Thermal Insolubilization of Electrically n-Doped Films Achieved Using 7-Alkoxy-Benzocyclobutene-Substituted Fullerene and Dopant Molecules

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KEYWORDS. n-doping, cross-linking, insolubilization, charge transport, immobilization

ABSTRACT: Insoluble electrically n-doped fullerene-containing films have been obtained by thermal annealing of a fullerene compound and a 1,3-dimethyl-2,3-dihydro-1*H*-benzo[*d*]imidazole n-dopant moiety, both of which are functionalized with a 7-butoxybenzocyclobutene group. The covalent tethering and electrical doping reactions are studied by mass spectrometry as well as electron paramagnetic resonance. Optical absorption spectra on BBCB-N-DMBI-H-doped BBCBP indicate films heated at 150 °C for 10 min are unaffected by immersion in *ortho*-dichlorobenzene for 10 min. Although films containing 10 mol% dopant showed electrical conductivity of values of $1.1 \times 10^{-5} \pm 3.4 \times 10^{-7}$ S cm^{-1} prior to heating, the thermal insolubilization process led to values around two orders-of-magnitude lower. However, the thermal insolubilization also leads to immobilization of the dopant molecule and the corresponding cation, reducing their ability to diffuse into an adjacent layer of a stronger electron acceptor.

1. INTRODUCTION

Electrical doping of organic semiconductors plays an important role in a variety of organic and hybrid (opto-)electronic devices including organic and metal-halide-perovskite photovoltaic cells, organic and metal-halide-perovskite light-emitting diodes, and organic field-effect transistors.[1-5] Strong molecular electron acceptors (p-dopants) or donors (n-dopants) can significantly increase the density of positive or negative charge carriers, respectively. This, in turn, permits one to tune the electrical conductivity of the semiconductor, as well as its Fermi level energy, allowing the alignment of the charge-transport levels of the doped materials at interfaces with other materials within an (opto-)electronic device stack to be manipulated.[6] However, dopant molecules or ions can be prone to diffuse or drift from their intended locations to other regions of the device in which their presence is unwanted. For example, Li^+ ions have been found to diffuse from doped layers in OLEDs into the emissive layer, negatively affecting device performance.[7] Furthermore, solution fabrication of multilayer devices is often challenging in that layers can be partially or completely dissolved during deposition of a subsequent layer. Accordingly approaches that immobilize and insolubilize the components of solution-processed electrically-doped films are potentially useful in improving device performance and stability.

In a few cases, such as that of PEDOT:PSS, the solubility of the doped material is “orthogonal” to that of typical organic semiconductor materials.[8] The use of large dopant molecules can in some cases lead to immobilization of the dopants,[9] but often the doped film remains substantially soluble in the types of organic solvent typically used to deposit subsequent layers. We have recently reported simultaneous n-doping, insolubilization, and dopant immobilization in a conjugated polymer using post-film-deposition thermal activation of dopant that forms a large tetracation that acts to “electrostatically cross-link” polymer chains.[10] However, the formation of covalent bonds between semiconductors and dopants, and/or between adjacent semiconductor moieties, subsequent to film formation is, in principle, a more general and reliable approach to achieving these goals. Several examples of this approach have been reported for the case of fullerene semiconductors. Deposition of poly(allylamine) onto C_{60} films, followed by annealing at 150 °C, led to chemical reactions, including amine-fullerene bond formation and electron-transfer reactions, resulting in insoluble n-doped films.[11] An azide-functionalized molecular dopant has been tethered to its $PC_{61}BM$ host by UV irradiation,[12] which results in the formation of a reactive nitrene that inserts into C—H bonds,[13] the immobilization of the tethered dopant being inferred by comparison of current-voltage characteristics of the irradiated doped films with those of control films, with the former showing much less hysteresis.[12] Undoped fullerene films have been insolubilized and/or immobilized in several ways including hydrolysis of a tri(alkoxy)silane-functionalized derivative,[14] thermal polymerization of styrene- or epoxide-functionalized examples,[15,16] and through heating of a fullerene with a pendant benzocyclobutene (BCB) moiety (PCBCB, Figure 1a).[14,17] In the last-mentioned approach, the BCB moiety is thermally ring-opened to an *ortho*-xylylene derivative that can then dimerize and/or react with a fullerene cage (Figure 1b) to form insoluble undoped fullerene dimers or oligomers, or, when the oligomeric BCB derivative (CL, Figure 1) is also used,[18] crosslinked material. n-Doped PCBCB:CL films have also been deposited and crosslinked, but the $IrCp^*Cp^+$ {$Cp = C_5H_5$; $Cp^* = C_5Me_5$} dopant ion is not completely immobilized and is partially lost on solvent exposure. Moreover, the thermal ring-opening of the benzocyclobutene ring of PCBCB occurs at 210 °C,[17] limiting the compatibility of the approach with other active materials and substrates. Here we report an extension of this BCB chemistry in which we (i) employ a BCB moiety that ring-opens at a lower temperature than that of PCBCB and (ii) incorporate BCB groups into a dopant molecule as well as the fullerene.

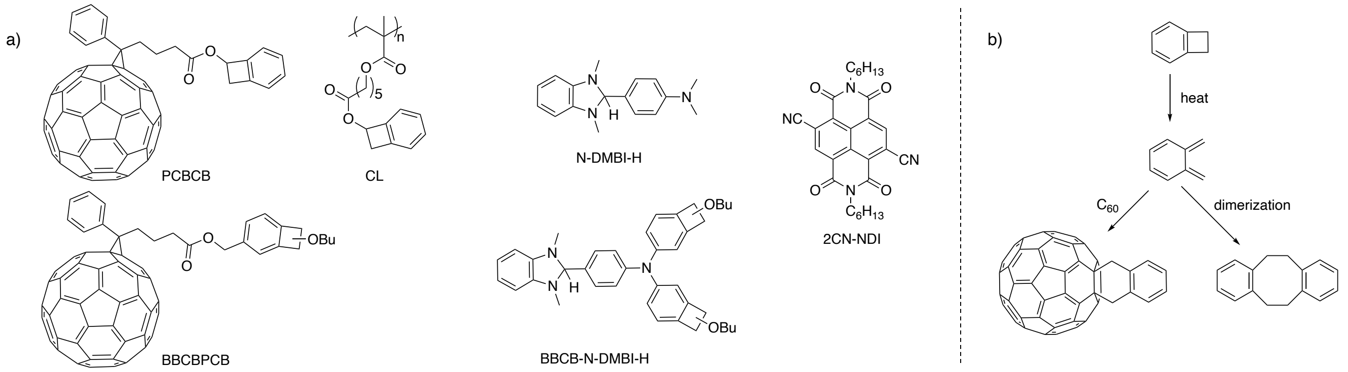


Figure 1. a) Chemical structures of compounds discussed in this work, including previously and newly reported benzocyclobutene-functionalized fullerenes (PCBCB and BBCBPCB respectively), an additive (CL) previously used with PCBCB, a widely reported n-dopant for fullerenes (N-DMBI-H) and a new benzocyclobutene-functionalized derivative (BBCB-N-DMBI-H), and an electron-transporting material more easily reduced than fullerenes (2CN-NDI) used here to examine dopant diffusion. b) Thermal ring-opening of benzocyclobutene to *ortho*-xylylene and examples of possible subsequent reactions.

2. EXPERIMENTAL SECTION

2.1. General Synthetic and Characterization Details. Chemicals were obtained from commercial sources and used as received unless stated otherwise. All operations involved in the synthesis were performed under an atmosphere of nitrogen using standard Schlenk techniques or in a glove box. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$, C_6D_6, or CD_2Cl_2, on Varian 500 or 700 MHz spectrometers. The chemical shifts (δ) are reported in parts per million (ppm). Differential scanning calorimetry data were acquired using a TA DSC Q 200 and heating and cooling rates of 10 °C min^{-1}.

2.2. Synthesis of BBCB-TTA. To a 250 mL two neck flask with a reflux condenser, $Pd(OAc)_2$ (224 mg, 1.0 mmol) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (0.086 g, 1.05 mmol), aniline (1.8 g, 10.4 mmol), compound BBCB-Br[17] 6.0 g, 23.5 mmol), and NaO^{t}Bu (3.4 g, 35.3 mmol) were added. The flask was sealed and evacuated and refilled with nitrogen three times. Anhydrous toluene (100 mL) added, and the mixture was heated at 80 °C for 2 d. The reaction mixture was cooled to room temperature. Water (30 mL) added, and the organic layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the crude product collected, and was purified through column chromatography (8:1 hexane: EtOAc) to yield the desired product, as a mixture of isomers (3.86 g, 83%). ^{1}H NMR (isomer mixture, 700 MHz, $CDCl_3$) δ [7.22–7.18 (m), 7.11–7.09 (m), 7.04–7.01 (m), 6.96–6.92 (m), 6.87 (s), 11H], [5.00–4.98 (m), 4.97–4.95 (m), 2H], [3.66–3.63 (m), 3.62–3.58 (m), 3.57–3.53 (m), 4H]. [3.41 (dd, J = 13.9, 4.4 Hz), 3.37 (d, J = 14.0 Hz), 2H], [3.07 (dd, J = 14.0, 2.0 Hz), 3.03 (d, J = 14.0 Hz), 2H], 1.69 – 1.57 (m, 4H), 1.49 – 1.37 (m, 4H), [0.96 (t, J = 7.4 Hz), 0.93 (t, J = 7.5 Hz), 6H]. ^{13}C{^{1}H} NMR (isomer mixture, 176 MHz, $CDCl_3$) δ 149.66, 148.72, 148.57, 147.63, 147.53, 147.10, 147.08, 147.06, 143.41, 143.37, 140.35, 137.30, 137.18, 137.00, 136.97, 129.17, 129.15, 127.13, 126.90, 126.89, 124.59, 124.57, 124.56, 124.04, 124.02, 123.86, 123.84, 123.46, 123.03, 122.07, 121.77, 120.07, 120.05, 119.83, 119.80, 119.78, 76.40, 76.39, 76.34,76.32, 68.99, 68.98, 68.86, 38.44, 38.42, 38.24, 38.19, 32.10, 32.04, 32.02, 19.54, 19.47, 19.46, 14.08, 14.03. HRMS (ESI) calcd for $C_{30}H_{36}NO_2$ ($M+H^+$), 442.2740; Found 442.2734. Anal Calcd. For $C_{30}H_{35}NO_2$: C, 81.59; H, 7.99; N, 3.17, Found C, 81.42; H, 8.18; N, 3.17.

2.3. BBCB-TTA-CHO. Phosphorus oxychloride (2.53 g, 16.5 mmol) was added into DMF (1.2 g, 16.4 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 30 min, a solution of BBCB-TTA (4.86 g, 11.0 mmol) in 1.2-dichloroethane (20 mL) was added into the reaction mixture at 0 °C. The reaction mixture was stirred at 60 °C for 15 h. The resulting mixture was poured into iced water (150 mL) and then neutralized with Na_2CO_3. The product was extracted with CH_2Cl_2 (2 × 100 mL). After removal of solvents, the crude product was purified through column chromatography on silica gel (5:1 hexane: EtOAc) and obtained as a yellow oil consisting of a mixture of isomers (1.6 g, 31%). ^{1}H NMR (major isomer peaks only, 700 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.63 (d, J = 8.8 Hz, 2H), 7.13–7.10 (m, 4H), 7.10–7.07 (m, 2H), 6.92 (dd, J = 8.9, 2.5 Hz, 2H), 4.97 (m, 2H), 3.62-3.58 (m, 2H), 3.57–3.53 (m, 2H), 3.44 (dd, J = 14.2, 4.4 Hz, 2H), 3.09 (dd, J = 14.2, 2.1 Hz, 2H), 1.63–1.57 (m, 4H), 1.43–1.35 (m, 4H), 0.91 (t, J = 7.5 Hz, 6H). ^{13}C{^{1}H} NMR (isomer mixture, 176 MHz, $CDCl_3$) δ 190.31, 153.94, 147.56, 147.56, 145.35, 145.34, 139.65, 139.60, 128.60, 128.56, 128.40, 128.38, 125.11, 125.08, 121.62, 121.60, 118.25, 118.20, 76.16, 76.14, 69.07, 38.36, 38.34, 31.90, 31.89, 19.35, 13.91. HRMS (ESI) calcd for $C_{31}H_{36}NO_3$ ($M+H^+$), 470.2690;

Found 470.2686. Anal Calcd. For $C_{31}H_{35}NO_3$: C, 79.28; H, 7.51; N, 2.98, Found C, 79.57; H, 7.79; N, 2.98.

2.4. BBCB-N-DMBI-H. In the glove box, to a 20 mL vial with Teflon septum, BBCB-TTA-CHO (1.4 g, 2.98 mmol) was added and dissolved in 12.0 mL anhydrous CH_2Cl_2 followed by addition of *N*,*N'*- dimethyl-1,2-phenylenediamine (490 mg, 3.59 mmol, 1.2 equivalent). The vial was capped and transferred outside the glove box. Two drops of acetic acid were added by syringe and the mixture was stirred at room temperature for 5 days. The solvent was evaporated, and the product was purified on silica gel (10:1 hexane/EtOAc) to obtain a yellow foam (700 mg, 1.19 mmol, 39%). ^{1}H NMR (major isomer peaks only, 700 MHz, CD_2Cl_2) δ 7.42–7.38 (m, 2H), 7.12 – 7.08 (br, 4H), 7.06–7.01 (m, 4H), 6.70–6.68 (dd, J = 5.4, 3.1 Hz, 2H), 6.44–6.41 (dd, J = 5.4, 3.2 Hz, 2H), 4.98 (dd, J = 4.4, 1.9 Hz, 2H), 4.81 (s, 1H), 3.63–3.59 (m, 2H), 3.58–3.55 (m, 2H), 3.44 (dd, J = 14.0, 4.4 Hz, 2H), 3.05 (dd, J = 14.0, 1.9 Hz, 2H), 2.59 (s, 6H), 1.63–1.58 (m, 4H), 1.45–1.39 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (isomer mixture, 176 MHz, C_6D_6) δ 150.12, 148.26, 147.90, 147.88, 142.75, 137.97, 137.90, 132.39, 130.18, 127.64, 127.60, 125.06, 125.03, 122.06, 120.63, 120.61, 119.85, 119.84, 106.21, 94.20, 76.69, 76.66, 68.80, 38.38, 38.34, 33.22, 32.42, 32.40, 19.74, 14.10, 14.08. ESI-MS 586.3433 (M-H$^+$), Anal Calcd. For $C_{39}H_{45}N_3O_2$: C, 79.69; H, 7.72; N, 7.15, Found C, 79.14; H, 7.93; N, 7.21.

2.5. BBCB-CHO. A solution of BBCB-Br[19] (1.0 g, 3.91 mmol) in THF (25.0 mL) was stirred at –78 °C under dry N_2 and treated dropwise with a solution of *n*-butyllithium (1.72 mL, 2.5 M in hexane, 4.30 mmol). The resulting mixture was kept at –78 °C for 60 min, and then DMF (0.500 mL, 6.45 mmol) was added dropwise. The mixture was stirred overnight (12 h), while the temperature was allowed to rise to room temperature. To the solution water added and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried over Na_2SO_4 and solvent evaporated. The residue was purified over silica gel (10:1 hexane/EtOAc) to obtain the product as a mixture of two isomers (90:10) as a pale- yellow oil (517 mg, 64%). ^{1}H NMR (major isomer peaks only, 500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.83 (dd, J = 7.6, 1.3 Hz, 1H), 7.75 (s, 1H), 7.31 (dd, J = 7.6, 1.0 Hz, 1H), 5.07 (dd, J = 4.5, 2.1 Hz, 1H), 3.71-3.66 (m, 1H), 3.53 (dd, J = 15.14.6 Hz, 1H), 3.55-3.51 (m, 1H), 3.20–3.15 (m, 1H), 1.68–1.58 (m, 2H), 1.47–1.35 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (major isomer, 126 MHz, $CDCl_3$) δ 192.43, 150.63, 147.46, 136.05, 132.51, 124.24, 123.60, 76.34, 69.25, 39.22, 32.02, 19.49, 14.05. ^{13}C{^{1}H} NMR (observed minor isomer peaks, 126 MHz, $CDCl_3$) δ 192.51, 153.52, 143.58, 137.78, 130.48, 124.40, 123.41, 78.51, 38.42. HRMS (ESI) calcd for $C_{13}H_{17}O_2$ (M+H$^+$), 205.1223; found 205.1221.

2.6. BBCB-CH$_2$OH. To a solution of BBCB-CHO (1.0 g, 4.9 mmol) in dry THF (15 mL) at 0 °C was added sodium borohydride (223 mg, 5.86 mmol, 1.2 eq); the reaction mixture was stirred for 2 h at room temperature. Excess sodium borohydride was quenched by addition of water. The mixture was extracted with EtOAc and the organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified through column chromatography (5:1 hexanes/EtOAc) to yield the desired product as a mixture of two isomers as a colorless oil (800 mg, 79%). ^{1}H NMR(major isomer, 500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.26 (s, 1H), 7.13 (dd, J = 7.5, 1.0 Hz, 1H), 5.02 (dd, J = 4.4, 2.0 Hz, 1H), 4.65 (s, 2H), 3.66 (m, 1H), 3.58 (m, 1H), 3.44 (dd, J = 14.1, 4.3 Hz, 1H), 3.13–3.06 (m, 1H), 1.69–1.57 (m, 2H), 1.48–1.33 (m, 2H), 0.94 (t, J = 7.4 Hz, 4H). ^{13}C{^{1}H} NMR (major isomer, 126 MHz, $CDCl_3$) δ 146.71, 142.18, 140.01, 128.52, 123.70, 121.81, 76.55, 68.92, 66.02, 38.45, 32.07, 19.51, 14.06. ^{13}C{^{1}H} NMR (observed minor isomer peaks, 126 MHz, $CDCl_3$) δ 145.86, 143.02, 142.31, 126.16, 122.98, 122.45, 76.51, 68.79, 38.47. HRMS (ESI) calcd for $C_{13}H_{19}O_2$ (M+H$^+$), 207.1380; Found 207.1378. Anal Calcd. For $C_{13}H_{18}O_2$: C, 75.69; H, 8.80, Found C, 75.54; H, 8.68.

2.7. BBCBPCB. PCBA[17] (200 mg, 0.222 mmol), BBCB-CH_2OH, (65.0 mg, 0.31 mmol) and 4-dimethylaminopyridine (41 mg, 0.33 mmol) was deoxygenated in a flask and then dissolved in 100 mL of dichlorobenzene. The solution was sonicated for 30 min to allow complete dissolution and then cooled to 0 °C (in an ice bath) and stirred for 5 min. *N*,*N'*-Dicyclohexylcarbodiimide, DCC, (46.0 mg, 0.22 mmol) was added to the solution and the mixture was stirred in ice bath for 3 h before warming it to room temperature. It was then allowed to stir at room temperature for 48 h. The crude product collected was purified through column chromatography (2:1 CH_2Cl_2/hexanes or toluene) to yield BBCBPCB as a mixture of isomers (120 mg, 49%). ^{1}H NMR (major isomer, 700 MHz, CD_2Cl_2) δ 7.96 (m, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.49 (m, 1H), 7.28–7.10 (m, 3H), 5.07 (s, 2H), 5.03–4.94 (m, 1H), 3.62 (q, J = 7.3 Hz, 1H), 3.55 (d, J = 7.3 Hz, 1H), 3.42 (dd, J = 14.1, 4.3 Hz, 1H), 3.04 (d, J = 14.1 Hz, 1H), 2.98–2.87 (m, 2H), 2.55 (t, J = 7.4 Hz, 2H), 2.21–2.12 (m, 2H), 1.59 (p, J = 7.0 Hz, 2H), 1.40 (q, J = 7.5 Hz, 2H), 0.93 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2) δ 172.73, 149.11, 147.99, 146.93, 145.98, 145.29, 145.20, 145.16, 145.06, 144.88, 144.79, 144.75, 144.69, 144.51, 144.39, 144.05, 143.78, 143.09, 143.02, 143.01, 142.99, 142.96, 142.94, 142.88, 142.27, 142.15, 140.95, 140.72, 138.18, 138.01, 137.47, 137.29, 136.91, 135.03, 132.24, 129.57, 129.01, 128.40, 128.22, 128.20, 127.19, 125.27, 123.64, 123.49, 122.77, 122.74, 80.07, 76.46, 68.84, 66.82, 53.86, 53.81, 53.70, 53.65, 53.50, 53.34, 53.26, 53.19, 52.12, 38.45, 34.03, 33.64, 32.05, 22.44, 22.43, 21.20, 19.46, 19.45, 13.79, 13.76. HRMS (MALDI) calcd for $C_{84}H_{28}O_3$ (M$^+$), 1084.2038; Found 1084.2056. Anal Calcd. For $C_{84}H_{28}O_3$: C, 92.97; H, 2.60, Found C, 91.56; H, 2.71.

2.9. Film Characterization. Stock solutions were prepared under a nitrogen atmosphere in an inert gas box using dried *o*-dichlorobenzene (o-DCB). The reported dopant concentrations are mole percentages, which are 100× the mole fraction, $n_D/(n_D + n_H)$, where n_D is the amount of BBCB-N-DMBI-H molecules and n_H is the amount of BBCBPCB molecules in the casting solutions. Thin films were prepared via spin-coating (at 1000 rpm for 1 min). UV-vis-NIR absorption data were acquired on a Cary 5000 instrument for both the solid and solution spectra. Electron spin resonance (ESR) measurements were performed using a Bruker Elexsys E580 spectrometer operating at 9.26 GHz with a MS-3 cavity and with 36 dB attenuation of the microwave power of 300 W.

Conductivity data were acquired with a custom-built 4-point probe system connected to a Keithley 6430 Source Meter. A solution of BBCBPCB (20 mg/mL) was stirred at a glove box in chlorobenzene overnight. A solution of dopant was prepared (in chlorobenzene) and mixed with BBCBPCB solutions (different mol%) and stirred for 2 h and finally, films were spin-coated (1500 rpm, 60 s) to achieve the thickness of 45 nm. The thickness of films was measured using a profilometer on different spots to ensure the films are uniform. Here, 45 nm is an average over 3 different spots on the glass substrate.

2CN-NDI[20] was deposited in a Kurt J. Lesker low-temperature evaporator Minispectros Series. The base pressure during the process was 10^{-6} Torr. The material was heated in a 10 cm^3 alumina crucible at 150 °C for 5 min prior to deposition. The deposition rate was controlled by a proportional-integral-derivative controller that uses a quartz crystal microbalance (QCM). The QCM was previously calibrated by crosschecking the thickness of layers deposited on silicon wafers with ellipsometry. The deposition rate oscillated around 0.4 A° s^{-1}, which was achieved with a source temperature of ca. 200 °C. The final thickness of 2CN-NDI layer was 190 nm.

3. RESULTS AND DISCUSSION

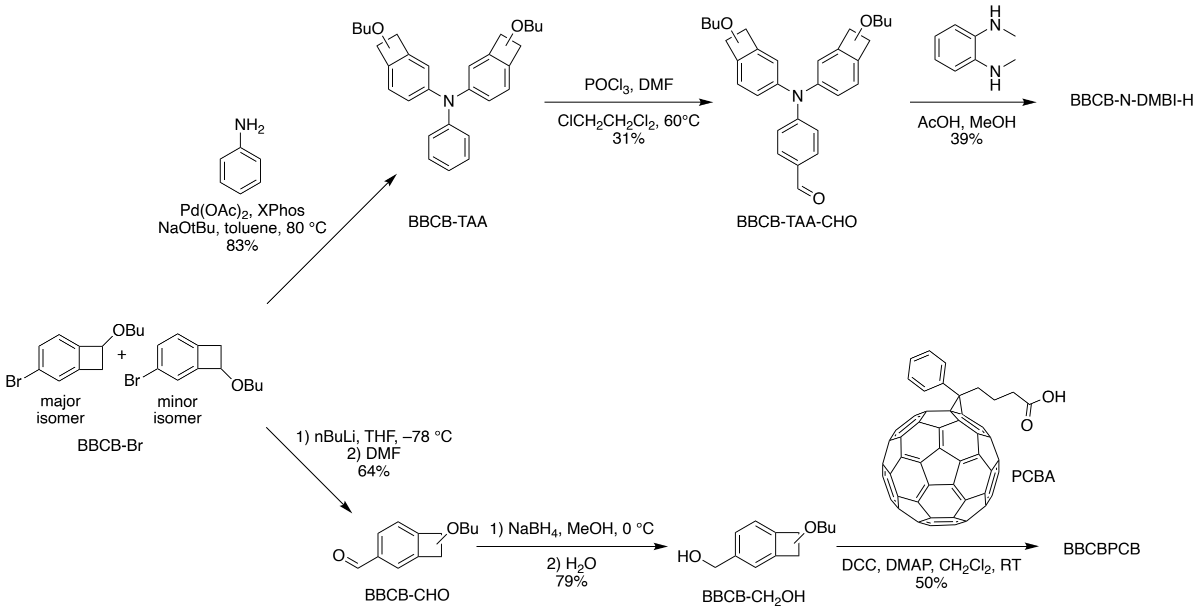
3.1. Design and Synthesis. The structures of the dopants and semiconductors used in this study are shown in Figure 1, along with those of some related molecules.

1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzoimidazole (DMBI-H) derivatives are air-stable n-dopants, which can be straightforwardly synthesized, and can successfully n-dope several classes of semiconducting host materials (A), to form $DMBI^+$ cations and AH^- with subsequent reactions leading to the formation of charge carriers, $A^{\bullet-}$.[21,22] In the present context, they are particularly effective n-dopants for fullerenes,[23,24] including a triarylamine-substituted derivative,[25] and their synthesis is easily modified to allow the incorporation of BCB moieties.

Electron-donating substituents on the four-membered ring of BCB are known to stabilize the reactive *ortho*-xylylene intermediates and thus lower the temperature required for ring-opening.[26,27] Indeed, the four-membered ring of PCBCB incorporates a mildly electron-donating RCO_2 substituent; however, alkoxy groups are more effective in this role and recently BuO substituents have been found to be particularly effective in facilitating low crosslinking temperatures for dielectric polymers.[19]

The synthesis of the new fullerene and dopant are shown in Scheme 1. Both syntheses begin with a mixture of 3- and 4-bromo-7-butoxybenzocyclobutene, BBCB-Br, which was obtained following the reported procedure.[19] For the synthesis of the dopant, a Buchwald-Hartwig amination reaction between aniline and 2.2 equivalent of BBCB-Br was used to synthesize the compound BBCB-TAA, also as a mixture of isomers.[28] BBCB-TAA was then formylated under Vilsmeier conditions to afford BBCB-TAA-CHO. The reaction of the aldehyde with *N*,*N'*-dimethyl-1,2-phenylenediamine in acidic conditions gave a moderate yield of BCB-N-DMBI-H, which was characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry (which, as is typical for DMBI-H derivatives, shows a peak assignable to the corresponding cation BCB-N-$DMBI^+$), and elemental analysis.

Scheme 1. Synthesis of 7-Butoxybenzocyclobutene-Functionalized Dopant and Fullerene



BBCBPCB - a PCBM-like fullerene with a BBCB substituent – was synthesized from the corresponding fullerene carboxylic acid, PBCA, and 3-/4-(hydroxymethyl)-7-butoxybenzocyclobutene, BBCB-CH_2OH, using *N*,*N*-dicyclohexylcarbodiimide (DCC)-assisted esterification conditions. PCBA was synthesized from commercially sourced PCBM as previously described,[17] while BBCB-CH_2OH was obtained by $NaBH_4$ reduction of the corresponding aldehyde, which itself was obtained from BBCB-Br by bromine-lithium exchange followed by quenching with DMF. BBCBPCB is readily soluble in common organic solvents, including benzene, toluene, and CH_2Cl_2, and was characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

3.2. Differential Scanning Calorimetry (DSC) and Optical Studies of Insolubilization. DSC of BBCBPCB was carried out in hermetically sealed Al pans heating from -50 °C to 300 °C at 10 °C per min; the first two heating scans and the first cooling scan are shown in Figure 2a. The first heating scan showed an exothermic feature with an onset of ca. 100 °C and peaking at ca. 150 °C, similar to that recently reported for a polymer containing 7-butoxycyclobutene side chains[17] This feature is not seen in subsequent scans and is, therefore, attributed to the dimerization of BBCB groups and/or their reaction with fullerene moieties following ring opening to the corresponding *ortho*-xylylenes. Significantly, the peak of the exotherm occurs at a considerably lower temperature than that of PCBCB (peak at ca. 210 °C)[17] or of BCBs with unsubstituted four-membered rings (>250 °C).[29]

The thermal insolubilization of BBCBPCB was assessed using absorption spectroscopy. Drop-cast films from the PCBBCB precursor were deposited on glass substrates and annealed at different temperatures for 10 min; these films were then washed and sonicated in solvent (CH_2Cl_2 or *o*-DCB) and UV-vis. spectra of the solutions were obtained (see Supporting Information, section 2.1). As the annealing temperature from 90 °C to 120 °C, the percentage conversion increased and at 120 °C negligible soluble PCBM-like material was obtained. For spin-coated (1000 rpm, 60 s) BBCBPCB films (with 30 nm thickness) a higher annealing temperature of 150 °C was found to be necessary. Films in which BBCB-N-DMBI-H (20 mol%) was co-deposited with BBCBPCB and the films subsequently annealed for 10 min at 150 °C also showed good solvent resistance to *o*-DCB (see Supporting Information, Section 2.2).

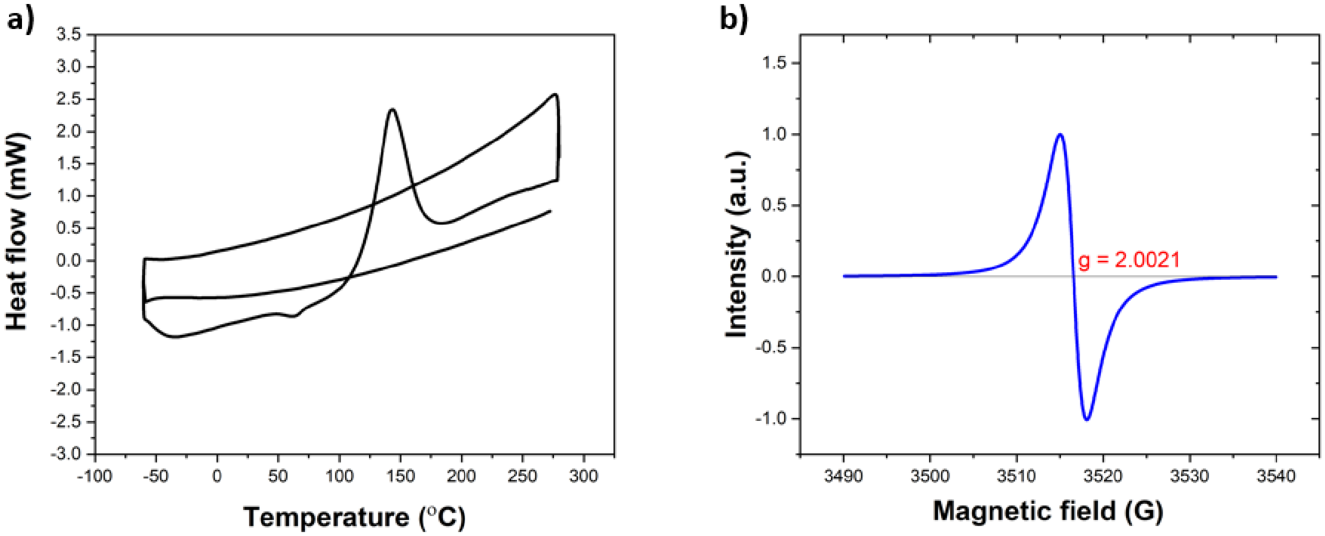


Figure 2. a) DSC thermogram of BBCBPCB (exothermic up; 10 °C min^{-1}) indicating an exothermic reaction, attributed to the reaction of the ring-opened BBCB units, on the first heating. b) First-derivative EPR Spectrum of a heated sample of (BBCB-N-DMBI-H)-doped BBCBPCB indicating a high *g*-value compared to PCBM$^{\bullet-}$, suggesting the relevant radical anions are primarily located on fullerene cores that have been further desymmetrized by reaction with BBCB moieties.

2.3. Electron Paramagnetic Resonance (EPR) and MALDI Investigations of BBCB-N-DMBI-H / BBCBPCB Reaction Products. The formation of fullerene radical anions is not unambigously demonstrated by the optical spectra of annealed doped films (see above and Supporting Information, section 2.2), which are rather broad, perhaps reflecting multiple environments for the fullerenes and their anions. Thus an EPR experiment was performed on BBCB-N-DMBI-H doped BBCBPCB (Figure 2b). To do so, a solution of BBCB-N-DMBI-H (20 mol%) and BBCBPCB was prepared in *o*-DCB, in 3 mm quartz EPR tubes and heated at 120 °C for 90 min. The solvent was evaporated under a high vacuum overnight to obtain a thin film deposited on the wall of EPR tube. Undoped BBCBPCB films and solutions exhibited no appreciable radical signal by EPR spectroscopy, whereas, as shown in Figure 2b, the sample obtained by co-deposition of BBCBPCB with BBCB-N-DMBI-H exhibited a strong signal. The signal is seen at $g = 2.0021$, higher than that reported for PCBM$^{\bullet-}$.[22] Previous studies have shown that larger *g*-values are often found when fullerene cores are multiply substituted in a low-symmetry fashion.[30] Accordingly, the high g-value in the present case suggests that the majority of the unpaired electrons are associated with radical monoanions of fullerenes that have reacted with one or more BBCB-derived *ortho*-xylylene crosslinking moieties.

BBCB-N-DMBI-H doped BBCBPCB was subjected to MALDI mass spectrometry (see Supporting Information section 2.4 for further details): signals are seen consistent with the formation of ions with the composition $[(\text{BBCB-N-DMBI})(\text{BBCBPCB})_n\text{H}]^+$ where n = 1, 2, i.e., suggesting the formation of the desired covalent dopant:host covalent bonds (either through reaction of dopant BBCB groups with fullerene BBCB groups and/or fullerene cores).

3.4. Electrical Conductivity. The in-plane bulk conductivities of BBCB-N-DMBI-H-doped BBCBPCB films spin-coated on glass substrates were measured with a four-point probe as a function of dopant concentration to quantify the impact of thermal insolubilization on the electrical properties of the doped films (Figure 3). Undoped BBCBPCB films yield an in-plane conductivity of 3.2×10^{-9} S cm^{-1}, one order-of-magnitude lower than that reported for PCBM films, but consistent with what is expected for a nominally undoped film. When the BBCB-N-DMBI-H is incorporated into the casting solution (10 mol%), the conductivity of BBCBPCB increases by up to four orders of magnitude to a value of $1.1 \times 10^{-5} \pm 3.4 \times 10^{-7}$ S cm^{-1}, and thermal annealing of the doped film at 70 °C for 1 h resulted in a slight increase of the conductivity to $5.5 \times 10^{-5} \pm 5.1 \times 10^{-6}$ S cm^{-1}. Although the increase in conductivity is clearly consistent with n-doping, the conductivity is much lower than the value of 1.9×10^{-3} S cm^{-1} previously reported for PCBM doped with N-DMBI-H at a similar concentration.[23] Higher dopant concentrations of 20 and 30 mol% led to successive decreases in the conductivity values.

To assess the impact of the thermal insolubilization on the in-plane electrical conductivity, the doped films were annealed at 150 °C for 10 min, which in all cases resulted in decreases in the conductivity; the highest values for insolubilized BBCB-N-

DMBI-H-doped BBCB seen at 10 mol% dopant was only $1.2 \times 10^{-7} \pm 3.8 \times 10^{-9}$ S cm^{-1}, two orders-of-magnitude lower than that of the unheated film. These values of conductivity are much lower than those obtained for insolubilized $(IrCp^*Cp)_2$-doped PCBCB films.[18]

One possibility is that the charge carriers are quenched by the reactive *ortho*-xylyene intermediates, resulting in lower effective doping levels in the latter case. However, similar conductivities are obtained using N-DMBI-H in place of BBCB-N-DMBI-H for a given loading, and the similar drops in conductivity on thermal annealing are found with both dopants, despite the lower density of BBCB moieties in the former (Figure 3). Furthermore, we observed a similar EPR intensity for a sample of $(N\text{-}DMBI)_2$-doped PCBM (where $(N\text{-}DMBI)_2$,[31] the structure of which is shown in Figure S16,[24] is a dimeric analogue of N-DMBI-H that readily dopes fullerenes to form the sample N-DMBI$^+$ cation) and a sample of thermally treated $(N\text{-}DMBI)_2$-doped BBCBPCB, suggesting no quenching of carriers in the thermal treatment of the latter sample (see Supporting Information, section 2.3).

Another possible explanation for the lower conductivity might be the BBCB reaction with fullerene cores might lead to increased energetic disorder in the fullerene sites and/or increased isolation of these sites from neighboring fullerenes. However, this is at odds with previous findings that the crosslinker CL does not adversely affect the conductivity of insolubilized $(IrCp^*Cp)_2$-doped PCBCB films,[18] and with the above-mentioned similarity in post-annealing conductivities obtained using N-DMBI-H in place of BBCB-N-DMBI-H (Figure 3), despite the potential for more BBCB/fullerene reactions in the latter case.

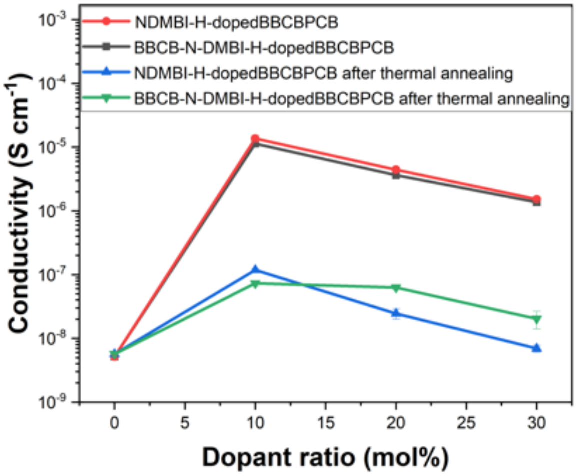


Figure 3. Electrical conductivity of BBCB-N-DMBI-H (or NDMBI-H) doped BBCBPCB before and after heating to 150 °C. Thermal annealing results in much lower conductivity values, perhaps attributable to morphology changes associated with the associated chemical reactions.

3.5. Dopant Diffusion. The immobilization of the dopant ion BBCB-N-DMBI$^+$ and/or the corresponding neutral dopant in thermally insolubilized BBCBPCB was investigated using UV-vis-NIR measurements of doped films with an overlayer of a small-molecule semiconductor 2CN-NDI (Figure 1). 2CN-NDI[20] was chosen as a potential host into which dopant ion and charge carrier migration might be possible because: firstly, it is a stronger electron acceptor than typical fullerenes, having a reduction potential of -0.54 eV vs. $FeCp_2$,[21] leading to a driving force for charge carrier and balancing dopant ion diffusion into this material; secondly, it is readily n-doped by N-DMBI-H and presumably other DMBI-H dopants meaning any neutral dopant diffusion into this material will lead to its doping;[21] and, finally, it can be evaporated allowing the fabrication of these bilayers for both unheated and insolubilized BBCB-N-DMBI-H-doped BBCBPCB.

A solution containing 60 mg of PPCBPCB and BBCB-N-DMBI-H (40 mol%) was prepared and stirred in the glove box overnight. The UV-vis-NIR of the solution was obtained to confirm that the doping reaction occurred (appearance of the signal for the fullerene radical anion around 1000 nm). Films were spin-coated (1000 rpm, 60 s). One of the films was insolubilized by heating at 150 °C for 10 min. 2CN-NDI was evaporated (at 200 °C) and deposited on the top of doped films to reach a total thickness of bilayer films to 300 nm. The films were sealed and the UV-vis-NIR spectra of the films were obtained (Supporting Information section 2.5).

The spectrum of the bilayer based on the unheated BBCB-N-DMBI-H-doped PPCBPCB shows several absorbance maxima throughout the visible that are characteristic of 2CN-NDI$^{\bullet-}$.[21] However, when the BBCB-N-DMBI-H-doped PPCBPCB films were thermally insolubilized these maxima were not seen, either initially or after heating at 70 °C for 1 h, indicating that the thermal annealing leads to dopant immobilization, as expected given the reactivity of the dopant BBCB moieties. The diffusion of fullerene radical anions into the 2CN-NDI film and of 2CN-NDI into the doped film would also result in formation of 2CN-NDI$^{\bullet-}$ given the more anodic redox potential of 2CN-NDI, so is evidently also minimized by the thermal treatment; on the other hand, we cannot rule out diffusion of neutral fullerene into the overlayer. Other analytical techniques, such as photoluminescence spectroscopy, near-edge X-ray absorption fine structure spectroscopy, and dynamic secondary ion mass spectrometry have been used to probe in- and through-plane diffusion of dopants and/or fullerenes in other cases.[9,32,33]

4. CONCLUSION

In conclusion, dopant and fullerene functionalization with 7-butoxybenzocyclobutene groups was investigated as an approach for the formation of thermally-annealed insoluble n-doped organic semiconductor films. The use of the butoxy substituent leads to thermal insolubilization in the range of 120–150 °C. The doping products of the DMBI-H derivative and BBCBPCB were characterized using MALDI-TOF-MS and EPR. Mass spectrometry confirmed the formation of covalently linked dopant and fullerene and EPR showed the signal for the formation of a fullerene radical anion. Furthermore, we demonstrate that dopant migration into an adjacent layer can be suppressed by the thermal treatment. Although unheated films of BBCPCB n-doped with BBCB-N-DMBI-H exhibit in-plane electrical conductivity of $1.1 \times 10^{-5} \pm 3.4 \times 10^{-7}$ S cm^{-1}, thermal insolubilization results in much lower values, perhaps attributable to morphology changes associated with the chemical reactions that result in insolubilization. Although the low electrical conductivity values obtained in this study will limit its utility, the general approach can potentially be developed further to yield better-performing materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra for all new compounds, optical spectra of films under various conditions, EPR spectra for N-DMBI)$_2$-doped PCBM and BBCBPCB, MALDI spectrum showing the reaction of BBCB-N-DMBI-H and BBCBPCB (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (through DMR-807797/2216857 and through the DMREF program, DMR-1729737), and the US Air Force of Scientific Research (FA9550-18-1-0499). The authors thank Dr. Raghunath R. Dasari for supplying 2CN-NDI, Dr. Robert Braga for collecting EPR data, and Prof. Juan-Pablo Correa-Baena and Andres Felipe Castro Mendez for evaporation of 2CN-NDI.

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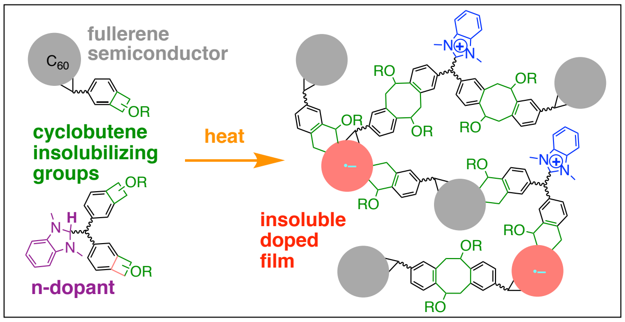

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