

Bi(benzimidazole)-Based Super-Electron-Donors in Redox Polymers as Battery Electrode Materials

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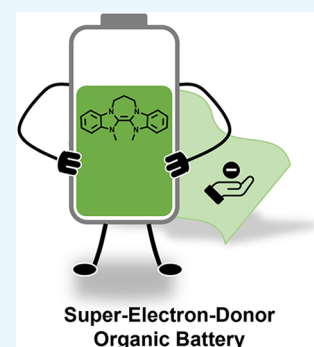
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ABSTRACT: Organic electrode-active materials (OAMs) represent an alternative to (transition-) metal-based materials used in conventional battery cells. Reversibly oxidizable p-type OAMs allow realization of full-organic battery cells operating in an anion-rocking-chair mechanism. In the search for p-type materials with a low redox potential, so-called super-electron-donors (SEDs) are a promising class of molecules. Herein, we incorporate a bi(benzimidazole) (BBI)-based SED into three polymers, **PBBI**, a conjugated homopolymer, **PSBBI** as a styrene-based side-chain polymer, and **X-PSBBI** as its cross-linked counterpart. Their properties as potential OAMs in lithium-organic half-cells were investigated, and **PBBI** was found to be electrochemically inactive. The side-chain polymers showed reversible cycling behavior in binder-free powder electrodes in LiBF_4 -based electrolytes with a low charge/discharge potential of 2.1 V *vs* $\text{Li}^{+/0}$, even though the accessible capacity quickly faded. As a possible degradation mechanism, we propose decomposition via a dicarbene species as a plausible, reactive key species. This study showcases bi(benzimidazole)s as redox-active groups in OAMs with a low redox potential and provides insight into challenges associated with obtaining reversible cycling behavior in battery electrodes.

KEYWORDS: organic battery, super-electron-donor, low-potential electrode material, redox polymer, benzimidazole, anionic battery, carbene



INTRODUCTION

With the ever-rising demand for electrochemical energy storage, conventional lithium-ion batteries are reaching their limitations, mainly due to the limited availability of lithium, the toxicity of transition metals used in those battery cells, and recycling challenges. Therefore, so-called post-lithium battery technologies are gaining more and more attention in current research.¹ As organic electrode-active materials (OAMs) consist of abundant elements (e.g., C, H, O, N), they offer a higher sustainability and open up the possibility to replace (transition-) metal-based electrode materials.^{2–6} Compared to their inorganic counterparts, OAMs bring several advantages, such as a lack of toxicity (in particular, for polymers), easier recyclability, and a synthesis without the need for high-temperature processes. However, by far one of the biggest advantages is the possibility of tuning the properties of the OAMs, like solubility, morphology, and redox behavior, with synthetic manipulations. To prevent the dissolution of the redox-active groups (RAGs) in battery electrolytes, different immobilization strategies can be applied, such as the implementation of the RAGs in frameworks, their salification⁷ or the synthesis of polymeric structures (often cross-linked),⁸ in addition to strategies applicable in battery fabrication (i.e., use of a mesoporous conductive carbon, electrolyte optimization, etc.).

According to Hünig's classification,⁹ OAMs are categorized by the nature of their RAGs, which determine the charge-

compensation mechanism: reversible anion uptake in p-type systems, reversible cation uptake in n-type systems, or both in bipolar materials. Under otherwise identical conditions, p-type redox-active moieties generally exhibit higher formal potentials than their n-type counterparts. Hence, p-type RAGs store charge via anion compensation, whereas n-type RAGs rely on cation compensation; bipolar systems combine both mechanisms. Therefore, the generation of positive charges upon oxidation in the solid state of p-type materials induces the ingress of anions from the electrolyte. Note that p-type RAGs exhibit, as a rule, higher formal potential values compared to those of n-type systems. P-type OAMs can be operated in so-called anion-rocking-chair and dual-ion batteries. Usually, the positive electrode OAMs are paired with metals or inorganic intercalation materials for the negative electrode, but also full-organic battery cells are possible cell designs.^{10,11}

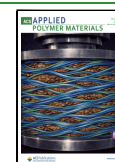
Regarding sustainability considerations and ease of recycling, full-organic cells are of specific interest. By using two p-type OAMs with anions as the charge carriers, one can even construct full-organic battery cells without the use of any

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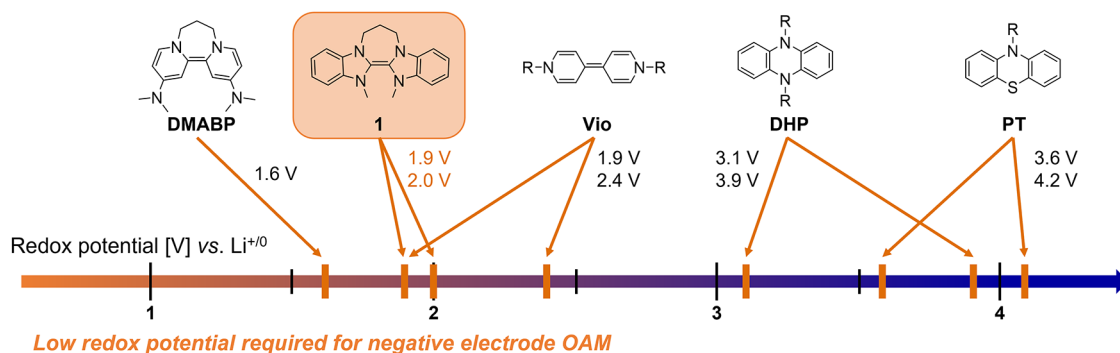
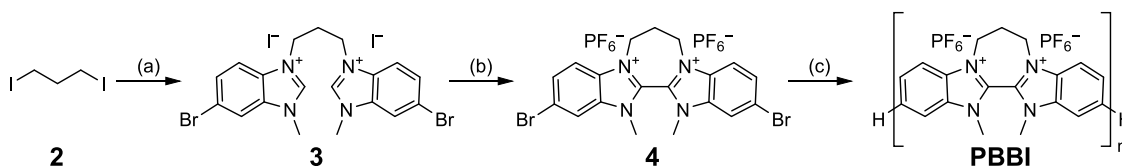


Figure 1. P-Type RAGs and their redox potentials vs $\text{Li}^{+}/0$. DHP and PT with high redox potentials and DMABP, Vio, and **1** with comparably low redox potentials. **1** is highlighted by an orange box as the herein investigated moiety.

Scheme 1. Synthesis of the Homopolymer Poly(bi(benzimidazole)) (PBBI) Starting from 1,3-Diiodopropane^a



^aReaction conditions: (a) 6-Bromo-1-methyl-1H-benzo[*d*]imidazole (2.5 equiv), MeCN, reflux, 15 h, 88%; (b) (i) KHMDS (0.5 M in toluene, 2.0 equiv), DMF/toluene (1:2), rt, 1 h; (ii) C_2Cl_6 (2.0 equiv), Et_2O , rt, 15 min; and (iii) NaPF_6 (2.8 equiv), MeOH/ H_2O (1:1), rt, 1 h, 58%; and (c) (i) $[\text{Ni}(\text{COD})_2]$ (1.3 equiv), 2,2'-bipyridine (1.3 equiv), COD (1.0 equiv), DMF, 60 °C, 40 h; (ii) HCl_{aq} (1 M), rt, 2 h, 75%.

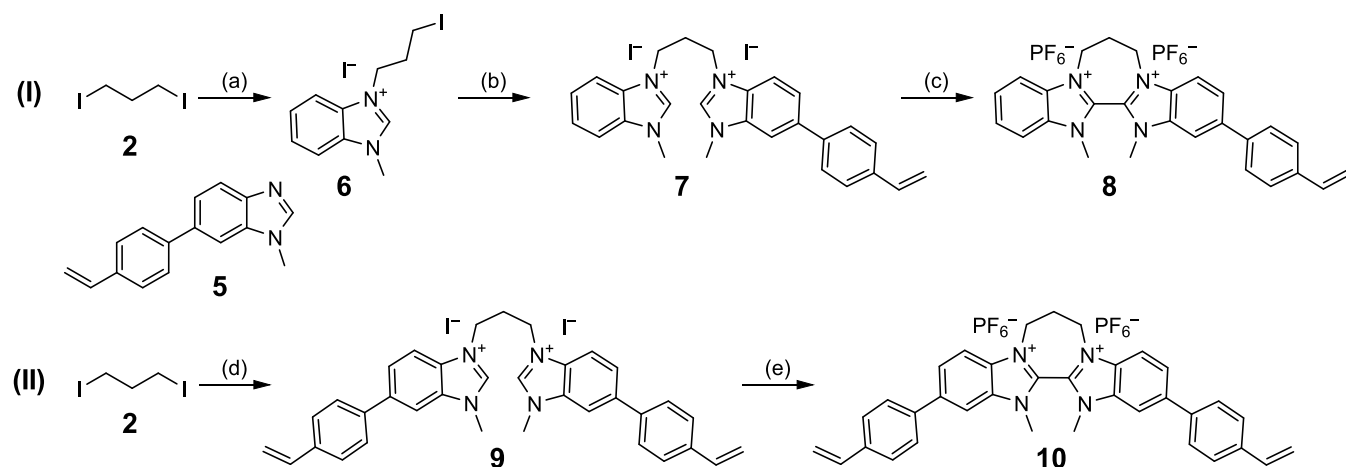
metals, also called “molecular ion batteries”.¹² To realize such a battery, two p-type OAMs with a significant potential difference between their redox processes are required. Many studies report RAGs with redox potentials of >3.4 V vs. $\text{Li}^{+}/0$.¹³ Examples are phenothiazine (PT),^{14,15} nitroxide radicals,^{16,17} or aryl amines,¹⁸ such as dihydrophenazine (DHP, Figure 1). Synthetic manipulations of the RAG can thermodynamically favor oxidation and lower the redox potentials, for example, by the introduction of electron-donating (i.e., methoxy) substituents on phenothiazine^{19–22} or an increase of the total electron density in the system, as in conjugated azines.²³ Unfortunately, the resulting potential shifts are not significant enough to enable the assembly of full-cells of usable cell voltage. P-type OAMs with low redox potentials (<2.5 V vs. $\text{Li}^{+}/0$), on the other hand, are much scarcer, with most of them focusing on pyridinium- or 4,4'-bipyridinium-salts, so-called viologens (Vio).^{12,24–32} Under ambient conditions, these compounds are handled in their oxidized, (di)cationic forms, as their neutral forms are very electron rich and highly reactive. Based on design principles similar to viologens, a molecule class of so-called *Super-Electron Donors* (SEDs) was introduced in the 1990s to early 2000s. In the neutral state, these molecules are highly reducing and are oxidized at low potentials (below 2.5 V vs. $\text{Li}^{+}/0$, Figure 1) while exhibiting an interesting apparent reversible two-electron redox process, as evidenced by cyclic voltammetry recorded in solution.³³ Due to this property SEDs are currently used as reducing agents in organic synthesis^{34,35} (e.g., for the activation of iodoarenes) and appear particularly promising for the design of negative electrodes in anionic rocking-chair batteries. For instance, a 2,2'-bipyridine SED (DMABP, Figure 1) exhibiting a reversible two-electron electrochemical process at a potential of -1.67 V vs. $\text{Fc}^{+}/0$ has been employed in a nonaqueous redox-flow battery,^{36,37} and we recently investigated DMABP-based polymers as battery electrode materials.³⁸

We herein investigate bi(benzimidazole) (BBI) SED **1** as an OAM. As expected, **1** features two electrochemical steps with close-by redox potentials that are lower than those of viologens (Vio, Figure 1). The benzannulation of the imidazole units of **1** offers the possibility to functionalize the molecule “away from” the redox-active center, which should maintain its redox properties. The 2,2'-bi(benzimidazolium) dication I^{2+} was first synthesized by Ames et al., and the properties of its neutral, reduced form (**1**) as an organic reducing agent were studied mainly by Murphy and co-workers.^{34,39–41} We decided to also use a C_3 -linker, as this is the only derivative that has been investigated as an SED so far, and other derivatives that, for example, possess a C_2 -linker, show irreversible redox processes.³⁹ Similar to the previously discussed viologens, the associated SED (**1**) is not stable under ambient conditions; therefore, the oxidized form or its precursors are used for synthetic manipulations. We herein present the implementation of the BBI core **1** in a conjugated homopolymer (PBBI) as well as in styrene-based side-chain polymers ((X)-PSBBI) and their electrochemical evaluation in lithium half-cells. While PBBI did not show any electrochemical activity in any battery setup, we were able to cycle the side-chain polymers PSBBI and X-PSBBI in binder-free electrodes with a LiBF_4 -based electrolyte, achieving initial discharge capacities of 62 and 88 mAh g^{-1} , respectively. The measurements confirmed the expected low operating potential with the reduction and oxidation processes centered at ~ 2.1 and ~ 2.2 V vs. $\text{Li}^{+}/0$, respectively. Despite these promising low potentials, a relatively fast capacity fading is observed, which we ascribe to a possible degradation via a dicarbene species.

RESULTS AND DISCUSSION

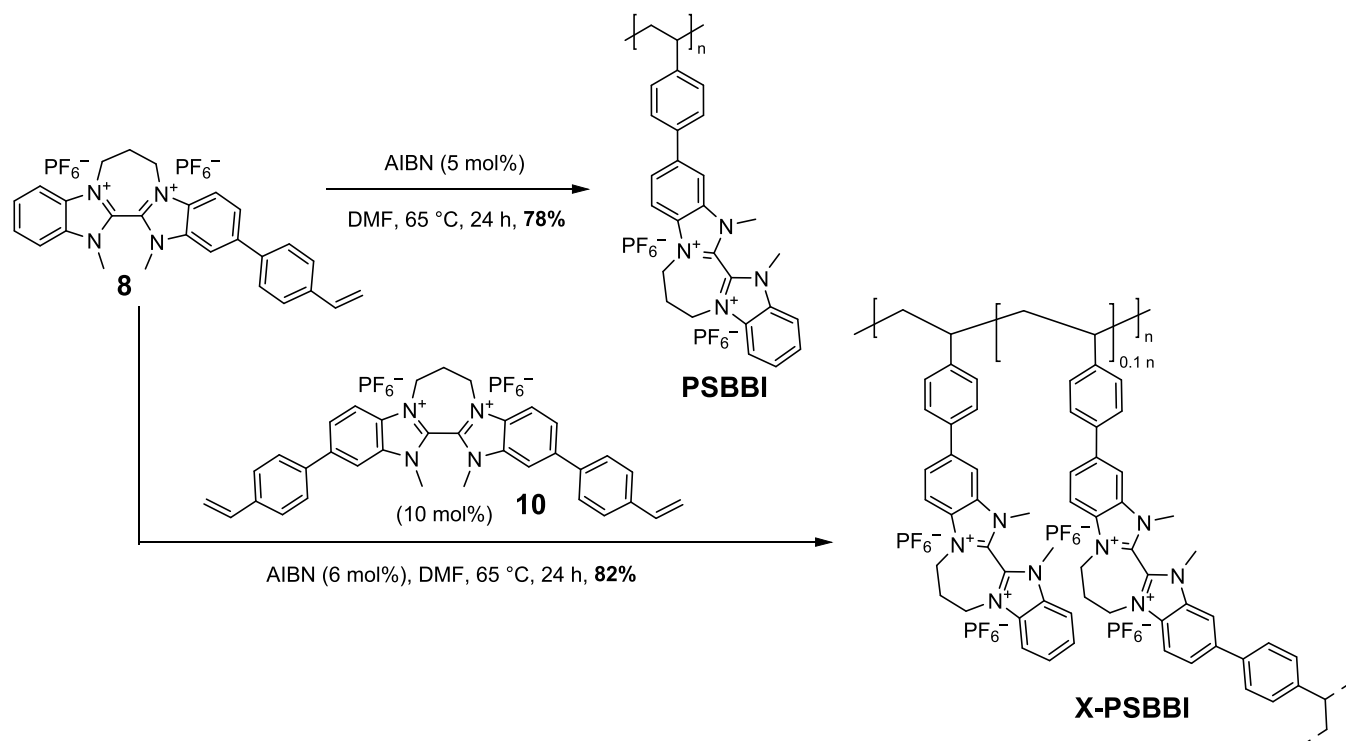
Synthesis and Characterization of BBI-Polymers

We first synthesized the conjugated homopolymer PBBI, as conjugated polymers usually exhibit an intrinsic semiconduc-

Scheme 2. Synthesis of the Styryl-BBI Monomer (I) and Cross-linker (II)^a

^aReaction conditions: (a) 1-Methyl-1H-benzo[d]imidazole, MeCN, reflux, 4 h, 56%; (b) **5**, MeCN, reflux, 36 h, 87%; (c) (i) KHMDS, DMF/toluene, rt, 1 h; (ii) C₂Cl₆, toluene, rt, 30 min; and (iii) NaPF₆, MeOH/H₂O, rt, 1 h, 53%; (d) **5**, MeCN, reflux, 4 d, 82%; and (e) (i) KHMDS, DMF/toluene, rt, 1 h; (ii) C₂Cl₆, toluene, rt, 30 min; and (iii) NaPF₆, MeOH/H₂O, rt, 1 h, 52%.

Scheme 3. Synthesis of the Linear and Cross-linked Polymers PSBBI and X-PSBBI



tivity that battery performance can benefit from.⁴² 1,3-Diiodopropane (**2**) was reacted in a nucleophilic substitution with commercially available 6-bromo-1-methyl-1H-benzo[d]imidazole, and the precipitated, 2-fold substituted product **3** was obtained in 88% yield via filtration (Scheme 1). The key step in the synthesis was the base-mediated dimerization of the two benzimidazole units, which first furnished the reduced form (SED) of **4** and was then oxidized. As in the literature procedure for unsubstituted derivatives, we used a solution of potassium bis(trimethylsilyl)amide (KHMDS) as the base,⁴⁰ followed by oxidation with perchloroethane instead of the iodine used in the literature. The resulting salt was then recrystallized in the presence of NaPF₆ to obtain the desired

monomer **4** as a PF₆ salt in 58% yield (from **3**). ¹⁹F and ³¹P NMR spectroscopy confirmed the presence of PF₆ anions (Figures S8 and S9). We then subjected monomer **4** to a nickel-mediated Yamamoto polymerization to obtain homopolymer PBBI (poly(bi(benzimidazole))) in a 75% yield. Due to its insolubility in all common organic solvents, PBBI could only be characterized via IR spectroscopy (Figure S26).

Even though conjugated polymers show an enhanced semiconductivity, the conjugation can also influence their performance in batteries in the form of polarization of the redox processes.⁴² In contrast, in side-chain polymers this conjugation is not present, but interactions (e.g., $\pi^*-\pi^*$ interactions) between the RAGs can occur.^{43,44} For the

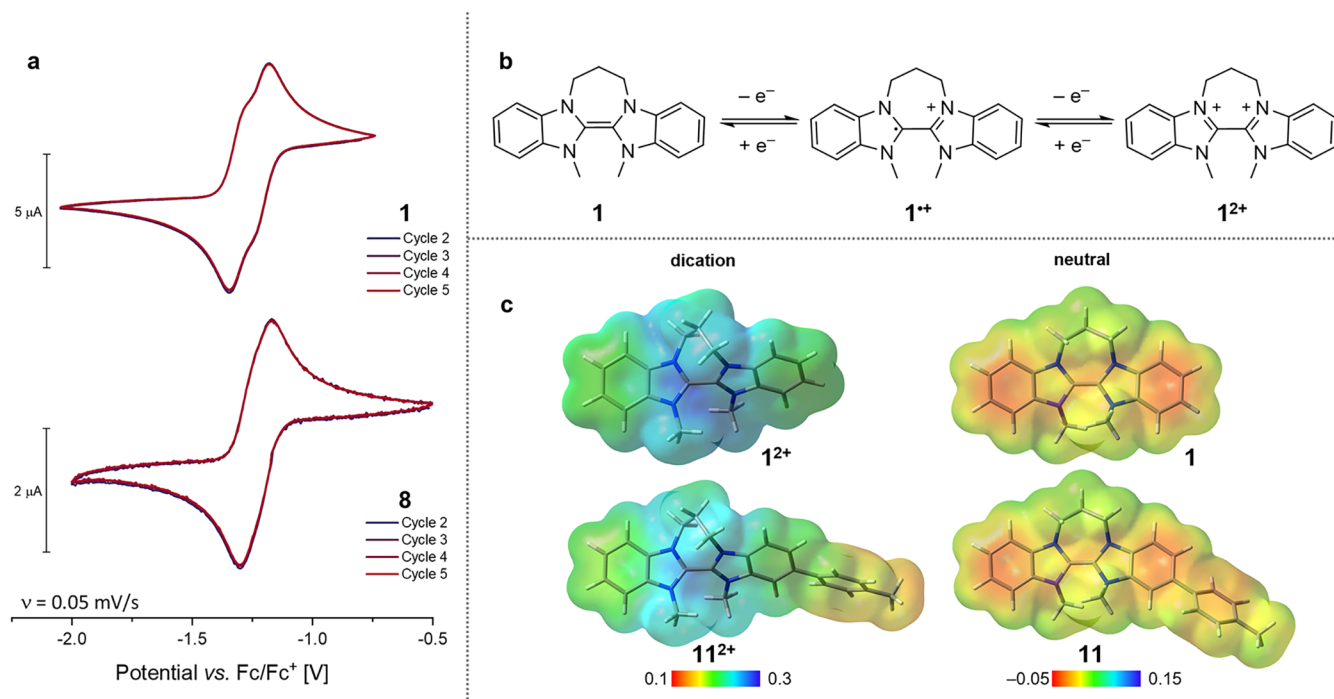


Figure 2. (a) Cyclic voltammograms of the salt of **1**(PF_6) $_2$ (1 mM in DMF, top) and of monomer **8** (1 mM in DMSO, bottom) with 0.1 M $n\text{-Bu}_4\text{NPF}_6$; working electrode: glassy carbon ($\varnothing = 2 \text{ mm}$). (b) Expected redox reactions of SED **1** to its dication $\mathbf{1}^{2+}$ via radical cation $\mathbf{1}^{\bullet+}$. (c) Electrostatic potential maps of dicationic and neutral BBI **1** and a tolyl-substituted BBI (B3LYP/6–311+G(d), isovalue 0.02).

synthesis of styrene-based side-chain polymers, an unsymmetrical precursor **7** was necessary, for which we reacted an excess of 1,3-diiodopropane with one equivalent of 1-methyl-1*H*-benzo[*d*]imidazole to furnish **6** in 56% yield (Scheme 2 (I)). Subsequently, the second iodide was replaced by 1-methyl-6-(4-vinylphenyl)-1*H*-benzo[*d*]imidazole (**5**) under similar reaction conditions, yielding **7** in 87% yield. The next key step was again the base-mediated dimerization of the two benzimidazole units, for which the previous conditions had to be slightly modified to ensure clean conversion. Compared to the literature, the equivalents of KHMDS and oxidant were partially increased, and the reaction mixture was slowly added to a dilute toluene solution of the oxidant instead of adding the perchloroethane to the reaction mixture.³⁴ This yielded **8** in 53% yield. For the synthesis of cross-linked polymers with anticipated lower electrolyte solubility, we synthesized a BBI-containing, redox-active cross-linker (Scheme 2 (II)). We reacted 1,3-diiodopropane with an excess of 1-methyl-6-(4-vinylphenyl)-1*H*-benzo[*d*]imidazole (**5**), and collected the 2-fold substitution product **9** via simple filtration in 82% yield. We then subjected **9** to the above-described optimized reaction conditions for the base-mediated dimerization, which furnished the bis-styryl-substituted cross-linker **10** in 52% yield. For both compounds, monomer **8** and cross-linker **10**, ^{19}F and ^{31}P NMR spectroscopy confirmed the presence of PF_6^- anions (Figures S18 and S19 for compound **8**, Figures S24 and S25 for compound **10**). We washed the target compounds with copious amounts of water to ensure removal of any iodide or chloride salts, as these are water-soluble.

With monomer **8** and cross-linker **10** in hand, we synthesized two polymers (Scheme 3): the linear poly(styryl bi(benzimidazole)) PSBBI and the cross-linked X-PSBBI, containing 10% cross-linker. For both, we used free-radical polymerization in DMF at 65 °C with AIBN as the initiator.

After a reaction time of 1 day, the respective reaction mixtures formed a gel, and stirring stopped. After washing and drying, both polymers were obtained as solids, PSBBI in 78% yield and X-PSBBI in 82% yield. Their insolubility in common organic solvents limited characterization options to IR spectroscopy (Figure S28).

Influence of Arylation of the BBI Core on the Electrochemical Properties

As described before, synthetic manipulations of the RAG can drastically change its redox behavior. To investigate the influence of arylation on the BBI core we measured cyclic voltammetry of $\mathbf{1}^{2+}$ and monomer **8** in solution (Figure 2a). $\mathbf{1}^{2+}$ can be reversibly reduced twice at half-wave potentials of 1.20 and 1.30 V vs. $\text{Fc}^{+/0}$ which would correspond to approximately 2.0 and 2.1 V vs. $\text{Li}^{+/0}$ (assuming 3.25 V for $\text{Fc}^{+/0}$ vs $\text{Li}^{+/0}$, redox reactions are shown in Figure 2b).⁴⁵ With 0.07 V the peak separation of the redox processes is similar to that of the $\text{Fc}^{+/0}$ redox couple (0.08 V). To our delight, styryl-substituted monomer **8** shows a broad two-electron redox process. Compared to the unsubstituted BBI $\mathbf{1}^{2+}$ with the two well-resolved and separate redox processes (Figure 2a), the broad peak for **8** is marginally shifted to the higher half-wave potential of -1.23 V vs $\text{Fc}^{+/0}$. We carried out quantum-chemical calculations on the unsubstituted BBI $\mathbf{1}^{2+}$ and a tolyl-substituted derivative in their dicationic ($\mathbf{11}^{2+}$), neutral and reduced form **11** (B3LYP/6–311+G(d)). The respective electrostatic potential maps show that arylation affects neither the distribution of the positive charges in the dicationic forms nor the displacements of charges in the reduced (neutral) BBIs (Figure 2c). These insights led us to the assumption that the arylation indeed does not affect the redox properties of the BBI.

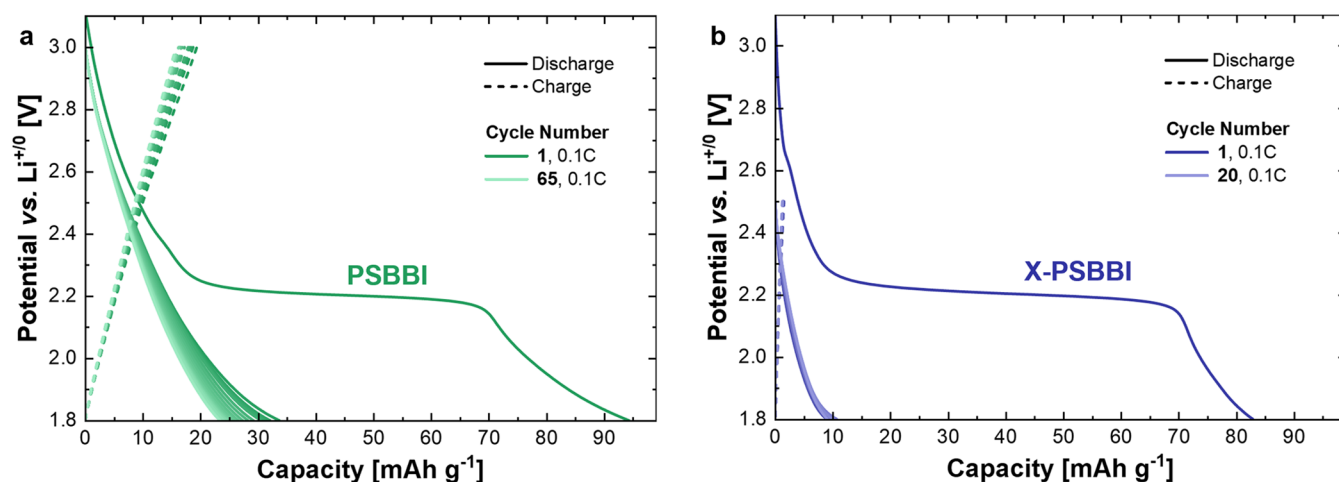


Figure 3. Electrochemical properties of PSBBI and X-PSBBI-based coated composite electrodes with 1M LiPF₆ in EC/DMC 1:1 (v/v) as electrolyte. (a) Charge/discharge curves at a rate of 0.1C of PSBBI electrodes (PSBBI/Super C65/KB600/PVDF (50:20:20:10), active material mass loading: 0.621 mg). (b) Charge/discharge curves at a rate of 0.1C of X-PSBBI electrodes (X-PSBBI/Super C65/PVDF (30:60:10), active material mass loading: 0.291 mg) (all: coated on carbon-coated Al-foil, CE = RE = Li, separator: GF/D).

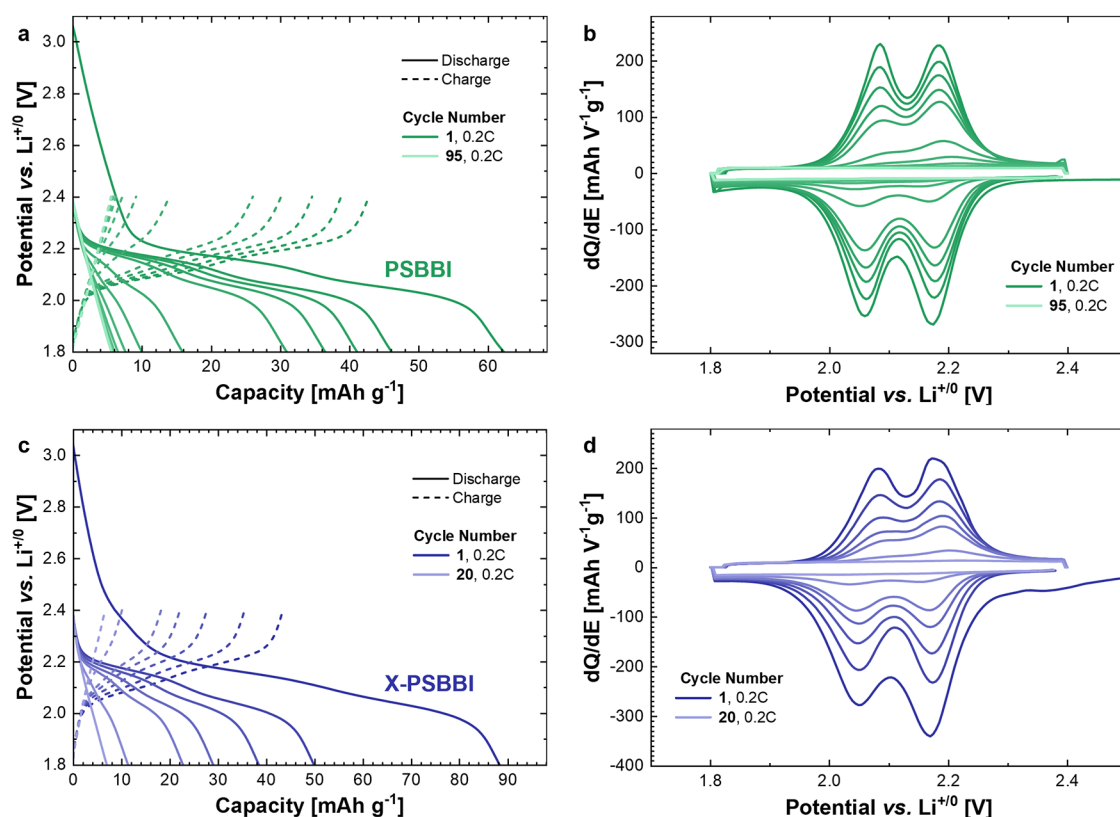


Figure 4. Electrochemical properties of PSBBI and X-PSBBI-based powder composite electrodes with 1 M LiBF₄ in EC/DEC 1:1 (v/v) as electrolyte. (a) Charge/discharge curves and (b) the corresponding differential capacity plot of PSBBI electrodes (PSBBI:KB600 (2:1), active material mass loading: 5.54 mg). (c) Charge/discharge curves and (d) the corresponding differential capacity plot of X-PSBBI electrodes (X-PSBBI:KB600 (2:1), active material mass loading: 5.92 mg) (all: separator: GF/D; plotted cycles: 1–5, then every fifth).

Electrochemical Investigations in Li Half-Cells

As all three polymers could not be characterized in solution, we directly moved to measurements in lithium-battery half-cells. For the conjugated homopolymer PBBI with a theoretical specific capacity of 90.5 mAh g⁻¹ (with PF₆ anions), we tested composite electrodes of different compositions, using the carbon additives Super C65, Ketjenblack EC-600J (KB600) and single-walled carbon

nanotubes (SWCNTs) vs. Li in three-electrode Swagelok-type cells. KB600 and SWCNTs should be beneficial for breaking up a potential π -stacking of the polymer and preventing dissolution.^{46,47} Despite these variations we were not able to detect any electrochemical activity of PBBI in lithium half-cells (see SI for details on electrode preparations, cell assembly and battery measurements, Figure S29).

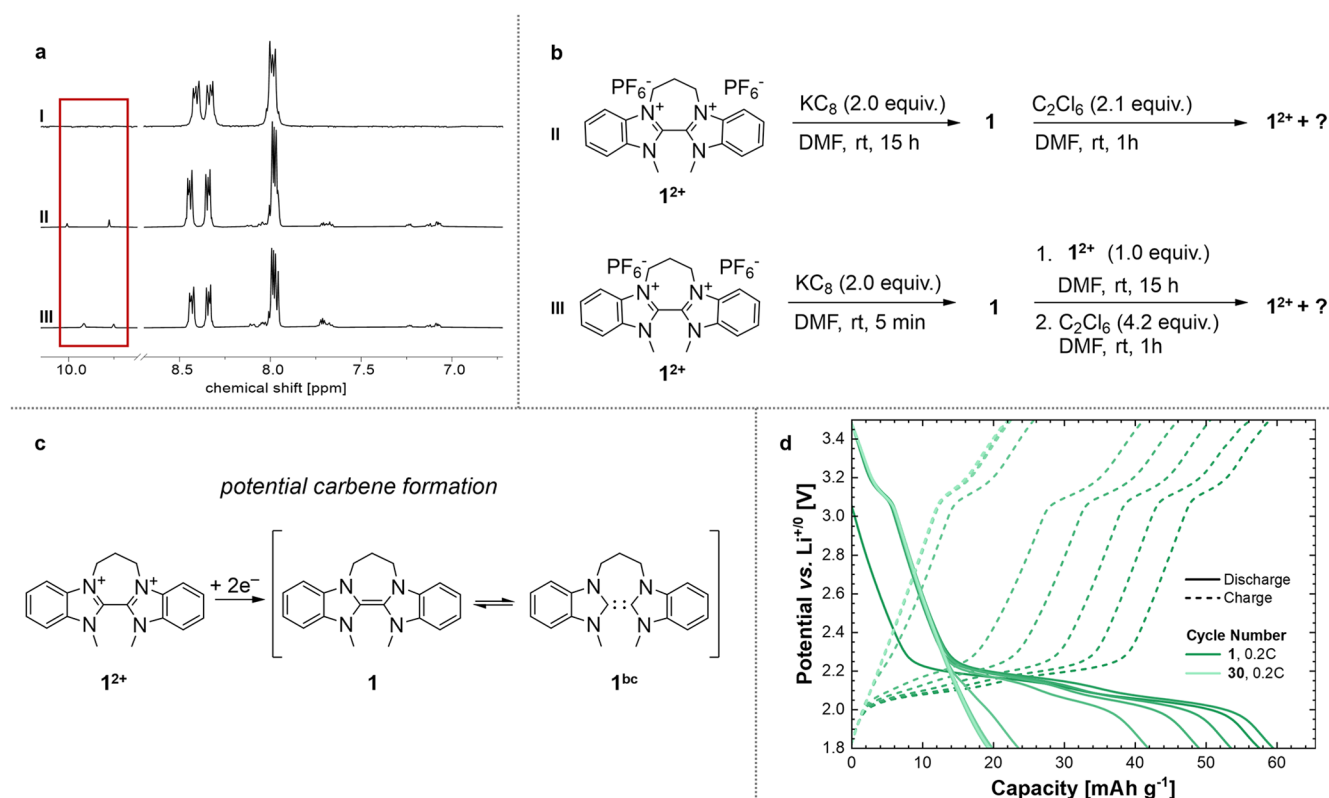


Figure 5. (a) Excerpt of the ^1H NMR spectra of (I) 1^{2+} , (II) the reduced and reoxidized 1^{2+} , and (III) the sample where 1^{2+} was reduced to **1**, more 1^{2+} was added and the mixture was then reoxidized. Spectra recorded in DMSO- d_6 (300 MHz, 300 K for (I); 400 MHz, 298 K for (II, III)). (b) Simplified reaction schemes for the decomposition experiment. (c) Potential formation of the bicarbene 1^{bc} from the reduced SED **1**, according to the Wanzlick equilibrium. (d) Galvanostatic cycling of a PSBBI powder composite electrode to high potential (1.8–3.5 V vs $\text{Li}^{+/0}$) (PSBBI/KB600 (2:1), separator: GF/D, electrolyte: 1 M LiBF_4 in EC/DEC 1:1 (v/v), active material mass loading: 5.81 mg); plotted cycles: 1–5, then every fifth.

For the side-chain polymers PSBBI and X-PSBBI, the theoretical specific discharge capacities are 77.0 mAh g^{-1} and 76.0 mAh g^{-1} , respectively (with PF_6^- anions). PSBBI and X-PSBBI composite electrodes were prepared similarly to the PBBI ones using Super C65 conductive carbon black and PVDF binder in a ratio of 60:30:10 (wt %). To check for electrochemical activity, different ether- and carbonate-based electrolytes were used in cyclic voltammetry experiments (Figures S31 and S32). Compared to the experiments with PBBI, we could now observe a reduction of the material at around 2.1–2.3 V vs. $\text{Li}^{0/+}$, depending on the electrolyte used. Since no reoxidation could be observed, we decided to change the electrode composition. For PSBBI we chose a Super C65/KB600 mixture as conductive carbon to compensate for the lack of intrinsic conductivity of PSBBI (with Super C65) and incorporate desolubilizing porous cavities (through KB600), resulting in electrodes consisting of 50 wt % PSBBI, 10 wt % Super C65, 30 wt % KB600, and 10 wt % PVDF binder. For X-PSBBI we tested composite electrodes consisting of 30 wt % of X-PSBBI, 60 wt % of Super C65, and 10 wt % PVDF binder, and constructed the cells as before, using 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) as the electrolyte. Galvanostatic charge/discharge measurements at a 0.1C rate show well-pronounced plateaus at 2.2 V vs. $\text{Li}^{0/+}$ during the first discharge (Figure 3a,b), and the reduction of the materials can clearly be seen in the respective dQ/dV plots (Figure S30). The first discharge capacities amount to 95 mAh g^{-1} for PSBBI (Figure 3a) and 83 mAh g^{-1}

for X-PSBBI electrodes (Figure 3b). After subtracting the capacitive contributions of the conductive carbon additives (25 mAh g^{-1} for PSBBI electrodes and 10 mAh g^{-1} for X-PSBBI electrodes), this leaves an amount of 70 mAh g^{-1} contributable to the active material PSBBI (91% of theory) and 73 mAh g^{-1} for X-PSBBI (96% of theory), which shows that both redox processes of the polymers are electrochemically addressable in the first discharge. Unfortunately, after the first complete discharge, no subsequent charging could be achieved in these electrodes, and we observed no more electrochemical activity of the active materials during cycling, only the remaining capacitive contribution of the conductive carbon.

Given that composite electrodes coated onto current collectors are highly sensitive to physicochemical and electrical parameters, we adopted the simplest electrode-processing approach. Widely used for decades including for the electrochemical assessment of inorganic active materials,^{48,49} this method consists of directly mixing the active material with carbon black (without any binder), thereby minimizing formulation-related effects and focusing on the intrinsic properties of the active material.

“Powder” composite positive electrodes were prepared without a binder by grinding the plain polymer powder with KB600 in a 2:1 weight ratio and tested electrochemically vs. Li in two-electrode Swagelok-type cells. Already by using the same electrolyte as before (1 M LiPF_6 in EC/DMC 1:1 (v/v)), we could achieve electrochemical reversibility (Figure S33a,b). Electrolyte screening showed that the use of LiBF_4 as the

supporting salt enabled the best electrochemical response for both **PSBBI** and **X-PSBBI**, likely due to the small size of the BF_4^- anion.⁵⁰ As solvents, both dimethoxyethane (DME) and a 1:1 EC/diethyl carbonate (DEC) mixture were found to be effective; however, EC/DEC provided slightly better performance. Figure 4 shows the outcome of one galvanostatic cycling experiment of a **PSBBI**- (a) and a **X-PSBBI**-based (c) powder electrode with 1 M LiBF_4 in 1:1 (v/v) EC/DEC as the electrolyte. Starting from an open-circuit potential of around 3.1 V vs. $\text{Li}^{+/0}$, both polymers behave similarly when being fully reduced to 1.8 V and then cycled between 1.8 and 2.4 V. At a charging rate of 0.2C, the **PSBBI** electrode delivers an initial discharge capacity of 62 mAh g^{-1} , and the **X-PSBBI** electrode delivers an initial discharge capacity of 88 mAh g^{-1} (nearing their theoretical specific capacities, considering carbon contributions). Interestingly, the differential capacity plots (Figure 4b,d) clearly show the two redox processes separately resolved at 2.07 and 2.18 V vs. $\text{Li}^{+/0}$, respectively; this is close to what is expected from the solution CV of compound **1**²⁺ (Figure 2a).

Even though there is a reversible capacity accessible, cycling is not stable. In the case of **PSBBI**, there are only 31 mAh g^{-1} left after five cycles (50% retention), while **X-PSBBI** only shows a retention of 25% after five cycles resulting in a specific discharge capacity of 22 mAh g^{-1} . The observed decay in capacity upon cycling could be due to either active-material dissolution in the electrolyte or a decomposition process. The first is commonly observed in OAMs, and even cross-linked polymers are not necessarily immune to dissolution. Since the reduced and oxidized forms of p-type OAMs have such different polarities, it is challenging to identify electrolytes that maintain immobilization. When opening cycled half-cells of **PSBBI** and **X-PSBBI**, however, we did not see indications of visible dissolution of the active material. On the other hand, decomposition was postulated to be the reason for the lack in cycling stability when using the 2,2'-bipyridinium SED **DMABP** in a redox-flow battery.³⁶ We therefore set out to investigate the stability of bi(benzimidazole) SED **1** in the presence of its oxidized form **1**²⁺, similar to the experiment reported by Sanford et al. using **DMABP** (structure see Figure 1).³⁶ In their case, a mutual reaction between the dicationic and reduced (neutral) forms of the SED led to decomposition. For this experiment, we prepared two solutions of the unsubstituted BBI **1**²⁺ in DMF (sample I) and chemically reduced them with KC_8 (samples II and III).^{51,52} We added one equivalent of **1**²⁺ to sample III and stirred both samples II and III overnight at room temperature (Figure 5b). We then reoxidized both samples with an excess of C_2Cl_6 , removed the solvent under vacuum and recorded ^1H NMR spectra (Figure 5a).

For **DMABP**, the Sanford group had observed degradation, as a new set of signals appeared in the NMR spectra that could be assigned to an open form, similar to **3**, **7**, or **9** in Schemes 1 and 2. The excerpts of the recorded NMR spectra of our experiment show that there might be degradation happening, as new signals appear upon reoxidation, even though they are not well pronounced. The signals highlighted by the red-colored box can be assigned to imidazole protons of an open form of BBI **1**²⁺; however, the signals with a chemical shift between 7.0 and 7.5 ppm would not belong to such a species. Another reason for the decay could be the formation of a carbene species upon reduction. According to Wanzlick, the reduced SED **1** could be in equilibrium with the bicarbene **1**^{bc}

(Figure 5c).^{53–56} Although Murphy et al. reported not to have observed carbene formation in solution, the battery electrode environment is very different.³⁴ To investigate a possible carbene formation in solution, we reduced **1**²⁺ with KC_8 in anhydrous DMF-*d*7 and recorded a ^{13}C NMR spectrum (Figure S1b). Confirming the observations of Murphy et al., we were not able to detect any carbene-carbon signal. Galvanostatic cycling of **PSBBI** electrodes leads to more anodic potentials (3.5 V vs. $\text{Li}^{+/0}$, Figure 5d, see Figure S34 for **X-PSBBI** cycling), showing a redox process at around 3.2 V vs. lithium that would fit to the oxidation of a typical N-heterocyclic carbene (NHC).^{57,58} Cycling to this higher cutoff potential and thereby including the oxidation of this (potential) carbene species, the charge capacity and the overall cycling performance are slightly enhanced. With a discharge capacity of 42 mAh g^{-1} after five cycles from an initial 60 mAh g^{-1} , the capacity retention increases to 70% compared to 50% in Figure 4a at the lower 2.4 V vs. $\text{Li}^{+/0}$ cutoff voltage. It is likely that such carbenes formed would be highly reactive and undergo side reactions, explaining the loss in capacity over time. We tried to slow down the proposed carbene formation by reducing the temperature during cycling to 0 °C. This did enhance the overall cycling stability, however, is no definite proof for the carbene formation (Figure S35).

CONCLUSIONS

We herein explored the use of a bi(benzimidazole)-based SED as a battery-active material. For this, we incorporated the bridged bi(benzimidazole) (BBI) unit into polymeric structures, namely, **PBBI** as a conjugated homopolymer, and **PSBBI** and **X-PSBBI** as two side-chain polymers, linear and cross-linked. The BBI unit itself and its styrene monomer undergo two closely spaced, reversible one-electron reductions in solution. In battery electrodes, the conjugated **PBBI** did not show any electrochemical activity, and only capacitive behavior could be observed, despite attempts to break up possible π -stacking by using KB600 and SWCNTs as conductive carbons. The side-chain polymers **PSBBI** and **X-PSBBI**, on the other hand, showed promising results and almost reached their theoretical specific discharge capacities in the initial discharge process when examined in classical coated electrodes. We obtained reversible cycling when employing these polymers in binder-free powder electrodes with LiBF_4 in EC/DEC as the electrolyte, furnishing initial discharge capacities of 62 and 88 mAh g^{-1} , respectively, close to theory, at an average voltage of 2.1 V vs. $\text{Li}^{+/0}$. As the electrodes lacked long-term cycling stability, we investigated a possible degradation based on the reactivity of the reduced BBI unit. Upon chemical reduction and reoxidation of the unsubstituted BBI in solution, some minor degradation could be observed, but still, most of the material underwent a clean reoxidation. When **PSBBI** or **X-PSBBI** electrodes were cycled in a wider potential window up to 3.5 V vs. $\text{Li}^{+/0}$, an electrochemical process at around 3.2 V appeared that could potentially be assigned to a carbene species. We claim that the reduced BBI units in the polymers undergo a Wanzlick equilibrium reaction to their dicarbene forms, which are highly reactive and can lead to degradation and capacity fading in the battery cell. This work demonstrates an example of a bi(benzimidazole) super-electron-donor-based polymer as a battery-active material with an attractively low redox potential of 2.1 V vs. $\text{Li}^{+/0}$. It showcases the challenges that such reactive species bring regarding battery cycling stability that may warrant more elaborate electrode design.

MATERIALS AND METHODS

Chemicals

Chemicals were purchased from ABCR, Acros-Organics, Fisher Scientific, BLDPharm, Sigma-Aldrich/Merck, or TCI and used directly without further purification, unless otherwise noted.

Inert Working Procedures

Moisture- or oxygen-sensitive reactions were carried out in glassware that was dried by heating under vacuum ($<10^{-2}$ mbar) beforehand, and standard Schlenk techniques were applied using dry argon (Argon 4.6 by MTI Industriegase). Anhydrous THF, DMF, MeCN, and toluene were obtained from an M. Braun solvent purification system (MB-SPS-800) and stored over activated molecular sieves (3 Å). Other solvents were used as purchased in analytical or HPLC grade. Solvents denoted as “degassed” were degassed by using three cycles of the freeze–pump–thaw procedure.

Chromatography

Flash column chromatography was carried out using silica gel 60, grain size 40–63 μm (230–400 mesh) from Macherey-Nagel. Analytical thin-layer chromatography (TLC) was carried out using silica-gel-coated aluminum plates with a fluorescence indicator (Macherey-Nagel ALUGRAM Xtra SIL G/UV254). Detection was carried out using UV light of two different wavelengths ($\lambda_{\text{max}} = 254$ or 365 nm).

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were recorded on a Bruker *Avance 400 Neo* [400.1 MHz (^1H), 100.6 MHz (^{13}C), 376.5 MHz (^{19}F), 162.0 MHz (^{31}P); 298 K] or Bruker *Avance III HD 300 MHz* [300.1 MHz (^1H); 300 K] spectrometer. Chemical shifts are reported in parts per million (ppm, δ scale). ^1H NMR spectra are referenced to tetramethylsilane as an internal standard or the residual solvent signal of the respective solvent: DMSO- d_6 : $\delta = 2.50$ ppm; acetone- d_6 : $\delta = 2.05$ ppm. ^{13}C NMR spectra are referenced to tetramethylsilane as an internal standard the residual solvent signal of the respective solvent: DMSO- d_6 : $\delta = 39.52$ ppm; acetone- d_6 : $\delta = 49.00$ ppm.¹ ^{19}F and ^{31}P NMR spectra are referenced to tetramethylsilane following the IUPAC recommendations.² The analysis followed first order, and the following multiplicity abbreviations were used: singlet (s), doublet (d), triplet (t), multiplet (m), and combinations thereof, such as doublet of doublets (dd). Coupling constants (J) are given in Hertz [Hz]. Chemical shifts (δ) are given in parts per million [ppm].

Elemental Analysis

Elemental analysis was carried out on an *Elementar vario Micro cube*. The reported values are the mean values from two measurements.

Polymerization Reaction Yields

Yields for polymerization reactions were calculated based on the mass conversions from the monomers. For cross-linked polymers, a full conversion of the cross-linking agent is assumed.

Cyclic Voltammetry in Solution

CV measurements in solution were performed in an argon-filled glovebox using a Metrohm *Autolab PGSTAT 128N*. Solvents were degassed using the freeze–pump–thaw method and were dried over a short plug of basic alumina. A glassy carbon disc electrode (2 mm diameter) was used as the working electrode, a platinum rod served as the counter electrode, and a silver wire served as the reference electrode. The redox pair ferrocene/ferrocenium ($\text{Fc}^{+/0}$) was used as an internal reference.

Electrochemical Measurements on Coated Composite Electrodes

Coated composite electrodes were fabricated by mixing the respective polymer with carbon black (*Timical Super C65* by MTI Corporation) and/or Ketjenblack 600JD by Weber and Schaer. The mixture was dried by heating to 60 $^{\circ}\text{C}$ under vacuum ($<10^{-3}$ mbar) overnight. PVDF (Kynar 761 by Arkema) predissolved in 1-methyl-2-pyrrolidone (NMP, 5 wt %) in the specified ratio was added as the

binder. This mixture was then dispersed in NMP (99.5%, Extra Dry, AcroSeal, Acros Organics). Polymer particles and conductive carbon(s) were ground in a mortar and were homogenized with a Thinky Mixer ARM-310 under subsequent addition of NMP. The resulting slurries were coated on carbon-coated aluminum foil (*EQ-CC-Al-16u-180-ss* by MTI Corporation) by using a ZAA2300 *blade coater* by Zehntner with a blade height between 150 to 250 μm . After coating, the films were first dried in a drying oven at 60 $^{\circ}\text{C}$ to obtain a “visually dry” film. Circular electrodes (12 mm diameter) were cut out of the obtained films by using a high-precision electrode cutter (*EL-Cut* by EL-Cell), before being transferred into a vacuum drying oven, where the electrodes were then dried at 60 $^{\circ}\text{C}$ under vacuum (10^{-2} mbar) overnight. Active material masses were obtained by weighing the dried electrodes on a *Cubis MSE3.6P-000-DM* micro balance by Sartorius and subtracting the average weight of ten blank electrodes (cut from areas of the respective foil that was not coated with slurry). Active material masses of the respective electrodes that were galvanostatically cycled are given in the captions of the figures. Electrochemical measurements of composite electrodes were conducted in three-electrode T-cells by Swagelok. Li-foil (GELON LIB, 99.9%, 0.75 mm) served as a reference electrode and as a counter electrode. Whatman GF/D glass fiber membranes served as separators in the main chamber of the cell and in the reference electrode. All cells were assembled inside an argon-filled glovebox containing less than 0.1 ppm of H_2O and O_2 . All measurements were conducted on an *MPG-2 battery cycler* (Bio-Logic S.A., Seyssinet-Pariset, France) at room temperature. After assembly, cells were allowed to equilibrate under open-circuit conditions for at least 12 h. Galvanostatic cycling experiments were started from an open-circuit state.

Electrochemical Measurements on Binder-Free Powder Composite Electrodes

Binder-free powder composite electrodes were prepared in an argon-filled glovebox by manually grinding the plain polymer powder with 33 wt % carbon black (Ketjenblack EC-600JD, AkzoNobel, KB600) using a mortar and pestle. The typical composite electrode mass was ~ 8 mg. Electrochemical measurements were performed in two-electrode Swagelok-type cells, employing a Li metal disc as the negative electrode and a fiberglass separator (Whatman GF/D) impregnated with ~ 150 μL of 1 M LiBF_4 in either dimethoxyethane (DME) or a 1:1 (v/v) ethylene carbonate/diethyl carbonate (EC/DEC) mixture. Galvanostatic cycling measurements were also conducted with an MPG-2 cycler (Bio-Logic S.A.) at 23 $^{\circ}\text{C}$.

Electrolytes

Electrolytes for composite electrode testing were either purchased pre-mixed from E-Lyte Innovations or were self-prepared with components from E-Lyte Innovations.

Synthesis of the Polymers

Poly(2,12-(14,15-dimethyl-7,8,14,15-tetrahydro-6H-benzo[4,5]imidazo[1,2-a]benzo[4,5]-imidazo[2,1-c][1,4]diazepine-5,9-diium) Hexafluorophosphate(V)) (PBBI). The synthesis of PBBI was performed following a modified procedure by Song et al.⁷ Bis(1,5-cyclooctadiene)nickel(0) ($\text{Ni}(\text{COD})_2$, 146 mg, 532 μmol , 1.33 equiv), 2,2'-bipyridine (bpy, 83 mg, 532 μmol , 1.33 equiv), and 1,5-cyclooctadiene (COD, 50 μL , 400 μmol , 1.0 equiv) were dissolved in degassed DMF (4 mL). A solution of **4** (300 mg, 400 μmol , 1.0 equiv) in degassed DMF (4 mL) was added to the first solution. The resulting mixture was heated to 60 $^{\circ}\text{C}$ for 24 h. As the reaction mixture solidified, the reaction was stopped, transferred into 1 M HCl_{aq} (50 mL), and stirred for 1 h at room temperature. The resulting yellow solid was washed with water (2 $\times$ 30 mL), MeOH (2 $\times$ 30 mL), acetone/MeOH (1:1, 2 $\times$ 30 mL), CH_2Cl_2 /cyclohexane (1:1, 2 $\times$ 30 mL), and cyclohexane (2 $\times$ 30 mL) via sonification and centrifugation. After drying *in vacuo* PBBI was obtained as a yellow solid (180 mg, 75%). **Elemental Analysis:** calcd. [%]: C: 38.40, H: 3.39, N: 9.43; found [%]: C: 33.67, H: 3.96, N: 7.86. A characterization in solution was not possible due to the insolubility in all common organic solvents.

Poly(styryl-bisbenzimidazolium Hexafluorophosphate(V)) (PSBBI). Monomer **8** (104 mg, 150 μ mol, 1.0 equiv) was added to a solution of azobis(isobutyronitrile) in anhydrous and degassed DMF (0.05 M, 150 μ L, 7.5 μ mol, 5 mol %) and stirred for 1 day at 65 °C. The formed orange gel was cooled to room temperature and was transferred into MeOH (30 mL). The precipitate was washed via sonification and centrifugation with MeOH (2 $\times$ 30 mL) and acetone (2 $\times$ 30 mL). After drying *in vacuo*, PSBBI was obtained as an orange solid (85 mg, 78%). **Elemental Analysis:** calcd. [%]: C: 46.56, H: 3.76, N: 8.04; found [%]: C: 44.26, H: 3.59, N: 7.47. A characterization in solution was not possible due to insolubility in all common organic solvents.

Poly(styryl-bisbenzimidazolium-stat-bisstyryl-bibenzimidazolium Hexafluorophosphate(V)) (X-PSBBI). Monomer **8** (139 mg, 200 μ mol, 1.0 equiv) and cross-linker **10** (16 mg, 20 μ mol, 0.1 equiv) were added to a solution of azobis(isobutyronitrile) in anhydrous and degassed DMF (0.05 M, 240 μ L, 12 μ mol, 6 mol %) and stirred for 1 day at 65 °C. The formed orange gel was cooled to room temperature and transferred into MeOH (30 mL). The precipitate was washed via sonification and centrifugation with MeOH (2 $\times$ 30 mL) and acetone (2 $\times$ 30 mL). After drying *in vacuo*, X-PSBBI was obtained as an orange solid (127 mg, 82%). **Elemental Analysis:** calcd. [%]: C: 47.11, H: 3.78, N: 7.95; found [%]: C: 45.00, H: 3.79, N: 7.32. A characterization in solution was not possible due to insolubility in all common organic solvents.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this study can be accessed on Zenodo (10.5281/zenodo.18399627).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.6c00515>.

Additional Materials and Methods, including the calculation of the theoretical specific capacities and C-rates, synthetic procedures and characterization data of **1** (PF₆)₂, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**, details on degradation experiments, NMR spectra, IR spectra, additional lithium half-cell measurements, and details on DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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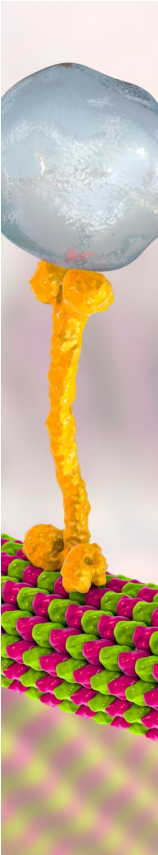
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