cl_2$) were obtained from a solvent purification system (MB-SPS-800) and stored over 3 Å molecular sieves. Other anhydrous solvents were obtained by drying over activated molecular sieves (3 Å) for several days. Ethyl acetate and cyclohexane for flash chromatography were purchased in technical grade and purified by distillation using a rotary evaporator. Other solvents were purchased and used in analytical or HPLC grade. $^{1}$H and $^{13}$C{$^{1}$H}NMR spectra were recorded on Bruker Avance dpx 400, dpx 300, III HD 300 and II 400 spectrometers at room temperature and referenced to the residual proton or carbon resonance of the deuterated solvent.[35] EI-MS spectra were recorded on a MAT 90 or a MAT 95 XL sector field device from Thermo Finnigan. HRMS spectra were measured on a Thermo Fisher Scientific Inc Exactive or LCQ Advantage *via* atmospheric pressure chemical ionization (APCI) with an orbitrap analyzer. Polymer molecular weights were determined using a GPC unit by Agilent Technologies. As eluent THF was used with a flow rate of 1 mL/min, and measurements were calibrated against polystyrene standards by PSS Polymer Standard Service GmbH. Cyclic voltammograms in solution were measured inside a glovebox using a PGSTAT128N by Metrohm Autolab. As working, counter, and reference electrode a glassy carbon disc electrode (2 mm diameter), a platinum rod, and a Ag/$AgNO_3$ electrode containing a silver wire immersed in an inner chamber filled with 0.1 M $AgNO_3$ and 0.1 M *n*-$Bu_4NPF_6$ were used, respectively. The ferrocene/ferrocenium redox couple was used as internal reference. For TGA measurements a TGA/STAA851© (SF 1100 °C, MT 1, $N_2$ atmosphere) by Mettler Toledo was used with an Alox 40 µL melting pot by Mettler Toledo. DSC measurements were done on a DSC823$^{e}$ (HSS7, $N_2$ atmosphere, liquid $N_2$ cooling) by Mettler Toledo with a standard aluminum 40 µL melting pot by Mettler Toledo.

**((1*E*,3*Z*,5*Z*,7*Z*)-1-(4-(Methyl)phenyl)cycloocta-1,3,5,7-tetraene (2).** Aq. NaOH (2.5 mL, 1 mM) was added to a mixture of 2-(4-methylphenyl)-4.4.5.5-tetramethyl-1.3.2-dioxaborolane[24] (**7**, 275 mg, 1.26 mmol) and (1*Z*,3*Z*,5*Z*,7*Z*)-1-bromocycloocta-1,3,5,7-tetraene[23] (**6**, 353 mg, 1.93 mmol) in THF (70 mL). The solution was degassed with three freeze-pump-thaw cycles, and $Pd(PPh_3)_4$ (80 mg, 0.069 mmol) was added. The mixture was stirred at 40 °C for 3 h. $H_2O$ (5 mL) was added, and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane) afforded **2** (168 mg, 68%) as a slightly yellow oil. $R_f$ 0.48 (cyclohexane); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.13-7.10 (m, 2H), 6.21-5.85 (m, 7H), 2.33 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ* 142.1, 137.6, 137.4, 133.3, 132.5, 132.3, 131.9, 131.6, 129.1, 127.3, 126.2, 21.2; HRMS (APCI+): *m/z* calculated for $C_{15}H_{15}O$: 211.1117 $[M+O+H]^+$, found: 211.1117. *One missing signal could not be assigned due to line broadening.

**(1*Z*,3*Z*,5*Z*,7*Z*)-1-(Phenethyl)cycloocta-1,3,5,7-tetraene (3).** A degassed solution of 9-borabicyclo(3.3.1)nonane (3.6 mL, 1.80 mmol, 0.5 M in THF) in dry THF (10 mL) was added to potassium vinyltrifluoroborate (**8**, 234 mg, 1.75 mmol). After stirring for 4 h at room temperature the mixture was added to $Pd(OAc)_2$ (8.5 mg, 38 µmol), RuPhos (35 mg, 75 µmol) and potassium fluoride (230 mg, 3.95 mmol). (1*E*,3*Z*,5*Z*,7*Z*)-1-bromocycloocta-1,3,5,7-tetraene (**6**, 320 mg, 1.75 mmol) was added, and the resulting mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and $Pd(OAc)_2$ (5 mg, 22 µmol), RuPhos (33 mg, 71 µmol), $K_2CO_3$ (725 mg, 5.2 mmol) and a degassed mixture of toluene (10 mL) and $H_2O$ (1 mL) were added. Bromobenzene (320 mg, 0.21 mL, 1.75 mmol) was added dropwise, and the mixture was stirred at 80 °C for 5 h and at 70 °C for 10 h. $H_2O$ (15 mL) was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane) afforded **3** (118 mg, 32%) as slightly yellow oil. $R_f$ 0.37 (cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.21-7.16 (m, 3H), 5.87-5.77 (m, 6H), 5.56 (s, 1H), 2.74 (t, *J* = 8.1 Hz, 2H), 2.34 (t, *J* = 8.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ* 144.0, 142.0, 134.3, 132.4, 132.0, 131.6, 131.1, 128.6, 128.4, 126.8, 125.9, 39.9, 35.4; MS (EI+), m/z (%): 208 (18) $[M]^{+\bullet}$, 117 (100) $[M–C_7H_7]^{+\bullet}$, 91 (45) $[M–C_9H_9]^{+\bullet}$; HRMS (APCI+): calculated for $C_{16}H_{16}$: 208.1252 $[M]^+$, found: 208.1254. *One missing signal could not be assigned due to line broadening. The $^{13}$C NMR spectrum contained some impurities due to cycloaddition reactions between COT units.

**(1*E*,3*Z*,5*Z*,7*Z*)-Cycloocta-1,3,5,7-tetraene-1-carbaldehyde.** A solution of *n*-BuLi (1.6 M in hexane, 8.19 mL, 13.1 mmol) was added dropwise to a solution of (1*E*,3*Z*,5*Z*,7*Z*)-1-bromocycloocta-1,3,5,7-tetraene (**6**, 2.01 g, 10.9 mmol) in dry THF (40 mL) at –78 °C. After stirring at –78 °C for 2.5 h, dry DMF (6.00 mL, 77.5 mmol) was slowly added, and the reaction mixture was stirred at room temperature for 2.5 h. The reaction mixture was quenched with aq. 1 M HCl (90 mL) and extracted with $Et_2O$ (5 x 50 mL). The organic layer was washed with $H_2O$ (5 x 200 mL) and brine (100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/$Et_2O$: 10/1) afforded (1*E*,3*Z*,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraene-1-carbaldehyde (350 mg, 24%) as an orange oil. $R_f$ 0.26 (cyclohexane/$Et_2O$: 10/1); $^1$H NMR (300 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.75 (bs, 1H), 5.76-6.01 (m, 6H).

**((1*E*,3*Z*,5*Z*,7*Z*)-Cycloocta-1,3,5,7-tetraen-1-yl)methanol (9).** $NaBH_4$ (50.9 mg, 1.34 mmol) was added to a solution of (1*E*,3*Z*,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraene-1-carbaldehyde (350 mg, 2.69 mmol) in THF (8 mL) and $H_2O$ (0.27 mL). The resulting mixture was stirred at room temperature for 1 h. After adding $H_2O$ (5 mL), the reaction mixture was extracted with $Et_2O$ (3 x 25 mL), washed with aq. 1 M HCl (50 mL) and brine (100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/$Et_2O$: 10/1) afforded **9** (337 mg, 93%) as a yellow oil. $R_f$ = 0.40 (cyclohexane/EtOAc: 2/1); $^1$H NMR (300 MHz, $CDCl_3$): δ 5.94-5.81 (m, 7H), 4.04 (s, 2H), 1.62 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ* 143.7, 133.5, 132.2, 131.9, 131.7, 131.6, 127.5, 66.5. *One missing signal could not be assigned due to line broadening.

**((1*E*,3*Z*,5*Z*,7*Z*)-Cycloocta-1,3,5,7-tetraen-1-yl)methyl acetate (4).** 4-Dimethylaminopyridine (3.23 mg, 26.1 µmol) and acetic anhydride (74 µL, 782 µmol) were added to a solution of ((1*E*,3*Z*,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraen-1-yl)methanol (**9**, 100 mg, 745 µmol) in dry pyridine (5 mL). The reaction mixture was stirred at room temperature for 3 h. $H_2O$ (10 mL) was added, and the organic layer was separated. The aqueous layer was extracted with cyclohexane (3 x 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/$Et_2O$: 10/1) afforded **4** (86.8 mg, 66%) as a yellow oil. $R_f$ = 0.85 (cyclohexane/EtOAc: 2/1); $^1$H NMR (400 MHz, $CDCl_3$): δ 5.91-5.75 (m, 7H), 4.49 (s, 2H), 2.07 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ 170.9, 138.7, 133.3, 132.3, 132.1, 131.9, 131.3, 131.2, 130.2, 67.3, 21.1.

**((1*E*,3*Z*,5*Z*,7*Z*)-Cycloocta-1,3,5,7-tetraen-1-yl)methyl benzoate (5).** Benzoyl chloride (170 µL, 1.49 mmol), triethylamine (260 µL, 1.86 mmol) and 4-dimethylaminopyridine (4.91 mg, 40.2 µmol) were sequentially added to a solution of ((1E,3Z,5Z,7Z)-cycloocta-1,3,5,7-tetraen-1-yl)methanol (**9**, 100 mg, 745 µmol) in dry $CH_2Cl_2$ (3 mL) at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was quenched with aq. 1 M HCl (3 mL), and the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (6 x 25 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/$Et_2O$: 20/1) afforded **5** (157 mg, 88%) as a yellow oil. $R_f$ 0.49 (cyclohexane/ $Et_2O$: 20/1); $^1$H NMR (300 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.56 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.47-7.42 (m, 2H), 5.95-5.83 (m, 7H), 4.75 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 166.3, 138.7, 133.4, 133.1, 132.3, 132.1, 131.9, 131.4, 131.2, 130.3, 130.1, 129.8, 128.5, 67.6.

**4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (10).** A solution of *n*-BuLi (1.6 M in hexanes, 9.40 mL, 15.0 mmol) was added dropwise to a solution of 1-bromo-4-vinylbenzene (1.79 mL, 13.7 mmol) in dry THF (90 mL) at −78 °C. After stirring for 1.5 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.62 mL, 17.8 mmol) was added dropwise. After stirring at −78 °C for another hour, the cold bath was removed, and the reaction mixture was stirred at rt for 2.5 h. The reaction mixture was quenched with sat. aq. $NH_4Cl$ (40 mL) and $H_2O$ (30 mL). The organic phase was separated, and the aqueous phase was extracted with $Et_2O$ (3 x 30 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane/EtOAc: 20/1) afforded **10** (2.92 g, 93%) as a colorless liquid. $R_f$ = 0.42 (cyclohexane/EtOAc: 20/1); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.73 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.81 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.29 (dd, *J* = 10.9, 0.9 Hz, 1H), 1.35 (s, 12H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ* 140.3, 137.0, 135.2, 125.7, 115.0, 83.9, 25.0; MS (EI+, 70 eV), m/z (%): 230 (95) $[M]^+$, 215 (60) $[M−CH_3]^+$, 147 (10) $[M−C_6H_{13}]^+$, 130 (100) $[M−C_6H_{13}O]^+$; HRMS (APCI+): *m/z* calculated for $C_{14}H_{20}BO_2$: 231.1551 $[M+H]^+$, found: 231.1552. *One missing signal could not be assigned because of signal broadening.

**(1*E*,3*Z*,5*Z*,7*Z*)-1-(4-Vinylphenyl)cycloocta-1,3,5,7-tetraene (11).** $Pd(PPh_3)_4$ (89.6 mg, 77.6 µmol) was added to a degassed solution of (1*E*,3*Z*,5*Z*,7*Z*)-1-bromocycloocta-1,3,5,7-tetraene (**6**, 284 mg, 1.55 mmol) 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (**10**, 393 mg, 1.71 mmol) and aq. NaOH (2.33 mL, 4.65 mmol, 1 M) in THF (15 mL). The reaction mixture was heated under reflux for 3 h. $H_2O$ (20 mL) was added, and the organic layer was separated. The aqueous layer was extracted with $Et_2O$ (3 x 50 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (silica gel, cyclohexane), afforded **11** (307 mg, 96%) as an orange oil. $R_f$ = 0.42 (cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 4H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.25-5.90 (m, 7H), 5.75 (ddd, *J* = 17.6, 0.8, 0.8 Hz, 1H), 5.25 (ddd, *J* = 10.9, 0.8, 0.8 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): δ* 141.8, 139.8, 137.0, 136.6, 133.0, 132.6, 132.4, 132.3, 131.8, 128.1, 126.4, 126.3, 113.9; MS (EI+, 70 eV), m/z (%): 206 (100) $[M]^+$, 191 (40) $[M-CH_3]^+$, 178 (28) $[M-C_2H_4]^+$, 91 (40) $[M-C_9H_7]^+$; HRMS (APCI+): *m/z* calculated for $C_{16}H_{15}$: 207.1168 $[M+H]^+$, found: 206.1167. *One missing signal could not be assigned due to line broadening.

**Poly[(1*E*,3*Z*,5*Z*,7*Z*)-1-(4-vinylphenyl)cycloocta-1,3,5,7-tetraene] (P1).** Azobisisobutyronitrile (2.4 mg, 14.6 µmol) was added to a solution of (1*E*,3*Z*,5*Z*,7*Z*)-1-(4-vinylphenyl)cycloocta-1,3,5,7-tetraene (**11**, 95.5 mg, 463 µmol) in dry and degassed toluene (0.1 mL) in an argon-filled glovebox. The resulting solution was immersed in an oil bath preheated to 60 °C and stirred at this temperature for 24 h. MeOH (5 mL) was added, and the reaction was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the polymer purified by successive precipitation from MeOH and *n*-pentane. **P1** (36 mg, 38%) was isolated as a yellow powder. $^1$H NMR (400 MHz, $CDCl_3$): 7.09 (br s), 6.46 (br s), 6.36 (br s), 6.01 (br s), 5.86 (br s), 1.93-0.85 (m); GPC (eluent THF, polystyrene standard): $M_n$ 1.09 × $10^4$ g $mol^{-1}$, $M_w/M_n$ 1.90; DSC (10 °C $min^{-1}$, $N_2$): $T_{exo}$ 258 °C; TGA (10 °C $min^{-1}$, $N_2$): $T_{d10\%}$ 438 °C.

**(1*Z*,3*Z*,5*Z*,7*Z*)-1-(4-Vinylphenethyl)cycloocta-1,3,5,7-tetraene (12).** 9-Borabicyclo(3.3.1)nonane (5.5 mL, 2.75 mmol, 0.5 M in THF) and dry THF (15 mL) were added to potassium vinyltrifluoroborate (**8**, 300 mg, 2.24 mmol). After stirring at room temperature for 4 h the mixture was added to $Pd(OAc)_2$ (11 mg, 49 µmol), RuPhos (52 mg, 111 µmol) and potassium fluoride (323 mg, 6.72 mmol). (1*E*,3*Z*,5*Z*,7*Z*)-1-bromocycloocta-1,3,5,7-tetraene (**6**, 446 mg, 2.44 mmol) was added, and the resulting mixture was stirred at room temperature for 24 h. The solvent

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was removed under reduced pressure, and a degassed mixture of toluene (12 mL), $H_2O$ (3 mL) and acetone (2 mL) was added. The resulting mixture was added to a mixture of $Pd(OAc)_2$ (12 mg, 54 µmol), RuPhos (47 mg, 101 µmol) and $K_2CO_3$ (930 mg, 6.73 mmol). 1-Bromo-4-vinylbenzene (520 mg, 0.29 mL, 2.84 mmol) was added dropwise, and the mixture was stirred at 60 °C for 41 h. $H_2O$ (20 mL) was added, and the mixture was extracted with $CH_2Cl_2$. The organic extracts were dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. Column chromatography (silica gel, cyclohexane) afforded **12** (231 mg, 44%) as a slightly yellow oil. $R_f$ 0.34 (cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.33 (d, $J$ = 8.1 Hz, 2H), 7.16 (d, $J$ = 8.1 Hz, 2H), 6.69 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.86-5.76 (m, 6H), 5.70 (dd, $J$ = 17.6, 1.0 Hz, 1H), 5.55 (s, 1H), 5.19 (dd, $J$ = 10.9, 1.0 Hz, 1H), 2.72 (t, $J$ = 8.1 Hz, 1H), 2.32 (t, $J$ = 8.1 Hz, 1H); $^{13}C$ NMR (101 MHz, $CDCl_3$): δ* 143.9, 141.8, 136.8, 135.4, 134.3, 132.4, 132.1, 131.7, 131.1, 128.8, 126.9, 126.3, 113.1, 39.8, 35.1; MS (EI, 70 eV), m/z (%): 234 (24) $[M]^{+\bullet}$, 117 (100) $[M–C_9H_9]^{+\bullet}$, 115 (40) $[M–C_9H_{11}]^{+\bullet}$; HRMS (APCI+): calculated for $C_{18}H_{18}$: 234.1409 $[M]^+$, found: 234.1414. *One missing signal could not be assigned due to line broadening.

**Poly[(1*Z*,3*Z*,5*Z*,7*Z*)-1-(4-vinylphenethyl)cycloocta-1,3,5,7-tetraene] (P2).** Azobisisobutyronitrile (3.0 mg, 18.3 µmol) was added to a degassed solution of (1*E*,3*Z*,5*Z*,7*Z*)-1-(4-vinylphenethyl)cycloocta-1,3,5,7-tetraene (**12**, 53.2 mg, 227 µmol) in dry toluene (70 µL). The resulting solution was immersed in an oil bath preheated to 60 °C and stirred at this temperature for 1.5 d. The reaction mixture was cooled to room temperature and evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the polymer was purified by successive precipitation from MeOH and acetone. **P2** (25.7 mg, 48%) was isolated as a yellow powder. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.03-6.25 (m, 4H), 5.78 (br s, 6H), 5.51 (br s, 1H), 2.63 (br s, 2H), 2.27 (br s, 2H), 1.84-1.06 (m, 3H); GPC (eluent THF, polystyrene standard): $M_n$ 1.28 × $10^4$ g $mol^{-1}$, $M_w/M_n$ 2.90; DSC (10 °C $min^{-1}$, $N_2$): $T_{exo}$ 286 °C; TGA (10 °C $min^{-1}$, $N_2$): $T_{d10\%}$ 419 °C.

**Computational details.** All density functional theory (DFT) calculations were performed using the Turbomole 7.0 software.[36] The resolution-of-identity (RI-J)[37,38] approximation for the Coulomb integrals was used in all DFT calculations. Further, the D3 dispersion correction scheme[39,40] with the Becke-Johnson damping function was applied. Geometry optimizations and harmonic vibrational frequency calculations were conducted at the TPSS[41]-D3/def2-TZVP[42] level of theory, the latter in order to characterize the nature of stationary points (no imaginary frequencies for local minima and one imaginary frequency for transition states). Accurate electronic energies were obtained from single point calculations at the PW6B95[43]-D3/def2-QZVP[44] level of theory on the TPSS-optimized geometries. The COSMO-RS continuum solvation model[45] was used to compute the solvation energies with benzene as the solvent (as closest match to a simulation in the melt). These calculations were done with the COSMOtherm program.[46] For this purpose, single-point calculations employing the default TPSS-D3/def2-TZVP level of theory were performed on the optimized gas-phase geometries for each molecule, and the solvation contribution was added to the gas-phase enthalpies. The final enthalpies in solution were calculated as the sum of the gas-phase single point electronic energies, the gas-phase thermal enthalpy contributions at 298.15 K, including zero-point vibrational energies, and the COSMO-RS solvation.

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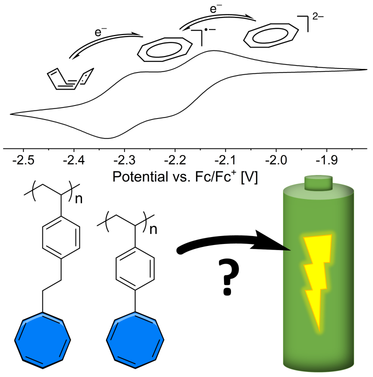
## Entry for the Table of Contents

## FULL PAPER

**COT battery?** Two novel aliphatic polymers, side-group functionalized with cyclooctatetraene (COT) units, and four COT model compounds were synthesized and investigated towards their ability to serve as electrode material in organic batteries. While the model compounds showed promising electrochemical reversibility, the polymers suffered from thermal dimerization and cross-linking reactions between the COT units.



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**Evaluation of cyclooctatetraene-based aliphatic polymers as battery materials: Synthesis, electrochemical and thermal characterization, supported by DFT-calculations**