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Supporting Information

Thermally Removable Sidechain Stabilized Benzodipyrrole as Electron-Rich Building Block Used in Donor-Acceptor Conjugated Polymers

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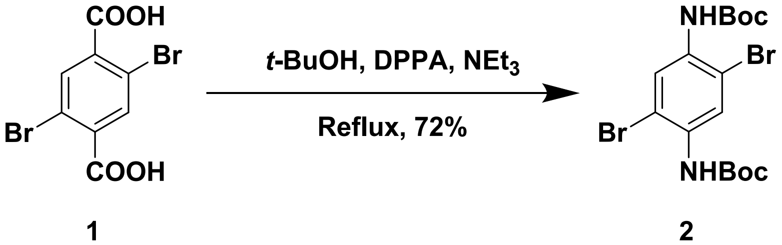
1. General Procedures and Synthesis

Chemical reagents and CYTOP were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled from sodium prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). ^1H NMR chemical shifts were referenced to TMS (0 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.0 ppm). Mass spectra were recorded on a Bruker BIFLEX III mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a TA Instrument Q2000 analyzer. Gel permeation chromatography (GPC) was performed on Polymer Laboratories PL-GPC220 at 150 °C using 1,2,4-tricholorobenzene (TCB) as eluent. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis spectrometer. Cyclic voltammetry (CV) was performed on BASI Epsilon workstation. Thin film measurements were carried out in acetonitrile containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum wire as a counter electrode, and all potentials were recorded versus Ag/AgCl (saturated KCl solution) as a reference electrode (scan rate: 50 mV s^{-1}). Grazing incidence wide-angle X-ray scattering (GIWAXS) were performed in vacuum on a Ganesha SAXSLAB instrument using the Cu Kα irradiation (wavelength of 1.54 Å).

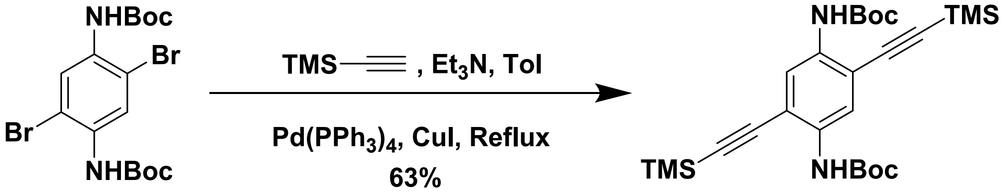
Synthesis and characterization.

Compound **1** is commercially available.



1 2

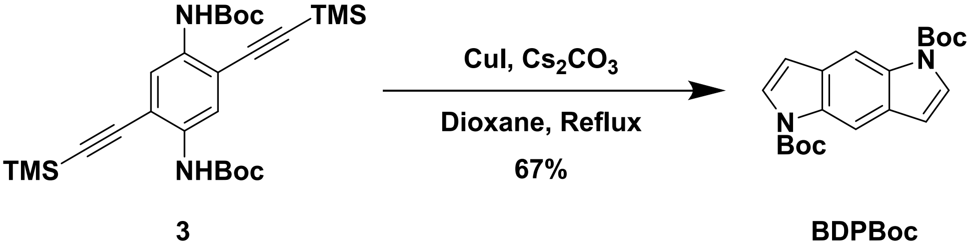
di-*tert*-butyl(2,5-dibromo-1,4-phenylene)dicarbamate (**2**): To a solution of 2,5-dibromoterephthalic acid (**1**, 11.247 g, 34.72 mmol) in *t*-BuOH (250 mL), Diphenylphosphoryl azide (28.666 g, 104.16 mmol) and triethylamine (25 mL) was added slowly. The reaction mixture was refluxed at 100 °C under a nitrogen atmosphere for 8 h. The resulting white precipitates were collected by filtration, then washed with methanol three times. The product was dried under vacuum to afford **2** as white powders (11.669 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.38 (s, 2H), 6.88 (s, 2H), 1.53 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 152.3, 131.9, 122.7, 111.6, 81.4, 28.3. HRMS (MALDI) m/z: $[M + H]^+$ calculated for $C_{16}H_{23}Br_2N_2O_4$, 465.0019; found, 465.0024.



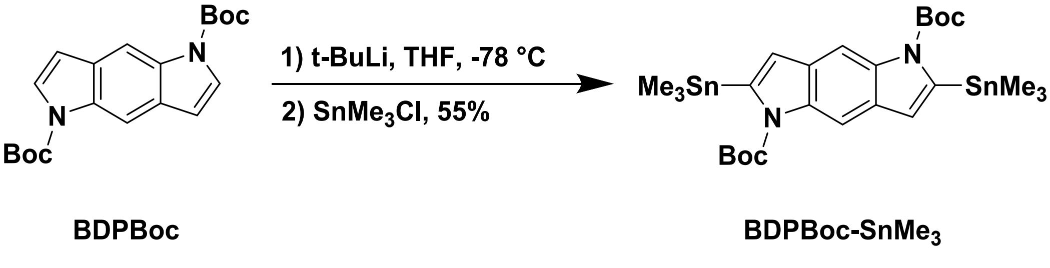
2 3

Compound 3: A solution of **2** (4.670 g, 10.02 mmol), $Pd(PPh_3)_4$ (1.165 g, 1.008 mmol) and CuI (157 mg, 0.801 mmol) in toluene (250 mL) was stirred under a nitrogen atmosphere. Trimethylsilylacetylene (5.588 g, 54.78 mmol) and triethylamine (25 mL) were slowly added to the system, and the mixture was refluxed at 120 °C for 18 h. After reaction, the mixture was cooled to room temperature, then the solvents were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (200 mL) and washed three times with water, then dried over with anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent ($PE:CH_2Cl_2$ = 2:1) to give **3** as yellow powders (3.169 g, 63 %).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.18 (s, 2H), 7.22 (s, 2H), 1.51

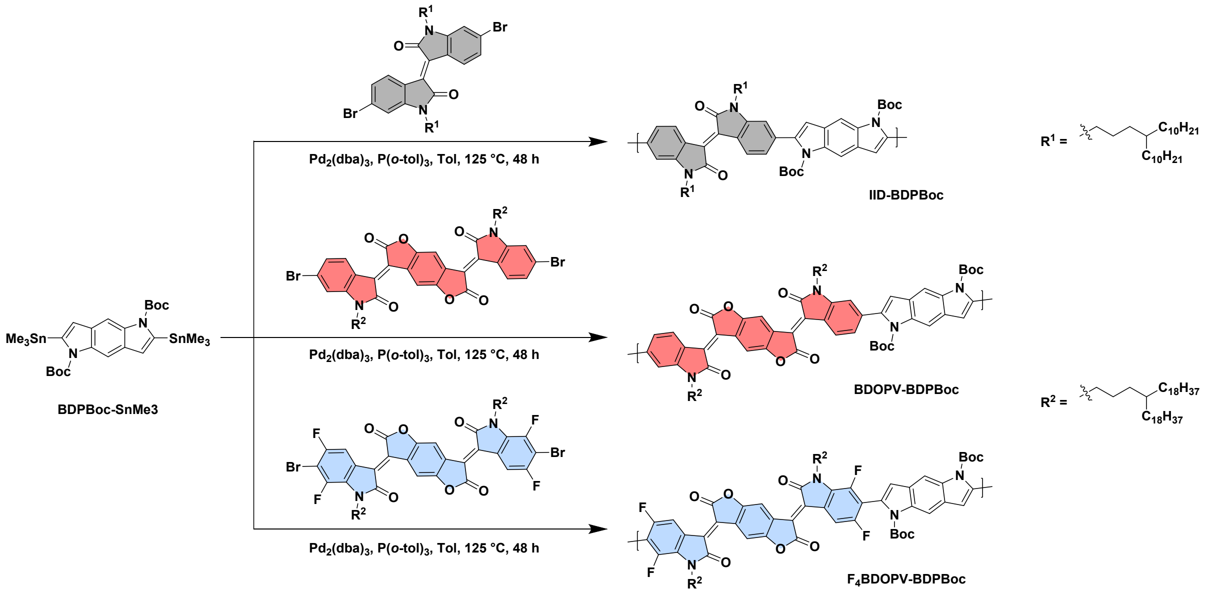
(s, 18H), 0.26 (s, 18H). ^{13}C NMR (101 MHz, CDCl$_3$, ppm): δ 152.6, 134.4, 120.0, 112.6, 103.8, 100.3, 80.9, 28.5. HRMS (MALDI) m/z: $[M + H]^+$ calculated for $C_{26}H_{41}N_2O_4Si_2$, 501.2599; found, 501.2607.



BDPBoc: A solution of **3** (1.460 g, 2.916 mmol), Cs_2CO_3 (2.805 g, 8.631 mmol) and CuI (177 mg, 0.903 mmol) in dioxane (100 mL) was refluxed at 120 °C under a nitrogen atmosphere. After reaction, the mixture was cooled to room temperature, acetic acid (3 mL) was added to the mixture, then the solvents were removed under reduced pressure. The residue was dissolved in CHCl$_3$ (100 mL) and washed three times with water, then dried over with anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified by silica gel chromatography with eluent (PE:CH_2Cl_2 = 2:1) to give **4** as pale-yellow powders (695 mg, 67 %).^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.32 (s, 2H), 7.60 (d, 2H), 6.64 (d, 2H), 1.69 (s, 18H). ^{13}C NMR (101 MHz, CDCl$_3$, ppm): δ 150.0, 132.3, 128.9, 126.3, 107.9, 106.5, 83.3, 28.3. HRMS (MALDI) m/z: $[M + H]^+$ calculated for $C_{20}H_{25}N_2O_4$, 357.1809; found, 357.1804.



BDPBoc-SnMe$_3$: A solution of **BDPBoc** (424.6 mg, 1.206 mmol) in THF (20 mL) was stirred at −78 °C under a nitrogen atmosphere. *t*-BuLi (2.4 mL, 1.3 M solution in *n*-pentane) was slowly added to the mixture in 15 min, then the mixture is stirred at −78 °C for 3 h. A solution of SnMe$_3$Cl (961.3 mg, 4.824 mmol) in THF (20 mL) was then added to the mixture, followed by stirring the mixture for another 6 h. After reaction, saturated NH$_4$Cl solution (10 mL) was added, then the mixture is slowly returned to room temperature, then the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed three times with water, then dried over with anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified by gel permeation chromatography with chloroform as eluent, then recrystallized to give **5** as colorless crystals (444.7 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.99 (s, 2H), 6.78 (t, 2H), 1.73 (s, 18H), 0.32 (t, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 152.4, 143.8, 134.3, 130.2, 118.9, 105.4, 83.8, 28.3, -7.1. HRMS (MALDI) m/z: $[M + H]^+$ calculated for $C_{26}H_{41}N_2O_4Sn_2$, 685.1105; found, 685.1140.



Polymerization reagent **IID-2Br**, **BDOPV-2Br** and **F_4BDOPV-2Br** were synthesized according to literature report[1-3].

IID-BDPBoc: IID-2Br (103.6 mg, 0.0947 mmol), **BDPBoc-SnMe$_3$** (64.6 mg, 0.0947 mmol), $Pd_2(dba)_3$ (4.40 mg, 5 mol%), P(*o*-Tol)$_3$ (5.97 mg, 21 mol%), and 10 mL of toluene were added to a Schlenk tube. The tube was charged with nitrogen through a *freeze-pump-thaw* cycle 3 times. The mixture was stirred for 48 h at 120 °C. *N*,*N'*-Diethylphenylazothioformamide (5 mg) was added and then the mixture was stirred for 0.5 h to remove any residual catalyst before being precipitated by addition of methanol. The precipitate was filtered through a PTFE filter and purified via Soxhlet extraction for 2 h with acetone, 18 h with hexane and finally collected with chloroform. The chloroform solution was concentrated by evaporation, precipitated with methanol and filtered off to afford dark solids (73.0 mg, 59%). M_n = 12.9 kDa, PDI = 1.61.

BDOPV-BDPBoc: BDOPV-2Br (89.9 mg, 0.0520 mmol), **BDPBoc-SnMe$_3$** (35.5 mg, 0.0520 mmol), $Pd_2(dba)_3$ (2.52 mg, 5 mol%), P(*o*-Tol)$_3$ (3.29 mg, 20 mol%), and 10 mL of toluene were added to a Schlenk tube. The tube was charged with nitrogen through a *freeze-pump-thaw* cycle 3 times. The mixture was stirred for 48 h at 120 °C. *N*,*N'*-Diethylphenylazothioformamide (5 mg) was added and then the mixture was stirred for 0.5 h to remove any residual catalyst before being precipitated by addition of methanol. The precipitate was filtered through a PTFE filter and purified via Soxhlet extraction for 2 h with acetone, 18 h with hexane and finally collected with chloroform. The chloroform solution was concentrated by evaporation, precipitated with methanol and filtered off to afford dark solids (74.3 mg, 74%). M_n = 44.2 kDa, PDI = 2.76.

F$_4$BDOPV-BDPBoc: F$_4$BDOPV-2Br (95.8 mg, 0.0552 mmol), **BDPBoc-SnMe$_3$** (36.3 mg, 0.0552 mmol), $Pd_2(dba)_3$ (2.58 mg, 5 mol%), P(*o*-Tol)$_3$ (3.48 mg, 20 mol%), and 10 mL of toluene were added to a Schlenk tube. The tube was charged with nitrogen through a *freeze-pump-thaw* cycle 3 times. The mixture was stirred for 48 h at 120 °C. *N*,*N'*-Diethylphenylazothioformamide (5 mg) was added and then the mixture was stirred for 0.5 h to remove any residual catalyst before being precipitated by addition of methanol. The precipitate was filtered through a PTFE filter and purified via Soxhlet extraction for 2 h with acetone, 18 h with hexane and finally collected with chloroform. The chloroform solution was concentrated by evaporation, precipitated with methanol and filtered off to afford dark solids (91.6 mg, 86%). M_n = 52.3 kDa, PDI = 2.87.

2. Electrochemical and Photophysical Properties

For UV-*vis* absorption measurements, all solution absorption spectra were tested using polymer solutions of 10^{-5} M concentration in 1-chloronaphthalene (1-CN). BDPBoc-based polymer thin films used for thin-film absorption spectra were prepared by spin-coating using a polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene) at 1000 rpm for 120 s on a glass substrate. BDP-based polymer films were prepared by heating corresponding spin-coated BDPBoc-based polymer films at 240 °C for 1 h.

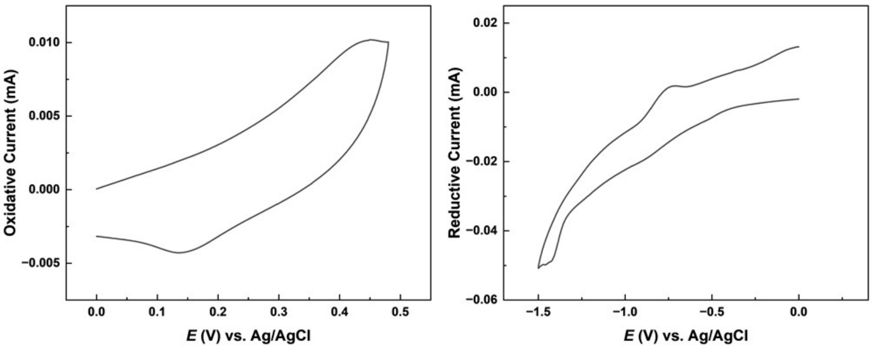


Figure S1. Cyclic voltammograms of IID-BDP.

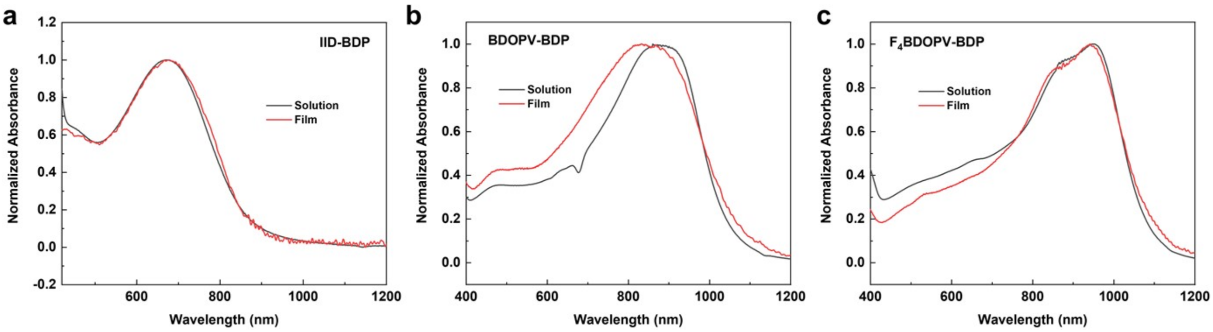


Figure S2. Comparison of UV-vis absorption spectra of 1-CN solution and thin films of BDP-based polymers.

3. Computational Studies

All calculations were performed using the Gaussian 16 software package[4]. The geometries of the polymer fragments were optimized at the B3LYP/6-311G(d,p) level and their energies were calculated at the same level. Galbraith *et al.* have proven that the length of alkyl chains in the molecule hardly affects the calculation results, especially dihedral angle potentials[5]. Therefore, alkyl chains were replaced by methyl groups in all calculations performed for simplicity.

4. Photoelectron Spectroscopy Measurements

Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out by Kratos AXIS Ultra-DLD photoelectron spectrometer under an ultrahigh vacuum of about 3×10^{-9} torr with an unfiltered He I gas discharge lamp source (21.2 eV) as excitation source. The instrumental energy resolutions for UPS spectra were 0.1 eV.

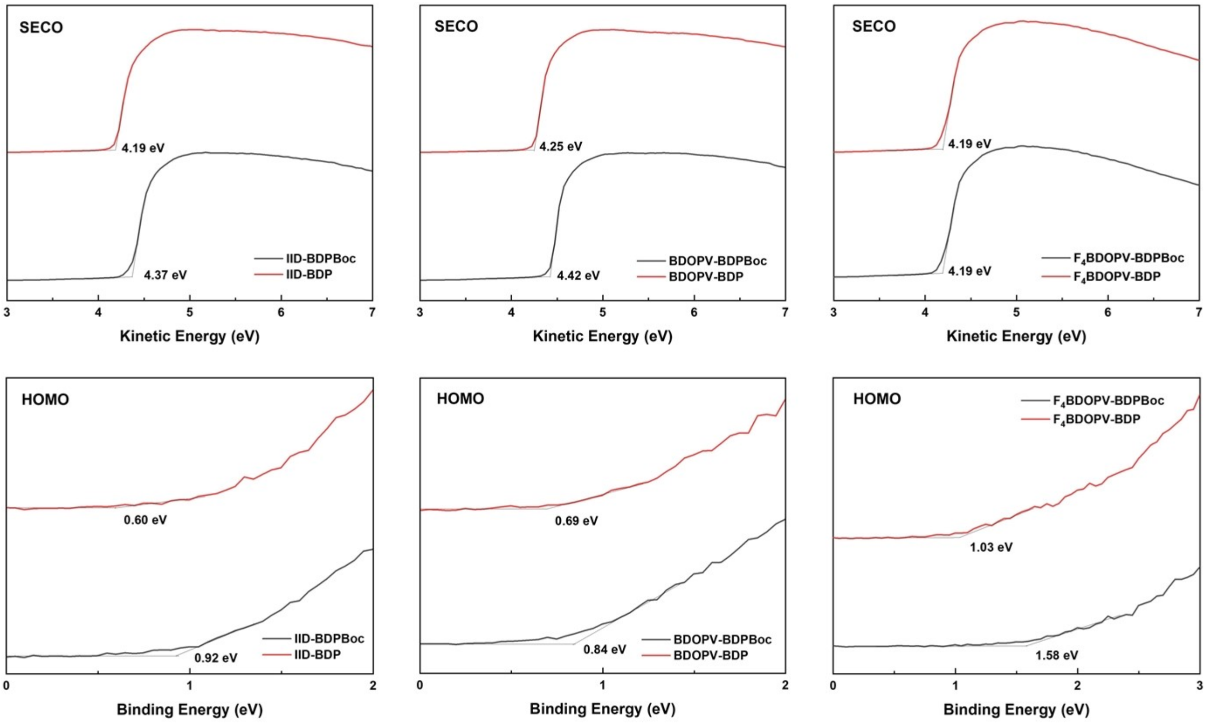


Figure S3. UPS data of IID-BDPBoc, BDOPV-BDPBoc and F_4BDOPV-BDPBoc (black) and corresponding deprotected polymers (red).

5. Microstructure Characterizations by GIWAXS

All thin films used for the GIWAXS test were prepared by drop-casting using a polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene) on a silicon substrate. BDP-based polymer films are prepared by heating the corresponding BDPBoc-based polymer film at 240 °C for 1 h.

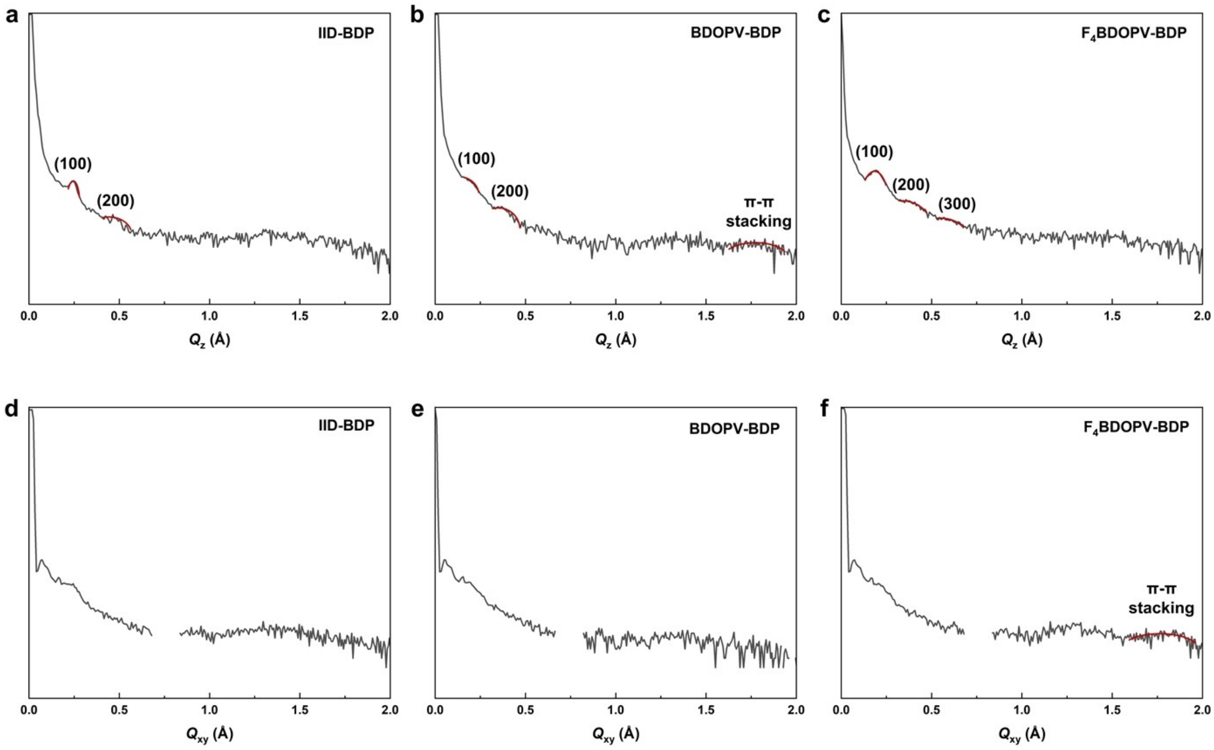


Figure S4. 1D-GIWAXS data of IID-BDP, BDOPV-BDP and F$_4$BDOPV-BDP thin films on **a-c.** Q_z direction and **d-f.** Q_{xy} direction. Red lines in the graphs show the peak fitting results.

6. Device Fabrication and Characterization

Top-gate/bottom-contact FET devices and complementary inverters were fabricated using glass substrates. The gold source and drain bottom electrodes were patterned by photolithography on the glass surface. The substrates were subjected to cleaning using plasma for 10 min before use. The substrates were transferred into a glovebox. A thin film of the polymer was deposited on the treated substrates by spin-coating using a polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene) at 2000 rpm for 60 s and annealed at 240 °C for 1 h to remove the Boc protection group. After polymer thin film deposition, a CYTOP solution (CTL809M: CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 60 s. The CYTOP layer was then baked at 120 °C for 1 h. Gate electrodes comprising a layer of Al (45 nm) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation. The OFET channel length (L) was 5, 10, 20, 50, or 100 μm while the ratio of channel width and length was kept as 20.

The evaluations of the FETs were carried out in air on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility, μ, was calculated from the data in the saturated regime according to the equation $I_{\mathrm{SD}} = \mu\ (W / 2L)\ C_{\mathrm{i}}\ (V_{\mathrm{G}} - V_{\mathrm{T}})^2$, where I_{SD} is the drain current in the saturated regime. W and L are the semiconductor channel width and length, respectively. C_{i} ($C_{\mathrm{i}} = 3.7$ nF cm^{-2}) is the capacitance per unit area of the gate dielectric layer. V_{G} and V_{T} are the gate voltage and threshold voltage, respectively. $V_{\mathrm{G}} - V_{\mathrm{T}}$ of the device was determined from the relationship between the square root of I_{SD} and V_{G} at the saturated regime.

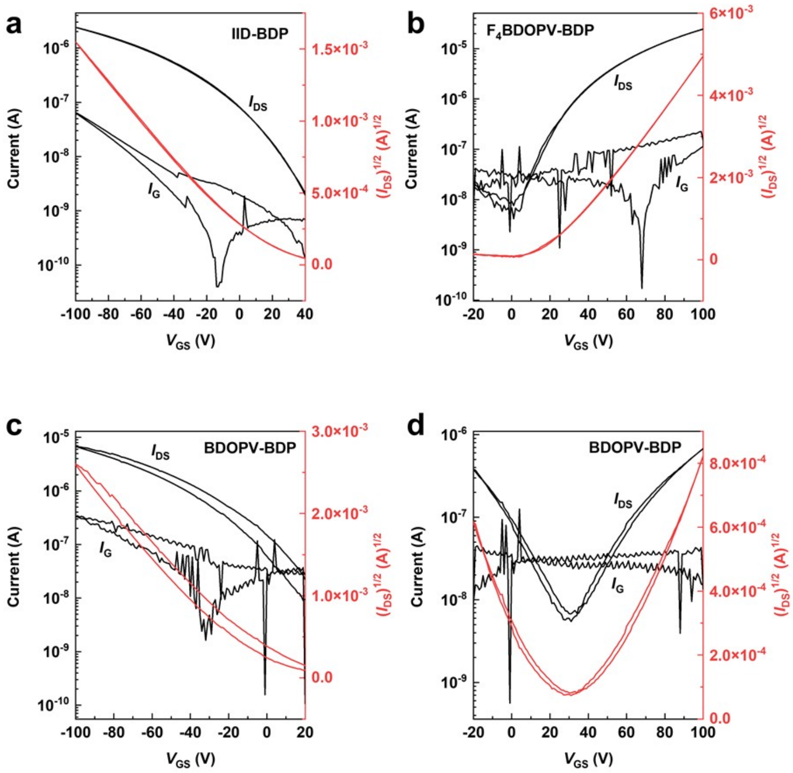


Figure S5. Transfer characteristic curve for IID-BDP (**a**), F_4BDOPV-BDP (**b**) and BDOPV-BDP (**c**, p-type; **d**, n-type) FET devices.

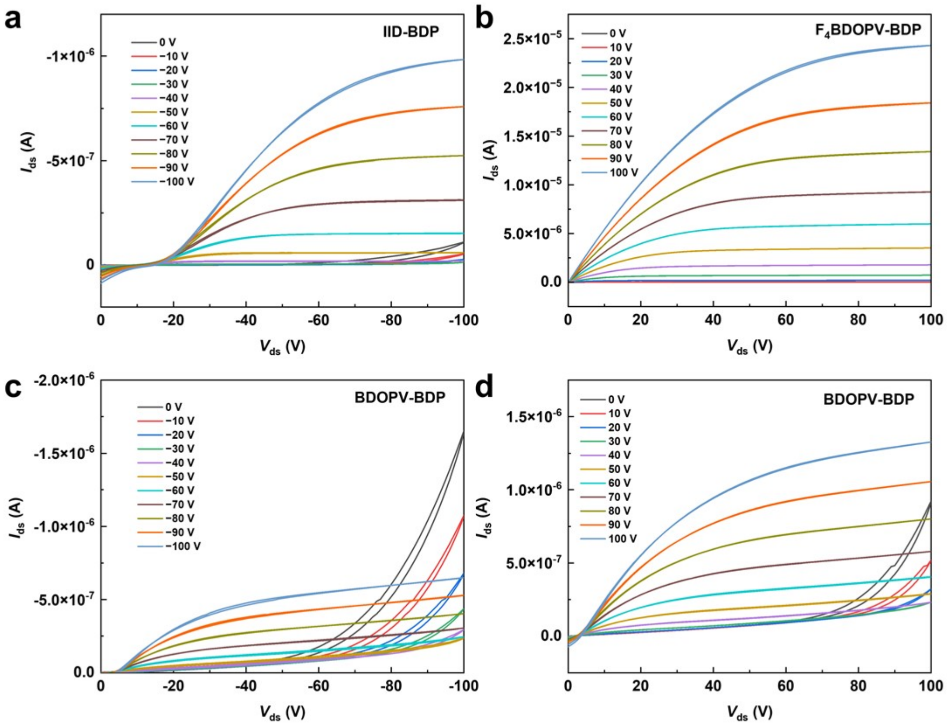


Figure S6. Output characteristic curve for IID-BDP (**a**), F_4BDOPV-BDP (**b**) and BDOPV-BDP (**c**, p-type; **d**, n-type) FET devices.

7. Scanning Electron Microscopy

SEM experiments were performed on a Hitachi S-4800 instrument. BDPBoc-based thin film samples were deposited on silicon substrates by spin-coating using a polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene) at 1500 rpm for 60 s. Corresponding BDP-based polymer film samples were prepared by annealing of BDPBoc-based polymer films at 240 °C for 1 h to remove the Boc protection group.

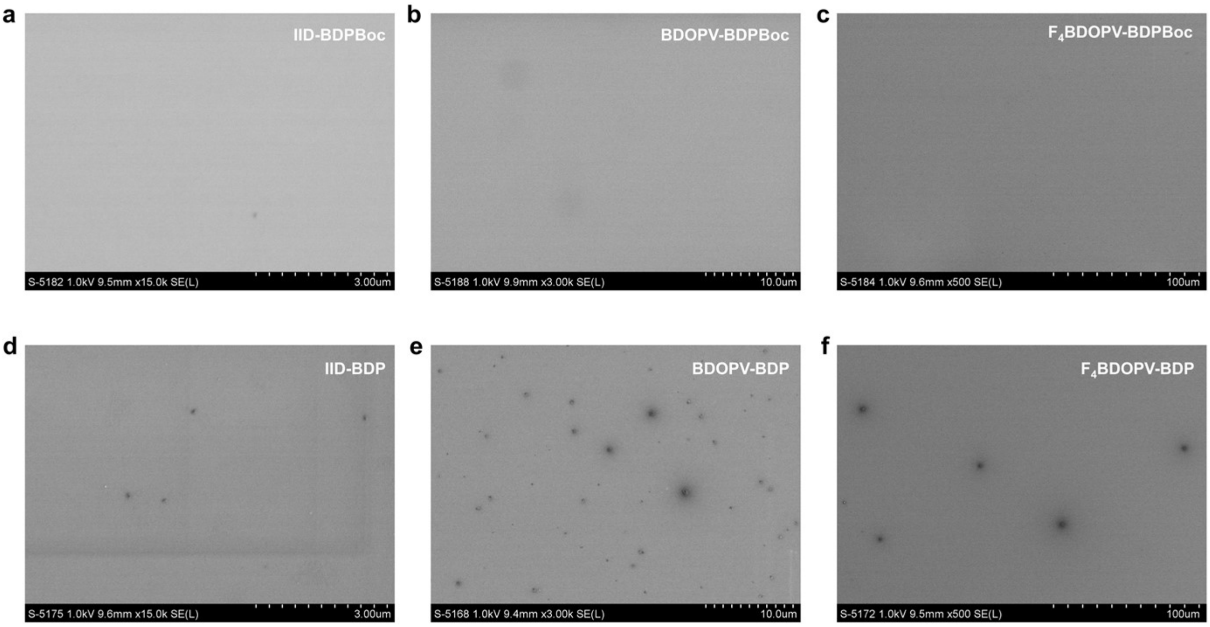


Figure S7. SEM images of BDP-based polymers before deprotection (**a-c**) and after deprotection (**d-f**). Black dents in **d-f** indicate pores in polymer films.

8. Atomic Force Microscopy

AFM experiments were performed on a Bruker Dimension Icon instrument. BDPBoc-based thin film samples were deposited on silicon substrates by spin-coating using a polymer solution (3 mg mL^{-1} in 1,2-dichlorobenzene) at 1500 rpm for 60 s. Corresponding BDP-based polymer film samples were prepared by annealing of BDPBoc-based polymer films at 240 °C for 1 h to remove the Boc protection group.

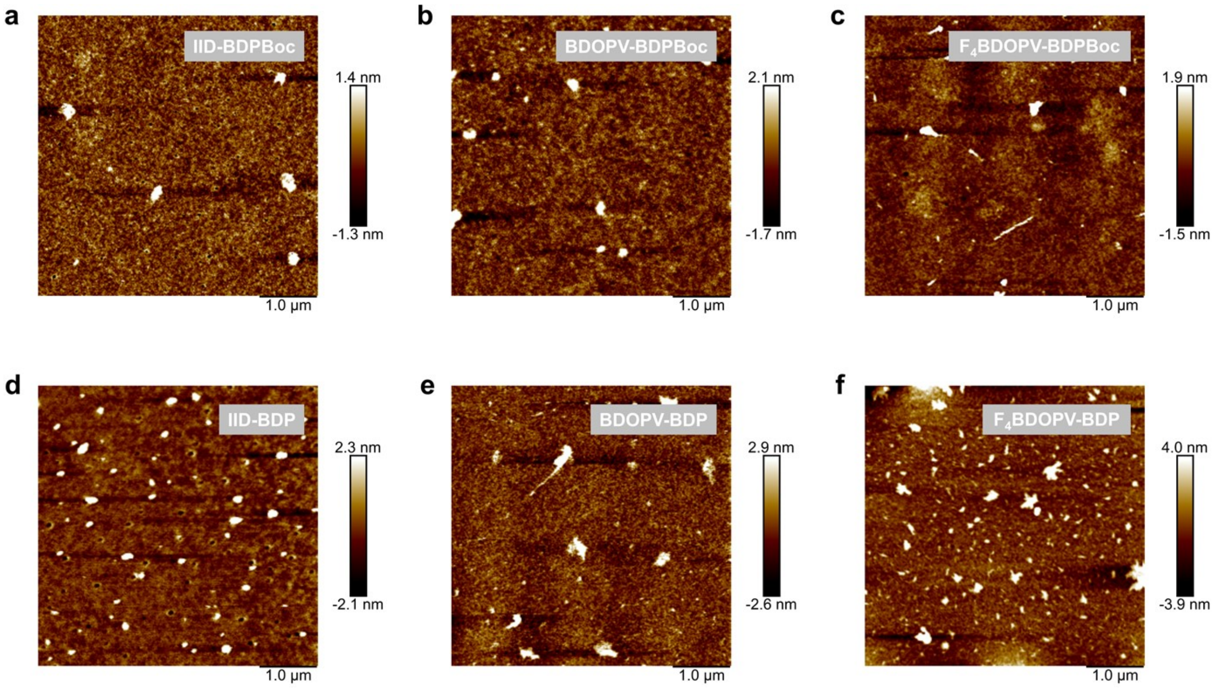
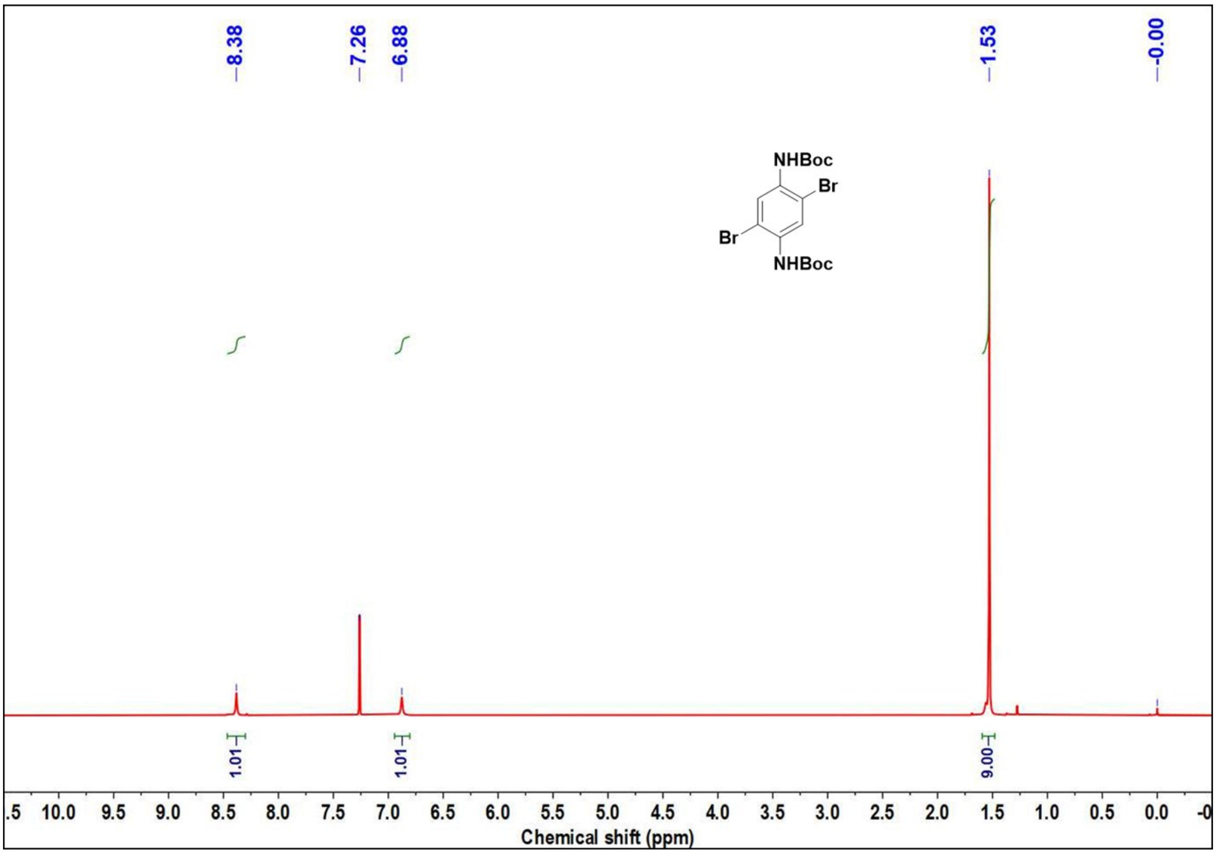
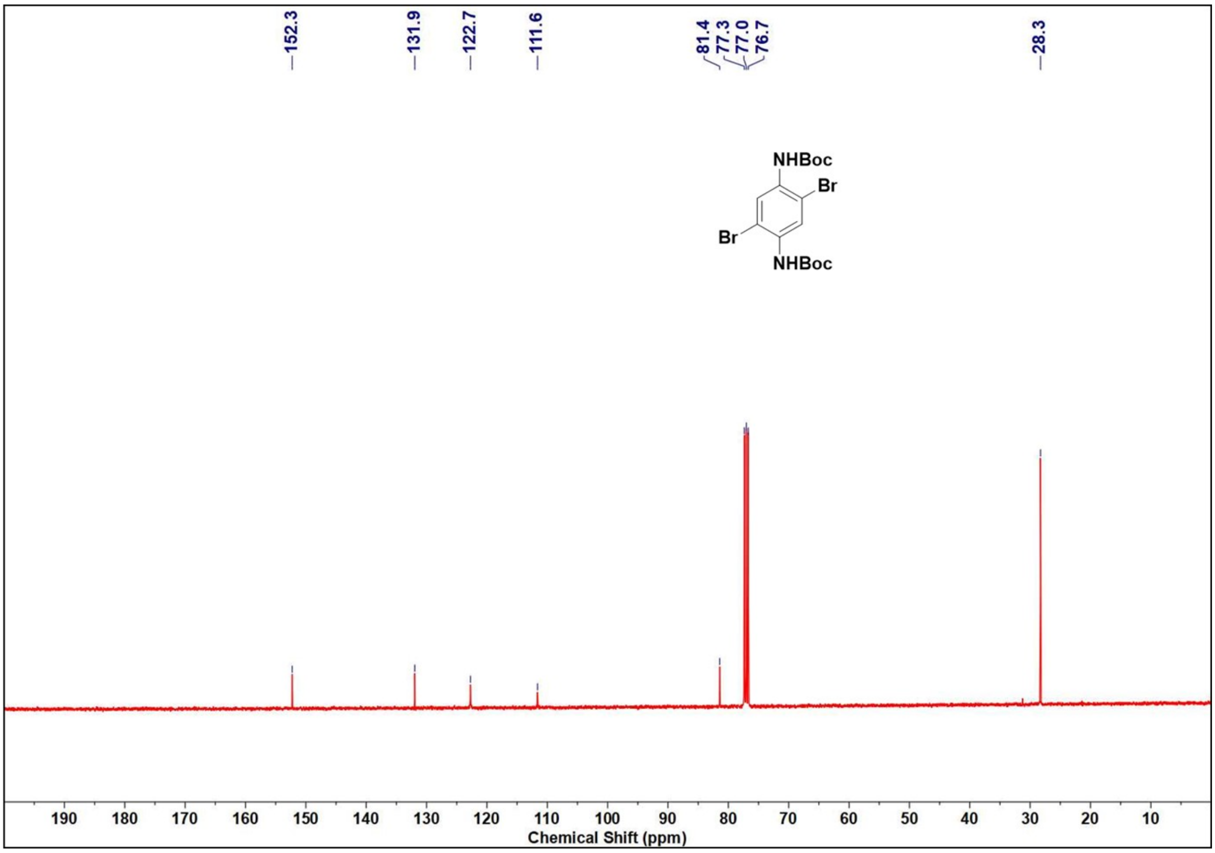
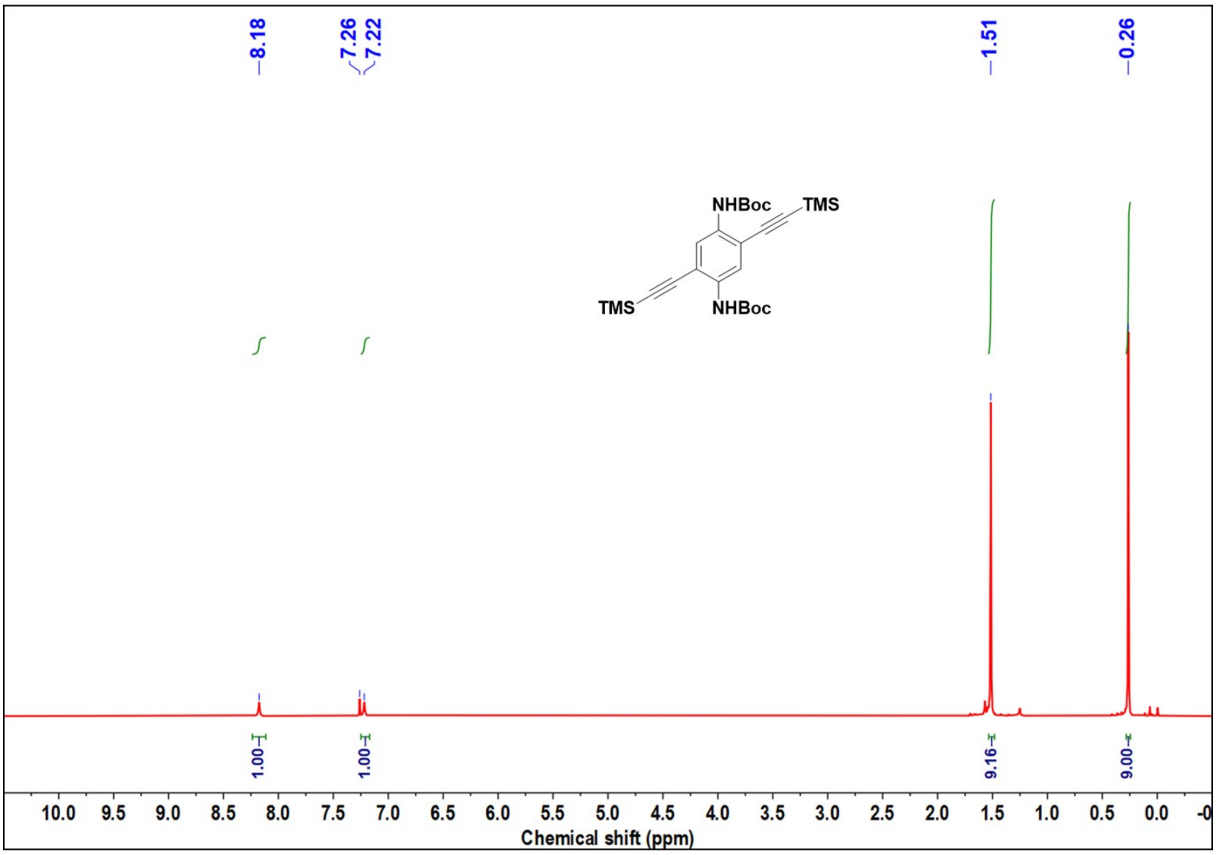


Figure S8. AFM images of BDP-based polymers before deprotection (**a-c**) and after deprotection (**d-f**).

9. NMR Spectra



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7.26
7.22
1.51
0.26
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TMS
TMS
NHBoc
1.00
1.00
9.16
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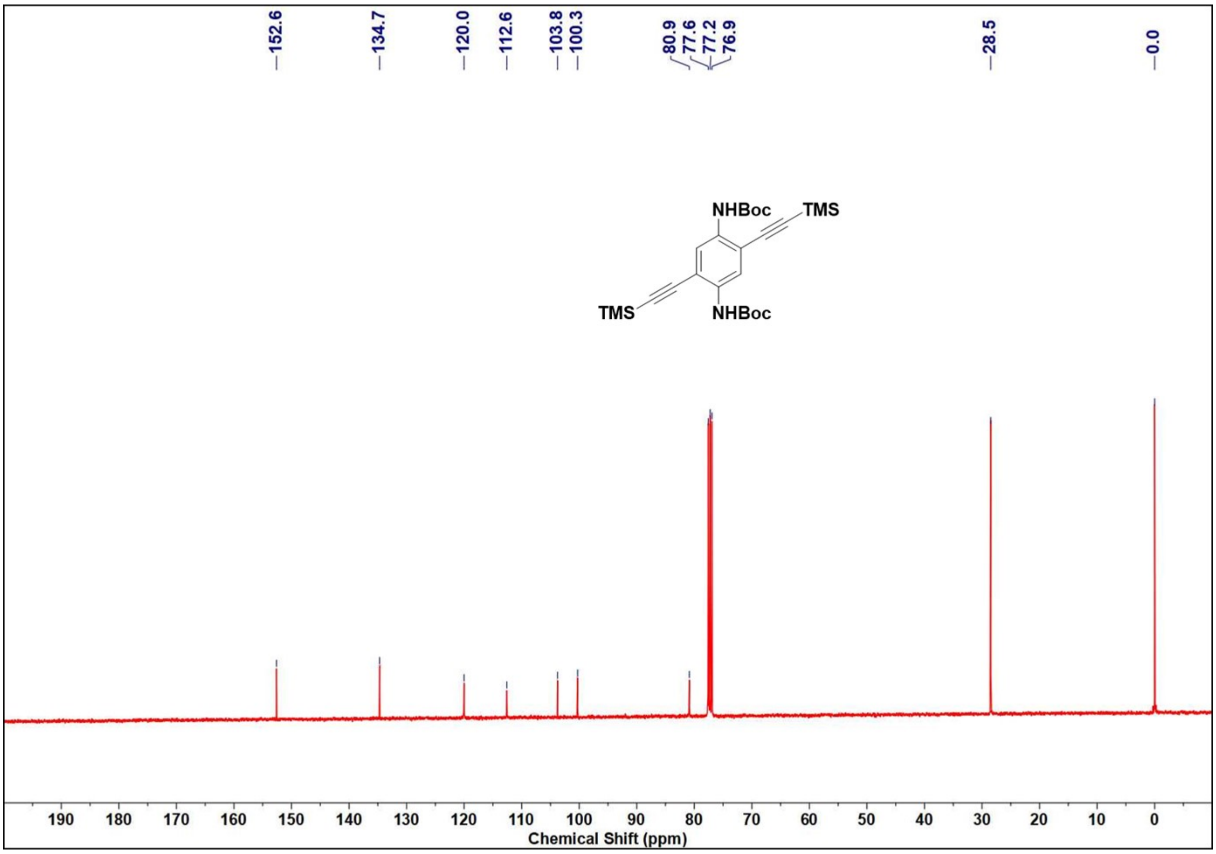
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)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103.8
100.3
80.9
77.6
77.2
76.9
28.5
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NHBoc
TMS
TMS
NHBoc
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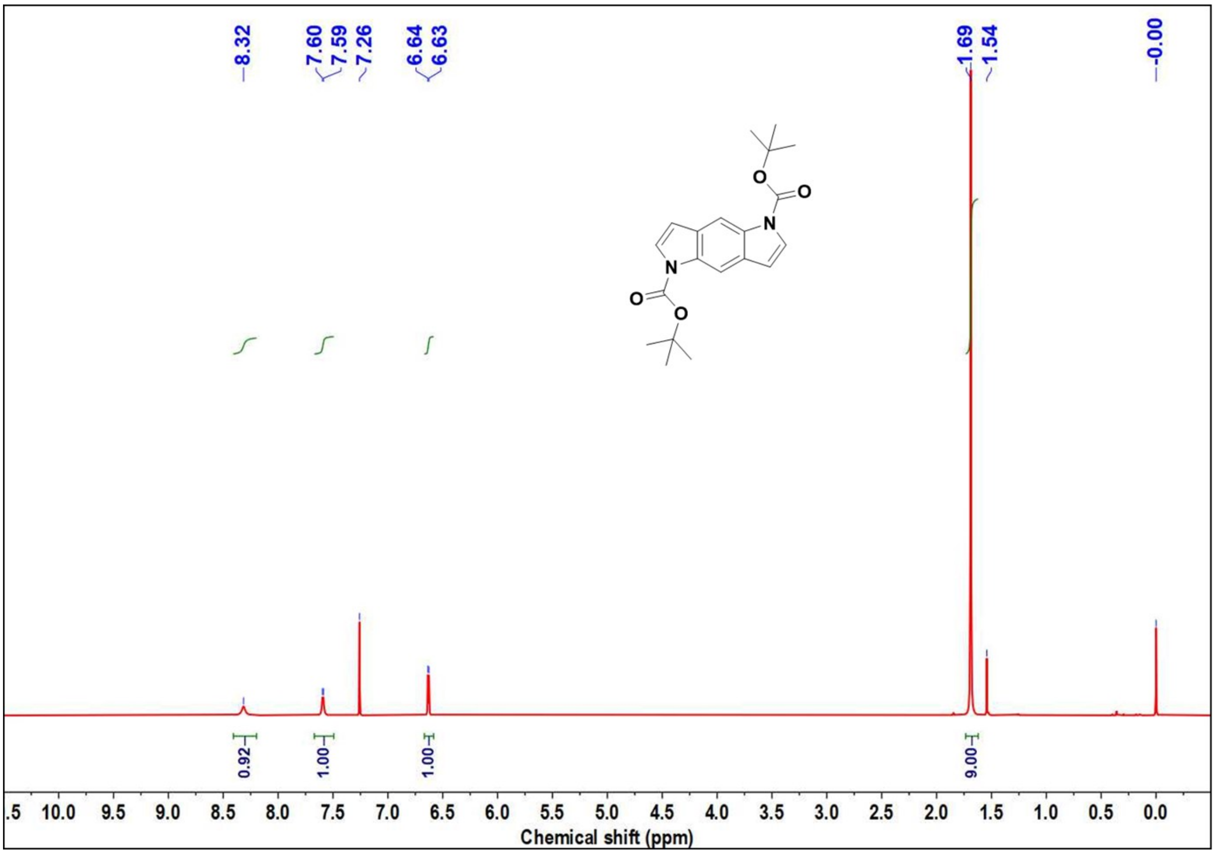
Chemical Shift (ppm)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O
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1.00
1.00
9.00
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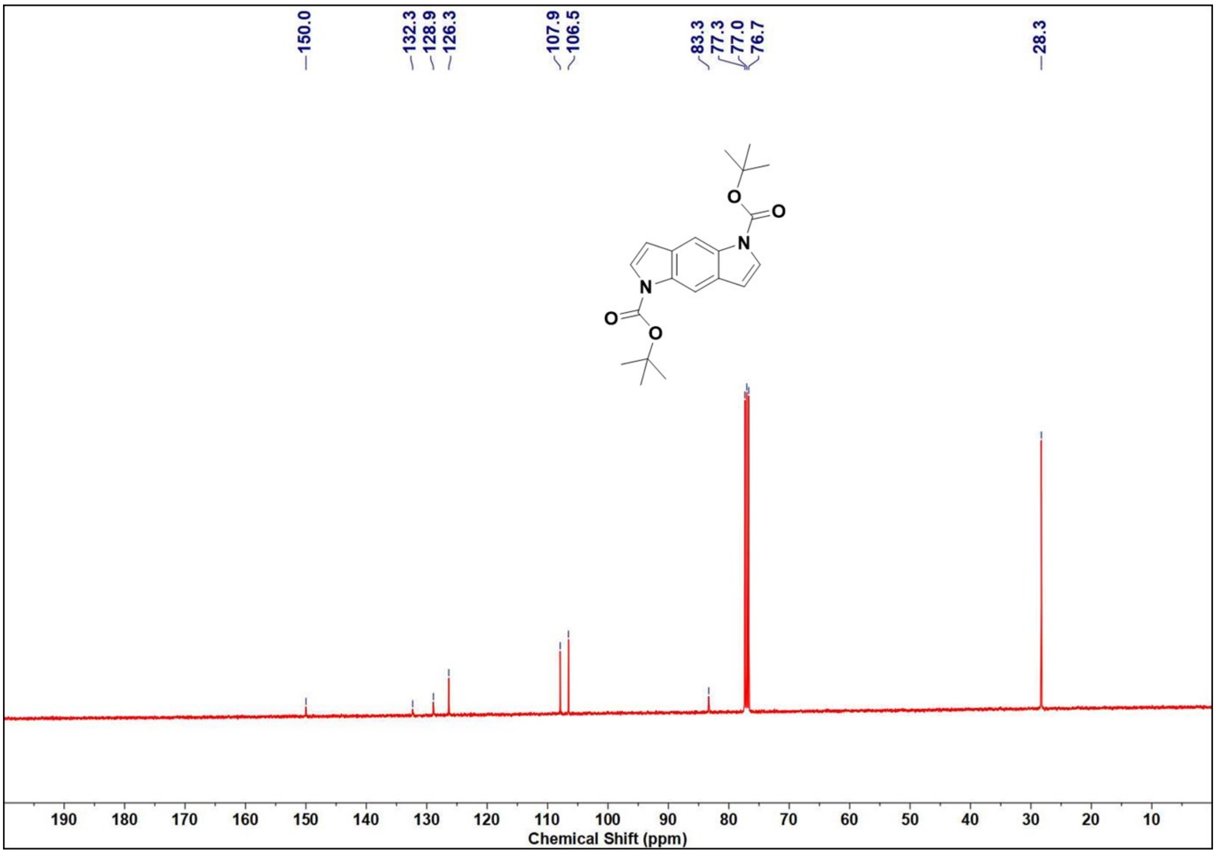
Chemical shift (ppm)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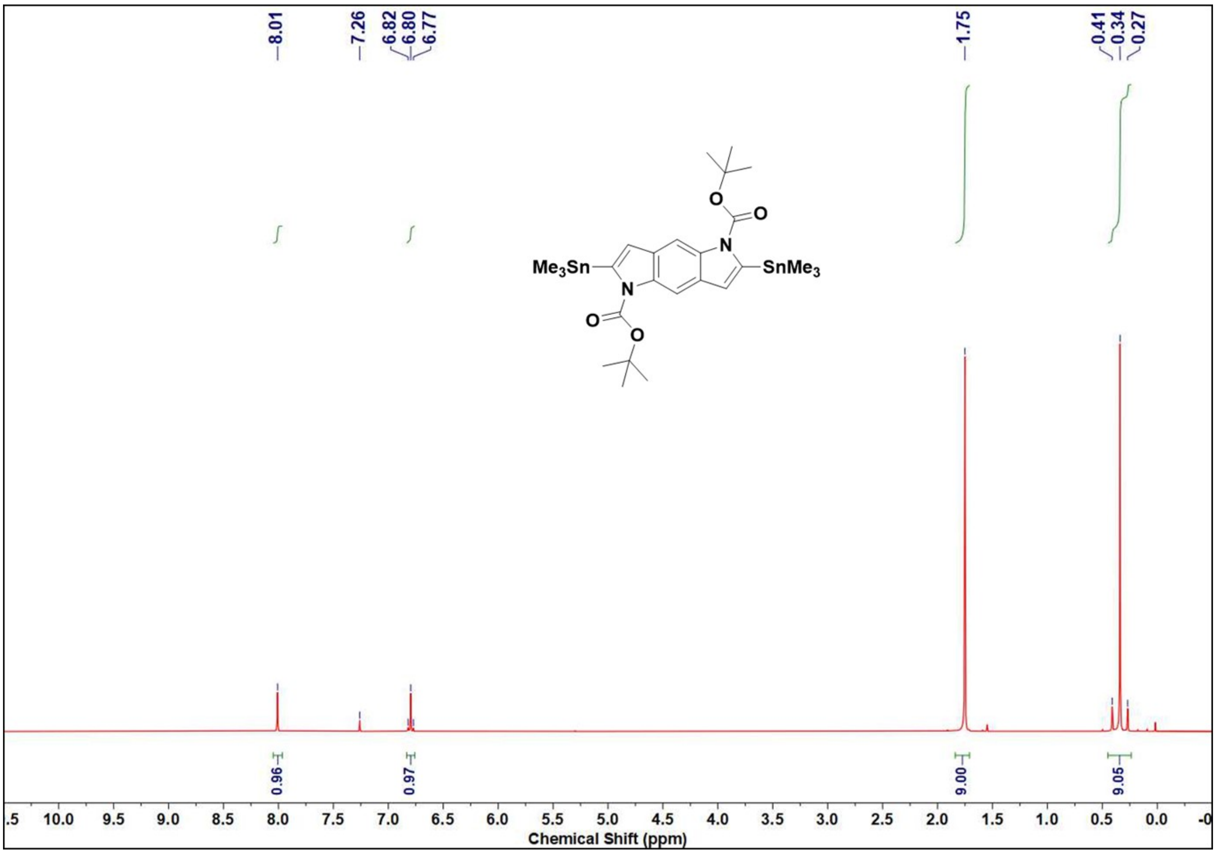
Chemical Shift (ppm)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0.41
0.34
0.27
Me$_3$Sn
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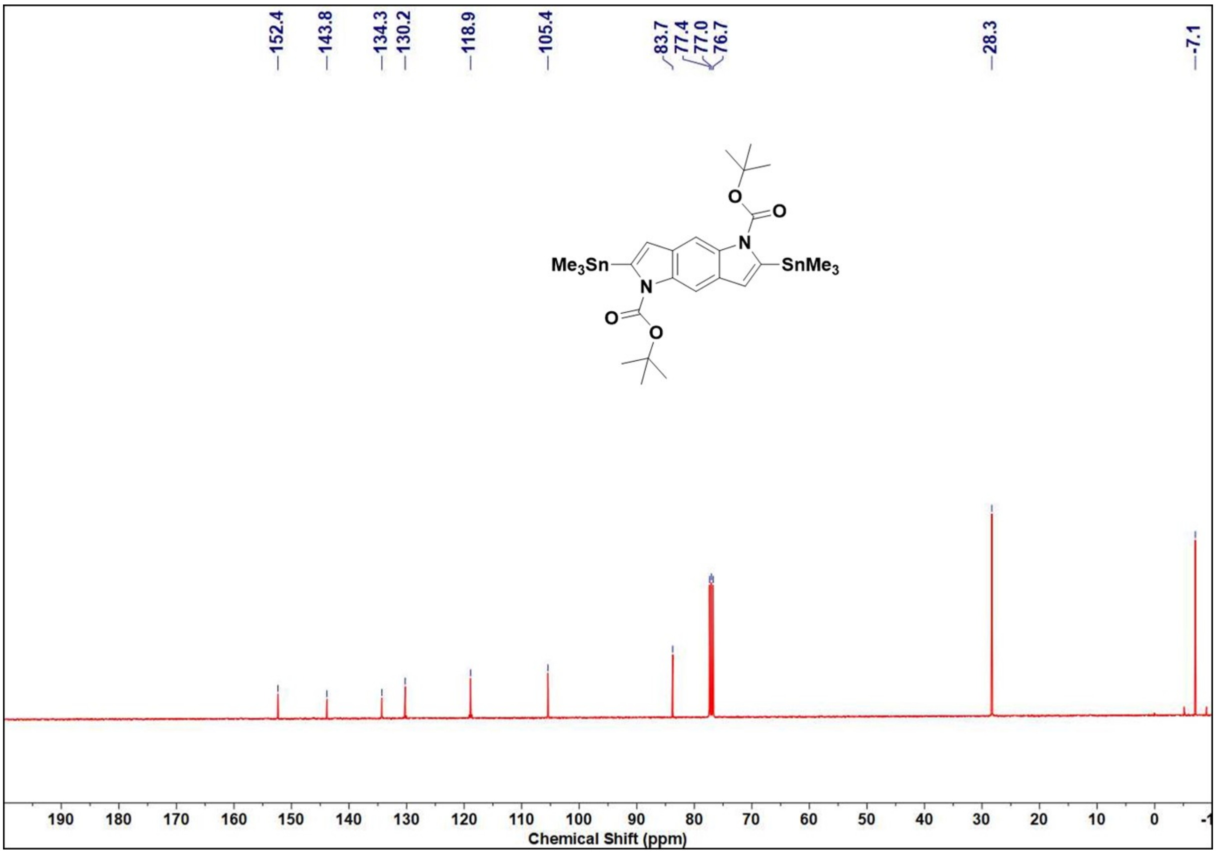
N
O
O
SnMe$_3$
0.96
0.97
9.00
9.05
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
Chemical Shift (ppm)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130.2
118.9
105.4
83.7
77.4
77.0
76.7
28.3
-7.1
Me$_3$Sn
N
O
O
N
O
O
SnMe$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
Chemical Shift (ppm)

Reference

[1] T. Lei, Y. Cao, Y. Fan, C.-J. Liu, S.-C. Yuan and J. Pei, *J. Am. Chem. Soc.*, 2011, **133**, 6099.

[2] T. Lei, J.-H. Dou, X.-Y. Cao, J.-Y. Wang and J. Pei, *J. Am. Chem. Soc.*, 2013, **135**, 12168.

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