1. Introduction

Organic electrode materials for batteries are gaining increasing interest.[1] Their higher sustainability and easier recycling relative to traditional, metal-oxide based electrode materials[2,3] make them attractive for next generation batteries,[4–6] and they can operate in a variety of battery configurations, including metal anode cells, metal-ion cells,[7–11] and full-organic cells.[12,13] Organic-based batteries often operate in dual-ion configuration.[14] For high performance of such cells, the organic electrode materials must show a reversible redox chemistry[15] and ideally possess a high specific capacity.[16,17] To obtain high cycling stabilities, dissolution of the organic active material in the liquid battery electrolyte has to be avoided, for which incorporation into a polymeric architecture has been proven a viable strategy.[18–20] Both p-type organic redox polymers with potentials of up to 4.1 V versus LiLi+[21] as prospective positive electrode materials as well as n-type redox polymers as negative electrode materials have been developed. To design full-organic batteries there is a continued quest for novel redox-active materials. Low redox potential polymers are particularly attractive to obtain full-organic cells with large operating voltages, and redox-active groups with two-electron processes will increase the specific capacities of the corresponding redox polymers.[16]

Cyclooctatetraene (COT, Figure 1) is a cyclic olefin with eight \( \pi \)-electrons. Upon two-electron reduction, COT is transformed into a 10 \( \pi \)-aromatic, planar, and stable dianion (as depicted in Figure 1 for its dibenzo-derivative 2).[22] Its ability...
to reversibly take up two electrons makes COT attractive for charge storage.[23–26] The conformational change upon reduction, which is also known for some heteroaromatics upon oxidation,[27,28] has rendered COT of interest for molecular actuators.[29,30] We recently investigated COT-functionalized aliphatic polymers as potential battery electrode materials.[31] However, the reversibility of their redox processes was limited due to cross-linking reactions occurring between COT units in the polymers. For this reason we turned our attention to its dibenzo-derivative dibenzo[a,e]cyclooctatetraene (DBCOT, 2 in Figure 1). Due to the aromaticity of the two annulated benzene rings, the central eight-membered ring in DBCOT is not prone to electrocyclic or cycloaddition reactions in contrast to COT itself.

The stepwise reduction of DBCOT to a dianion has been known for more than 50 years,[32,33] and the planarity of the dianion was proven by X-ray crystallography.[34,53] For an application as battery electrode material, insolubility in common battery electrolytes has to be obtained.[18] One strategy to this end is to attach DBCOT units as side groups to polymers, for which monofunctionalized derivatives are required. Since this approach is scarcely reported in the literature, we first set out to develop synthetic routes to monofunctionalized DBCOT derivatives and herein report three different synthetic pathways to bromo-DBCOT 3 as well as one route to Me-DBCOT 4 and finally report a synthesis of para-tolyl-functionalized DBCOT derivatives 5 and polymers P1–P3 synthesized and investigated in this study.

2. Results and Discussion

2.1. Synthesis of Bromo-DBCOT 3

The first report of a synthesis of DBCOT (2) by Fieser and Pechet dates back to 1946 in three steps from o-phthalaldehyde and o-phenylene diacetonitrile.[36] 2012, a three-step, gram-scale synthetic protocol was published by Helmchen and co-workers, which is likely the most convenient way to access unsubstituted DBCOT.[37] Derivatives, which are monofunctionalized in 2-position, on the other hand, are scarce in the literature. These were required to synthesize aliphatic polymers with DBCOT units as side groups. Of particular interest was 2-bromo-DBCOT (3, Figure 1) due to its ability to undergo Pd-catalyzed cross-coupling reactions. In 1972, Mislow and co-workers published a five-step synthesis of 3 (yield not given) under harsh conditions, with the last step being a two-fold decarboxylation with Cu/CrO3 in quinoline at >200 °C.[38] Hence, our first goal was to develop a new synthetic protocol to bromo-DBCOT 3. We reasoned that the central eight-membered ring in 3 could either be constructed in one step from two unsymmetric precursors (Routes a,b in Scheme 1), or the two double bonds in the eight-membered rings could be formed in successive reactions (Route c in Scheme 1; and Route d in Supporting Information, which was unsuccessful in the last step). In the first case, the Wittig reaction seemed suitable due to the required asymmetry of the coupling partners. This reaction has been employed on several occasions in the synthesis of DBCOT itself or derivatives thereof.[39–45] Unsubstituted DBCOT 2, for instance, was synthesized through Wittig reaction already in the 1960s.[39,40] Our first two synthetic routes therefore make use of this reaction (Scheme 1a,b).

We attempted both modes of connection. In the first (a), the bromo-substituent was connected to the dialdehyde coupling...
partner 6, which was accessed through reduction of 4-bromophthalic anhydride (7) to diol 8[46] followed by Swern oxidation to 6.[47] In the second mode (b), the bromo-substituent was attached to the phosphonium salt 9, which we synthesized from 4-bromo-1,2-dimethylbenzene (10) through NBS-bromination to 11 followed by nucleophilic substitution with triphenylphosphine. The Wittig reaction between o-phthalaldehyde (12) and 9 furnished bromo-DBCOT 3 in a low yield of only 4% (Scheme 1b). This was likely due to this reaction proceeding via the cis,trans-derivative trans-3, shown in Scheme 1, in which one of the double bonds in the eight-membered ring possessing a trans-configuration. This compound is highly reactive due to its significant strain energy. The reason for its formation is the low stereoselectivity (cis or trans) of the Wittig reaction. In 2008, Herges[42] and Nuckolls[41] independently reported that the double Wittig reaction between o-phthalaldehyde (12) and the 1,2-bis(triphenylphosphonium ylide) 13 proceeded via the corresponding cis,trans-derivative of 2. This highly reactive species with a calculated strain energy of 18 kcal mol−1[41] immediately underwent further reactions or decomposed, diminishing the yield of the cis,cis-derivative of 2. In his doctoral thesis, Bornhöft therefore recommended to use irradiation subsequently to the Wittig coupling step to immediately transform the trans to a cis double bond.[48] Since the synthesis and purification of the coupling partners 6 and 13 required for Route a was more facile, we optimized the reaction conditions for the Wittig coupling reaction for these partners. A detailed overview of tested conditions can be found in the Supporting Information. We obtained the best yield of 34% when the Wittig coupling step was performed in isopropanol at reflux for 90 min, the reaction mixture was then diluted with cold isopropanol and irradiated with a medium pressure mercury lamp for 30 min to isomerize the trans to a cis double bond. This corresponds to a total yield of 13% for 3 over three steps from 7.

As third strategy we investigated a step-wise ring closure of the eight-membered ring in 3, which has been successfully used for other DBCOT derivatives[43,44] (Scheme 1c). Making use of the Z-selectivity of alkyne to alkene hydrogenation, the synthesis proceeded through diarylkyne 14. 14 was accessed in a Sonogashira coupling reaction between 2-ethynylbenzaldehyde (15) and aryl iodide 16, and these two coupling partners were synthesized in two steps each from 2-ethynylbenzaldehyde (17) and 4-bromo-1-iodo-2-methylbenzene (18), respectively. The partial hydrogenation of 14 to stilbene derivative 19 proceeded very slowly using Lindlar’s catalyst in benzene as solvent. With palladium on carbon, on the other hand, a faster conversion was observed, however, the reaction had to be closely monitored to avoid overhydrogenation to a CC-single bond. 19 was obtained in 72% yield. The final McMurry coupling of the two aldehydes using Fürstner’s conditions[49] afforded bromo-DBCOT 3 in 59% yield. The total yield for this route is 17% over five steps from 18. However, two further steps to prepare 15 were also required, adding up to a total of seven steps. Inspite of the higher yield of this Route c with potential for improvement, the shortness of Route a with only three steps makes it more attractive.

2.2. Synthesis of Polymers P1–P2 and p-tolyl-DBCOT 5

With bromo-DBCOT 3 in hand, we proceeded to synthesize the vinyl- (20) and styryl- (21) DBCOT monomers...
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(Scheme 2). Suzuki–Miyaura coupling of 3 with 2-ethenyl- or 2-(4-ethenylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[31] afforded 20 and 21, respectively, in quantitative yield. Free radical polymerizations were effected using AIBN in toluene and furnished DBCOT-based polymers P1 and P2 in good yields. Analytical GPC versus polystyrene standard provided molecular weights of $5.8 \times 10^4$ g mol$^{-1}$ for P1 and $2.3 \times 10^4$ g mol$^{-1}$ for P2.

To further decrease their potential solubility in battery electrolyte solution, we synthesized cross-linked derivatives X-P1 and X-P2 using divinylbenzene as cross-linker. X-P1 and X-P2 showed high thermal stabilities with onsets for decomposition at 448 and 444 °C, respectively, from thermal gravimetric analysis (TGA) measurements. As opposed to the COT-functionalized polymers reported by us before,[31] no exothermic events took place in differential scanning calorimetry (DSC) measurements, indicating no rearrangement processes of the DBCOT units to occur. As small molecule-reference compound for P2 and X-P2 para-tolyl-functionalized DBCOT 5 was accessed from bromo-DBCOT 3 by Suzuki–Miyaura coupling with 2-(p-tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[50]

2.3. Synthesis of Methyl-DBCOT 4 and Polymer P3

As third DBCOT derivative, we synthesized methyl-DBCOT 4 (Scheme 3), which was also used as precursor for polymer P3. The same strategy as for 3 (Scheme 1a) using a Wittig one-step ring formation of 4-methylphthalaldehyde (22) and the 1,2-bis(triphenylphosphonium ylide) 13 furnished 4 in 7% yield. Likely, the cis-trans-isomer of 4 was formed in this reaction, diminishing the yield, which could – in the future – be transformed to the cis,cis-derivative through irradiation, as described for 3 above. 22 was accessed in two steps through reduction of 4-methylphthalic acid (23) to the corresponding diol followed by its Swern oxidation.[47] NBS-bromination of 4 afforded 24, which was hydrolyzed under basic conditions to benzyl alcohol 25 and transformed into methacrylic ester 26 by reaction with methacryloyl chloride. Free-radical polymerization using AIBN as radical starter in toluene furnished DBCOT-functionalized poly(methacrylate) P3 in 40% yield. P3 showed a glass transition at 123 °C in the DSC measurement and no exothermic events, indicative of rearrangement processes of the DBCOT units. With an onset
for decomposition at 289 °C (TGA) its thermal stability was somewhat lower than those of X-P1 and X-P2.

2.4. Electrochemical Characterization in Solution and Thin Film

CV measurements in solution were first performed on 4 and 5 as reference compounds for the obtained polymers. As shown in Figure 1, DBCOT can undergo a two-step reduction to a dianion. 4 showed a reversible first reduction at −2.58 V and a quasi-reversible second reduction at −2.92 V, while para-tolyl-substituted DBCOT 5 featured one reversible reduction at a half-wave potential \( E_{1/2} = -2.55 \) V in THF (Figure 2, all versus Fc/Fc\(^+\)). We measured the CV of compound 5 at different scan rates and plotted the peak current versus the scan rate (Figure S7, Supporting Information), which provided a linear relationship. This indicates a reversible redox process.

Whether the quasi-reversible reduction for 5 corresponded to a one- or two-electron redox process is not clear, but for 4 two separate redox events were observed for both reduction steps.

We next turned to the DBCOT polymers. In THF solution, poly(vinyl-DBCOT) P1 showed one quasi-reversible reduction with a half-wave potential of \( E_{1/2} = -2.50 \) V versus Fc/Fc\(^+\) (Figure 3). When measured as thin film on a glassy carbon electrode in DMF solution, two reductions appeared at cathodic peak potentials of \( E_{\text{cp}} = -2.58 \) and −2.99 V versus Fc/Fc\(^+\) (Figure 4). These were irreversible, likely due to dissolution of the polymer film after the first reduction. Concerning the redox activity of the DBCOT groups, the redox potentials obtained for P1 matched well with those found for Me-DBCOT 4.

Poly(styryl) derivative P2 featured a quasi-reversible reduction in solution with \( E_{1/2} = -2.40 \) V (Figure 3), while in film two quasi-reversible reductions appeared at \( E_{1/2} = -2.46 \) and −2.76 V (all versus Fc/Fc\(^+\)) (Figure 4). These again correspond well to the half-wave potential measured in solution for reference compound 5. The incomplete reversibility of the reductions in thin film were likely due to a partial dissolution of the polymer upon reduction and a diffusion away from the electrode, which furnished a smaller current on the reverse anodic scan.

Figure 2. Cyclic voltammograms of Me-DBCOT 4 (top) and p-tolyl-DBCOT 5 (bottom) (1 × 10\(^{-3}\)m in THF, scan rate 100 mV s\(^{-1}\) with 0.1 M n-Bu\(_4\)NPF\(_6\) glassy carbon electrode).
For poly(methacrylate) $P_3$, an irreversible reduction with a cathodic peak potential of $E_{\text{cp}} = -2.67$ V was observed and a quasi-reversible reduction at $E_{1/2} = -2.93$ V (Figure 3). The first reduction likely stemmed from both the DBCOT units and the connecting ester groups, which can be reduced in this potential range, but in an irreversible way. The resulting anion radicals can undergo dimerization reactions in analogy to the Acyloin condensation. The second reduction can be attributed to the DBCOT groups.

These redox properties on the DBCOT polymers show that poly(vinylene) $P_1$ and poly(styrene) $P_2$ are generally suitable as electrode materials for batteries, since their reduction proceeded with (partial) reversibility in solution or thin film.

2.5. Electrochemical Characterization in Battery Test Cells

Based on the CV results for $P_1$ and $P_2$, we turned our attention to three electrode half-cell measurements in battery cells. We chose the cross-linked polymers $X-P_1$ and $X-P_2$ to ensure their insolubility in the battery electrolyte in both the charged and discharged state. A high solubility would lead to loss of active material and therefore result in a strong capacity fade during electrochemical cycling. For composite electrodes, such a phenomenon needs to be avoided. In order to investigate the performance of DBCOT polymers $X-P_1$ and $X-P_2$ as battery electrode materials, we fabricated composite electrodes consisting of 50 wt% polymer, 45 wt% carbon additive (KS6L, Imerys Graphite & Carbon) as conductive additive, and 5 wt% poly(vinylidene difluoride) (PVdF) as binder. We chose KS6L since this graphite-based conductive additive does not show activity in the investigated potential window (0.5–2 V versus Li$|$Li$^+$, Figure 5b gray). Metallic lithium served as the counter and reference electrode, and 1 m LiPF$_6$ in EC:DMC (1:1) as electrolyte. Scanning electron microscopic measurements showed the pristine structure of the carbon additive to be maintained in the composite electrodes (Figure 5a). The distribution of polymers $X-P_1$ and $X-P_2$ was uneven on the micrometer scale due to their insolubility in $N$-methyl-2-pyrrolidone during electrode preparation.

We next measured CVs of the composite electrodes (Figure 5b), which showed a behavior reminiscent of pseudo capacitors. While in the solution and thin film CVs for $P_1$ and $P_2$ (Figures 3 and 4) clear redox peaks were visible, these merged to broad curves when using thicker composite electrodes. For $X-P_1$, a shoulder peak at 0.8 V versus Li$|$Li$^+$ can be identified, which corresponds well with the cathodic peak potential obtained for $P_1$ in solution of (estimated) 0.66 V versus Li$|$Li$^+$ (assuming 3.25 V for Fc$|$Fc$^+$ versus Li$|$Li$^+$). Hence, it is likely that Faradaic redox processes take place, but only at the surface of the electrodes. In comparison to the conductive carbon KS6L by itself, the CV curves of the $X-P_1$ and $X-P_2$-based composite electrodes showed a significantly higher redox activity, which must stem from the DBCOT polymers. Integrating the areas provided a specific capacity of 56 mAh g$^{-1}$ for $X-P_1$ and 31 mAh g$^{-1}$ for $X-P_2$. These values correspond to 48% and 36% of the theoretical specific capacities for $P_1$ (116 mAh g$^{-1}$) and $P_2$ (87 mAh g$^{-1}$), respectively.

Figure 3. Cyclic voltammograms of polymers $P_1$–$P_3$ in THF ($\approx 1 \times 10^{-3}$ m with regard to the redox-active units, scan rate 100 ($P_1$ and $P_2$) or 20 mV s$^{-1}$ ($P_3$) or with 0.1 m n-Bu$_4$NPF$_6$, glassy carbon electrode).

Figure 4. Cyclic voltammograms of polymers $P_1$ and $P_2$ in thin film on a glassy carbon electrode (in DMF, scan rate 100 mV s$^{-1}$ with 0.1 m n-Bu$_4$NPF$_6$).
3. Conclusions

DBCOT is promising redox-active group for low-voltage battery electrode materials due to its ability to undergo reversible two-electron reduction. We herein presented three aliphatic DBCOT-polymers in view of their suitability as negative electrode materials. We first established three synthetic routes to bromo-functionalized DBCOT 3 and a synthesis to methyl-DBCOT 4. The best synthetic path to 3 involves three steps in 13% total yield and uses a Wittig reaction for the formation of the two double bonds in the COT group. To increase the yield for the product with two Z-double bonds, we employed irradiation in the last (Wittig reaction) step. Using these monofunctionalized DBCOT derivatives, we synthesized three linear DBCOT polymers with a poly(vinylene) (P1), poly(styrene) (P2), and poly(methacrylate) (P3) backbone as well as two cross-linked derivatives X-P1 and X-P2. Electrochemical characterization of the linear polymers in solution and thin film showed well-defined redox events for the two-fold reduction of the DBCOT unit. Battery half-cell measurements with cross-linked X-P1 and X-P2 demonstrated the redox-activity of the polymers, however, with more pseudo capacitive like behavior. This was likely due to Faradaic redox processes occurring mostly near the electrode surface. Hence, while the DBCOT-functionalized polymers presented herein may be suitable as low-voltage electrode materials, electrode composition, thickness, and porosity will play important roles in accessing their full redox activity. Due to the conformational change of the DBCOT units upon reduction, these polymers are also of interest to molecular actuators.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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anode materials, cyclooctatetraene, molecular actuators, organic batteries, redox polymers, Wittig reaction

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[1] P. Poizot, J. Gaubicher, S. Renault, L. Dubois, Y. Liang, Y. Yao, Chem. Rev. 2020, 120, 6490.
[2] R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, Nat. Energy 2018, 3, 267.
[3] M. Winter, B. Barnett, K. Xu, Chem. Rev. 2018, 118, 11433.
[4] B. Esser, F. Dolhem, M. Becuwe, P. Poizot, A. Vlad, D. Brandell, J. Power Sources 2021, 482, 228814.
[5] S. Lee, J. Hong, K. Kang, Adv. Energy Mater. 2020, 2, 2001445.
[6] S. Dühnen, J. Betz, M. Kolek, R. Schmuch, M. Winter, T. Placke, Small Methods 2020, 4, 2000039.
[7] Y. Lu, J. Chen, Nat. Rev. Chem. 2020, 4, 127.
[8] J. J. Shea, C. Luo, ACS Appl. Mater. Interfaces 2020, 12, 5361.
[9] J. Cui, Z. Guo, J. Yi, X. Liu, K. Wu, P. Liang, Q. Li, Y. Liu, Y. Wang, Y. Xia, J. Zhang, ChemSusChem 2020, 13, 2160.
[10] A. V. Desai, R. E. Morris, A. R. Armstrong, Acc. Chem. Res. 2019, 52, 1802151.
[11] J. Xie, Q. Zhang, Small 2019, 15, 1805061.
[12] C. Friebe, A. Lex-Balducci, U. S. Schubert, Angew. Chem., Int. Ed. 2020, 13, 2232.
[13] P. Poizot, F. Dolhem, J. Gaubicher, Curr. Opin. Electrochem. 2018, 9, 70.
[14] T. Placke, A. Heckmann, R. Schmuch, P. Meister, K. Beltrop, M. Winter, Joule 2018, 2, 2528.
[15] F. Otteny, G. Studer, M. Kolek, P. Bieker, M. Winter, B. Esser, ChemSusChem 2020, 13, 2232.
[16] P. Acker, M. E. Speer, J. S. Wössner, B. Esser, J. Mater. Chem. A 2020, 8, 11195.
[17] F. Otteny, M. Kolek, J. Becking, M. Winter, P. Bieker, B. Esser, Adv. Energy Mater. 2018, 8, 1802151.
[18] B. Esser, Org. Mater. 2019, 01, 063.
[19] S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U. S. Schubert, Chem. Rev. 2016, 116, 9438.
[20] M. D. Hager, B. Esser, X. Feng, W. Schuhmann, P. Theato, U. S. Schubert, Adv. Mater. 2020, 32, 2000587.
[21] M. E. Speer, M. Kolek, J. J. Jassoy, J. Heine, M. Winter, P. M. Bieker, B. Esser, Chem. Commun. 2015, 51, 15261.
[22] R. D. Allendoerfer, P. H. Rieger, J. Am. Chem. Soc. 1965, 87, 2336.
[23] C. D. Stevenson, J. P. Davis, WO2011142777 A1, 2010.
[24] M. Bovenkerk, B. Esser, Eur. J. Org. Chem. 2015, 2015, 775.
[25] P. Auchtcher-Krummel, K. Müllen, Angew. Chem., Int. Ed. 1991, 30, 1003.
[26] C. D. Stevenson, R. C. Reiter, L. F. Szczepura, S. J. Peters, J. Am. Chem. Soc. 2005, 127, 421.
[27] F. Otteny, V. Perner, D. Wassy, M. Kolek, P. Bieker, M. Winter, B. Esser, ACS Sustainable Chem. Eng. 2020, 8, 238.
[28] M. Kolek, F. Otteny, P. Schmidt, C. Mück-Lichtenfeld, C. Einholz, J. Becking, D. Schleicher, M. Winter, P. Bieker, B. Esser, Energy Environ. Sci. 2017, 10, 2334.