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Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers

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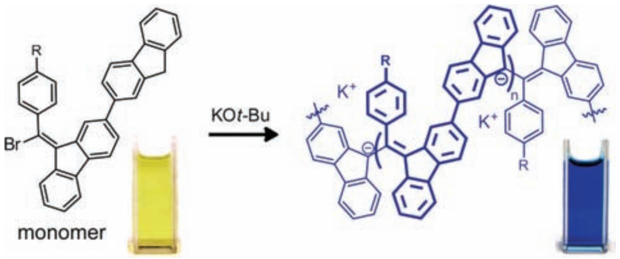
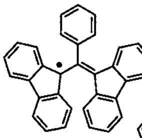
ABSTRACT



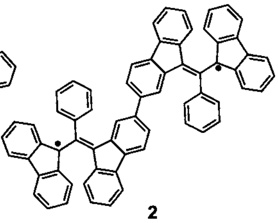
The synthesis of poly-1,3-bisdiphenylene-2-phenyl allyl (BDPA) radicals via a new anionic oligomerization strategy is reported. The material displays a reversible reduction from the orange-red radical to the blue carbanion in solution.

We report electroactive conjugated materials containing a carbon-centered radical based on the 1,3-bisdiphenylene-2-phenylallyl (BDPA) radical (**1**)[1] that can be reversibly reduced to a delocalized carbanion.[2] Our synthesis of these materials is based on a new anionic oligomerization that produces a soluble carbanionic polymer. The ability of biradical **2** and oligomer **3** to be readily reduced to give anionic materials is critical to several applications, including battery anodes, in which polycarbanions with lithium counterions are used for charge storage.[3] Additionally, *n*-dopable (electron-conducting) organic conjugated materials that become conductive upon reduction are essential elements of photovoltaic and field effect transistor devices.[4] Conjugated polymer semiconductors that are *p*-dopable are abundant, but there remains a limited number of stable *n*-dopable materials.[4] Finally, **2** and **3** are electrochromic because they can be switched between the orange-red colored radical and the deep blue carbanion.[5]

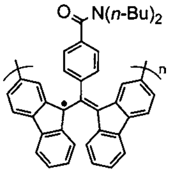


BDPA radical

1



2



3

The BDPA carbanion is remarkably stable for a material containing no electronegative heteroatoms and can persist

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[1] (a) Koelsch, C. F. *J. Am. Chem. Soc.* **1957**, *79*, 4439. (b) Kuhn, R.; Neugebauer, F. A. *Monatsh. Chem.* **1964**, *95*, 3. (c) Azuma, N.; Ozawa, T.; Yamauchi, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 31.

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[4] (a) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656. (b) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Brdas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.

[5] Reviews: (a) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147. (b) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268.

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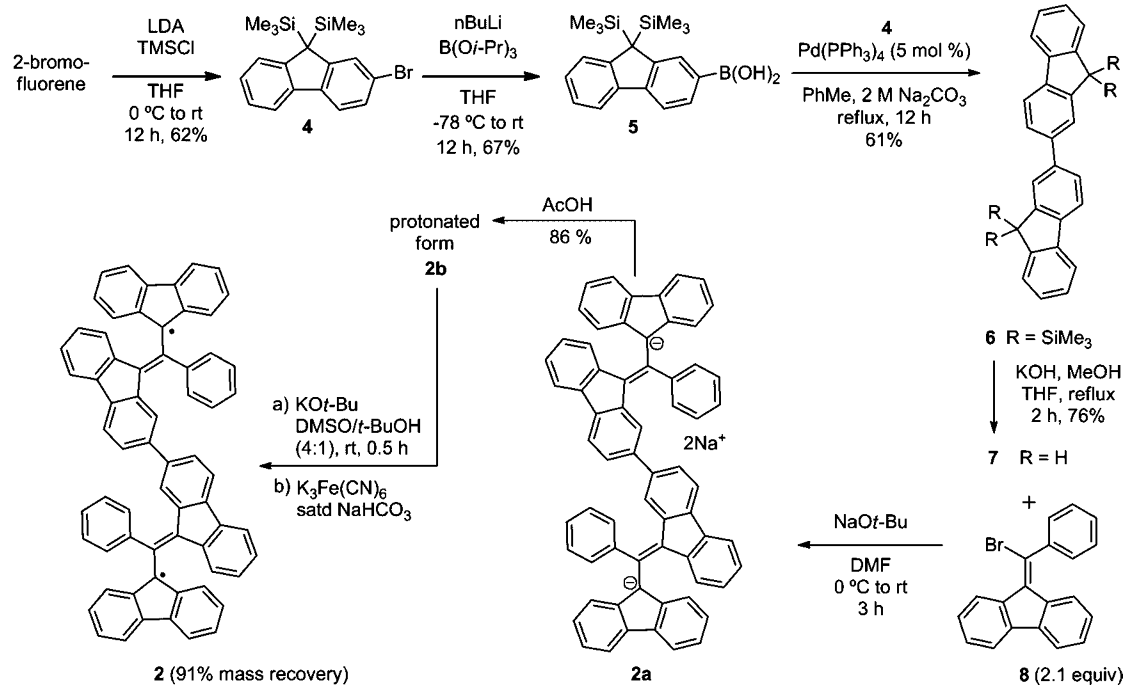
Scheme 1. Synthesis of **2**



for days under 1 atm oxygen in polar aprotic solvents, such as DMF and DMSO, when generated electrochemically.[2a] The predominant decomposition pathway of the BDPA carbanion under ambient conditions is via oxidation to the radical.[2a] Previous electrochemical studies have found that the BDPA radical and closely related derivatives with substitution at the 4-position of the phenyl ring behave as semiconductors with energy gaps of 1.5−1.7 eV in the solid state.[6]

Building on Kuhn and Neugebauer's synthesis of BDPA,[1b] an anionic oligomerization method was pursued. In this approach, the BDPA oligomer is synthesized as a polycarbanion (**3a**), which can then be oxidized to the polyradical. The incorporation of the BDPA radical into the main chain of a conducting polymer or oligomer has not been previously investigated. However, polyacetylenes with a pendant BDPA connected through the 4-position of the phenyl ring have been previously studied.[7] In addition, there have been extensive efforts reported in the literature to develop materials based on the related triphenylmethyl radical and its derivatives.[8]

To test the viability of an anionic oligomerization strategy and to study the effect of linking two BDPA radicals through the 2-position of a fluorene ring, dimer **2** was synthesized as a model system (Scheme 1). Previously reported bis-BDPA biradicals have been limitted to those linked through the phenyl ring.[9] Bifluorene **6**, synthesized by Pd-catalyzed coupling of **4** and **5** followed by deprotection of the 9-positions, was reacted with 2.1 equiv of bromide **8** to obtain dianion **2a**. Protonation of **2a** resulted in a complex mixture of tautomers, *E*/*Z* double bond isomers, and rotamers (^{1}H and ^{13}C NMR spectra included in Supporting Information).[10] However, **2a** offered a simplified ^{1}H and ^{13}C NMR spectrum due to its increased symmetry.[11] Figure 1 (top) shows a portion of the ^{1}H NMR spectrum of the carbanion of a previously reported BDPA derivative with a bromide at the 4-position of the phenyl ring (Br-BDPA).[1b] Figure 1 (bottom) shows a portion of the ^{1}H NMR spectrum of **2a** and the proton assignments, which were determined using gCOSY 2D NMR. Oxidation of **2a** with potassium ferricyanide produces biradical **2**, which shows an EPR signal very similar to that of BDPA at room temperature in solution.[12] Biradial **2** was observed in HRMS but could not be isolated as an analytically pure compound.

On the basis of the success of the dimer synthesis, monomer **9** was prepared, beginning with the condensation

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(6) Eley, D. D.; Jones, K. W.; Littler, J. G. F.; Willis, M. R. *Trans. Faraday Soc.* **1967**, 902.

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(11) Carbanions for NMR study were generated by adding 2.0 equiv of potassium *tert*-butoxide per acidic proton to a d_6-DMSO solution of the protonated precursor.

(12) Solution EPR spectra and effective magnetic moment measurements are available in Figure S1 of Supporting Information. Solid-state EPR and the magnetic properties of the materials will be a focus of future investigations.

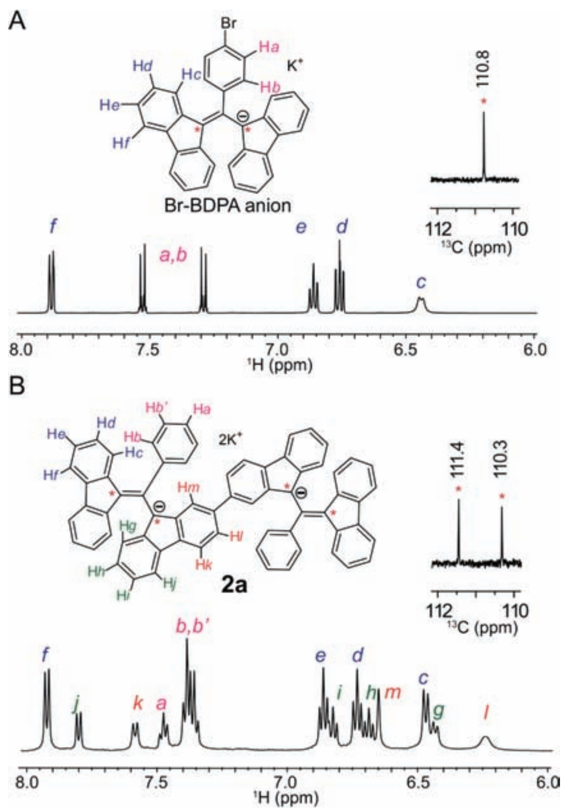
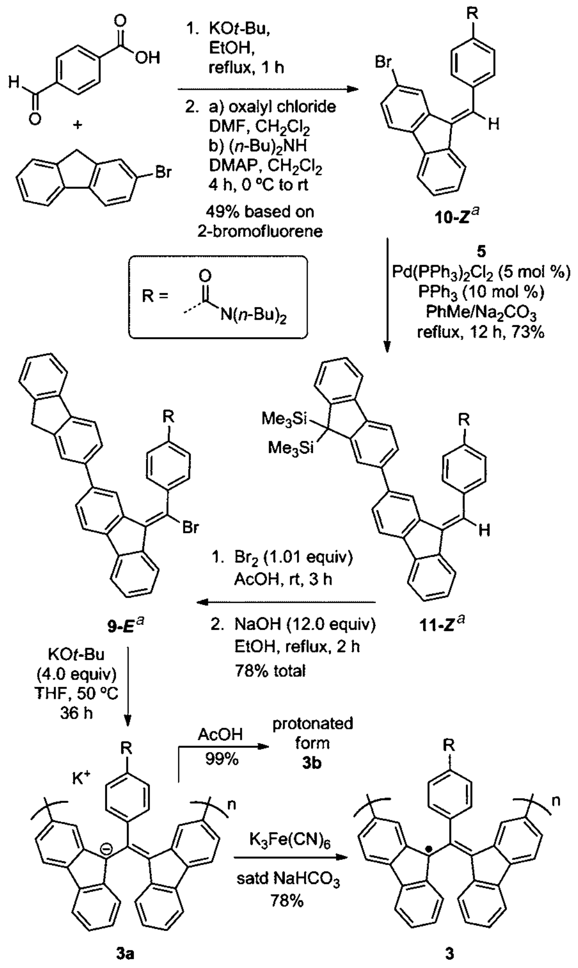


Figure 1. Selected regions of ^{1}H and ^{13}C NMR of Br-BDPA anion (a) and **2a** (b) are shown. Spectra were collected in d_6-DMSO (a, 20 °C; b, 40 °C).

of 2-bromofluorene and 4-carboxybenzaldehyde (Scheme 2). The crude carboxylate salt was converted to a dibutylamide via the acid chloride, and the *E* and *Z* isomers were separated by chromatography for characterization. We have previously shown that amides are compatible with the polymerization conditions,[10a] and the *n*-butyl groups were chosen to provide greater solubility to both the monomer and the oligomer. After Pd-catalyzed coupling of **10-*E*/*Z*** with boronic acid **5**, the alkene of **11-*E*/*Z*** was dibrominated in acetic acid. Hydrogen bromide was eliminated with sodium hydroxide in refluxing ethanol with concurrent removal of the trimethylsilyl groups to provide **9-*E*** and **9-*Z***, which could be separated by chromatography.

Several conditions for oligomerization were screened, but in all cases *tert*-butoxide was used as the base because it deprotonates fluorene at the 9-position without attacking the alkenyl bromide. The effects of solvent (THF, DMA) and counterion (Li, Na, K, Mg, Ba, Zn) were explored (see Table S1 in Supporting Information), and the extent of oligomerization was analyzed on the basis of the M_n, as determined by GPC (DMF) of the crude polyanions. Potassium *tert*-butoxide in THF was chosen as the preferable method and was used to synthesize **3b**, which is a light yellow powder that is readily soluble in CH_2Cl_2, THF, and chloroform (GPC (THF): $M_n = 6.5$ kDa, degree of polymerization (DP) = 11). The ^{1}H and ^{13}C NMR of **3b** showed broadened signals that are in agreement with the proposed structure. In the ^{13}C spectrum, the resonance at 52.7 ppm, which is specific to the carbon attached to the acidic proton of BDPA precursors, supports the proposed structure (see Supporting Information). To isolate the radical form of the oligomer, **3a** was treated with potassium ferricyanide. After precipitation into methanol, a dark red powder (GPC (THF): $M_n = 9.4$ kDa, DP = 16) was isolated. The higher M_n may be a result of **3** having a larger persistence length in THF as compared to **3b**. Fractionation of the polymer during precipitation may also contribute to the discrepancy. In addition to the expected IR absorbances, the isolated oligomers **3** and **3b** display a weak ketone stretch at approximately 1720 cm^{-1} that we attribute to 9-fluorenone end-groups (see Figure S2 in Supporting Information).[13] Oligomer **3** showed a featureless EPR absorption in THF at room temperature (see Figure S1 in the Supporting Information).

Scheme 2. Synthesis of **3**



[a] *E*/*Z* isomers were synthesized in a 1:1 ratio but were isolated and characterized separately.

The UV−vis spectra of the protonated precursor, the carbanions, and the radicals are presented in Figure 2.

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(13) The results of combustion analysis for **3** and **3b** are reported and discussed in Supporting Information. Additionally, oligomer **3** showed no detectable level (<0.1%) of bromide in combustion analysis.

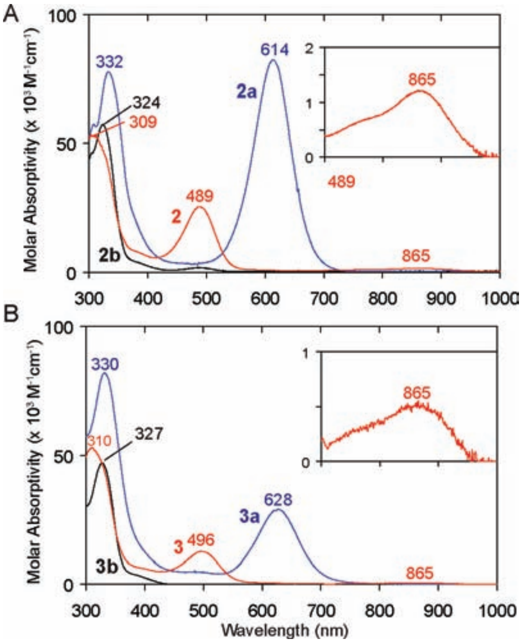

Figure 2. Absorption spectra of **2a**, **2b**, **2** (a) and **3a**, **3b**, **3** (b) are shown. All spectra were collected in THF except for **2a** and **3a**, which were collected in DMSO purged with nitrogen.

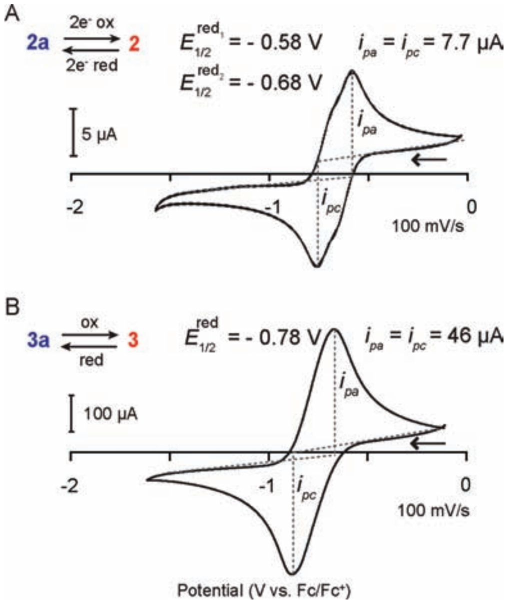

Figure 3. Cyclic voltammograms of **2** (a) and **3** (b) showing the reversible redox couple between the carbanion and the radical. Conditions: (a) 0.10 M $LiClO_4$ in DMF, Pt-button electrode, [**2a**] ≈ 1 mM, **2a** formed by deprotonation with LiO*t*-Bu in DMF; (b) 0.10 M (n-Bu)$_4$NPF$_6$ in MeCN, Pt-wire electrode with **3** dropcast from a chloroform solution.

Dianion **2a** shows a strong absorbance at 614 nm in DMSO similar to the BDPA anion absorbance at 600 nm in DMF. The polyanion **3a** is red-shifted and appears broadened. Biradical **2** and polyradical **3** show strong absorbances near 490 nm and weak absorbances at 865 nm in THF, which are comparable to the reported values for BDPA in dioxane (485 and 860 nm).[1b]

Biradical **2** shows two closely spaced, reversible one-electron reductions to form the dianion **2a** (Figure 3). Polyradical **3** displays a broad, reversible reduction peak, presumably attributable to multiple radicals undergoing one-electron reduction. The electrode displays a visible change in color from reddish brown to deep blue upon reduction to the blue polyanion. In general, **3** did not form quality films. Future work will examine how cross-linking through the solubilizing groups can aid in film formation.

In conclusion, materials that join BDPA radicals through the 2-position of the fluorene ring have been synthesized via a new anionic oligomerization strategy. The carbanions have been characterized with ^{1}H and ^{13}C NMR. The absorption spectra of the protonated, anionic, and radical forms of **2** and **3** are reported, as is the ability to reversibly perform one-electron reductions to form the carbanions from the radicals. Further work will investigate how to improve the film forming abilities of **3** and investigate how changing the connectivity between the fluorene rings affects the electronic and magnetic properties of the materials.

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Supporting Information Available: Experimental details and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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