

Supporting Information

Elucidating Charge Carrier Reactivity, Conversion, and Degradation in n-Doped Oligo- and Poly(Benzodifurandione)

Jinhyo Hwang,¹ Xiaojuan Ni,² Michael F. Espenship,¹ Kan Tang,³ Junxiang Zhang,³ Aniruddha Basu,³ Suman Kuila,³ Stephen Barlow,³ Seth R. Marder,^{3,4} Jean-Luc Brédas,² Julia Laskin,¹ Jianguo Mei^{1}*

1 Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

2 Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ, 85721, USA

3 Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, CO 80309, USA

4 Departments of Chemistry and of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO 80309, USA

Correspondence to: jgmei@purdue.edu

Experimental Section

Materials

All reagents and solvents for the synthesis and analysis were purchased from Aldrich, Alfa Aesar, TCI and were used without purification unless otherwise mentioned. Synthetic intermediates and final monomers were purified by column chromatography with silica gel (General-Reagent, 200–300 mesh) using dichloromethane and hexane as described in detail in Supporting Information.

Characterization

UV–Vis–NIR Absorption Spectroscopy: UV–vis–NIR absorption spectra were measured with an Agilent Technologies (Cary 5000/6000i) Cary Win UV–vis–NIR spectrophotometer. Solution UV–vis–NIR spectra were recorded at a concentration of 0.05 mM in a quartz cuvette with a 1 cm path length.

Cyclic Voltammetry: CV measurements were carried out using a Shanghai Chenhua Instrument CHI760E potentiostat with a three-electrode setup. Redox properties of the molecules (0.5 mM solutions prepared in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte dissolved in dichloromethane) were tested in a three-electrode cell using a Pt-button working electrode, a Ag/AgCl reference electrode, a Pt wire counter electrode, and the ferrocene/ferrocenium couple (Fc/Fc⁺) was used as an external standard to estimate the E_{LUMO} . Cyclic voltammetry was performed at a scan rate of 20 mV s⁻¹, unless specified otherwise. Differential pulse voltammetry was also done over the same potential range. All measurements were performed under inert conditions.

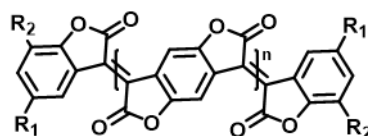
Spectro-Electrochemistry: Spectro-electrochemical measurements were performed by fitting the CV setup inside a quartz cuvette in the UV–vis–NIR absorption spectrophotometer. Potentials were applied for 15 s prior to recording the UV–vis–NIR absorption spectrum at each voltage to ensure stabilization of the optical trace. the molecules (0.05 mM solutions prepared in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte dissolved in dichloromethane) were tested in a cuvette of 1 mm path length using a honeycomb-electrode with a built-in counter electrode. The same Ag/AgCl reference electrode used for the CV and DPV measurements were used in these experiments. Potential steps of 0.1 V were then used to evaluate the electrochromic

behavior of the polymers. Smaller potential steps were chosen as the oxidation potential was approached.

ESI-Mass spectrometric measurements: ESI-MS were acquired using an Agilent 6560 ion mobility quadrupole time-of-flight (IM Q-TOF) mass spectrometer (Santa Clara, CA, USA) fitted with a custom-designed electrospray ionization (ESI) source. A 1000 μM solution of sample species was infused into the inlet of the instrument via a fused-silica capillary (50 μm ID, 150 μm OD) at a flow rate of 1 $\mu\text{L}/\text{min}$. ESI conditions include a spray voltage of -3.5kV and inlet temperature of 250°C. Negative ions were analyzed in the mass range of m/z 100 – 3200 with a resolution ($m/\Delta m$) of 25,000 for m/z 751. The solvent composition was an 80:20 mixture of acetonitrile-DMSO (%v/v). The instrument also includes a collision cell filled with nitrogen where select precursor ions underwent collision induced dissociation (CID) to form product (fragment) ions. The collision energy value was set to 20 eV.

Electron-paramagnetic resonance: Chemically doped solutions (0.2 mM solutions in THF) were measured at room temperature on a Bruker EMX EPR Spectrometer using WinEPR Acquisition Software.

Computational Methods: The ground-state geometry optimizations and electronic-structure calculations of the BFD2/3 oligomers were performed at the density functional theory (DFT) level using the range-separated ωB97XD functional and the 6-31G** basis set. The range-separation parameters (ω) was optimized to be 0.114 bohr⁻¹ for the neutral BFD3 molecule, and this value was also applied to other systems. All the calculations were performed using the Gaussian 16 package.¹



BFD1: $n=0$, $R_1=t\text{Bu}$, $R_2=\text{H}$

BFD2: $n=1$, $R_1=t\text{Bu}$, $R_2=t\text{Bu}$

BFD3: $n=2$, $R_1=t\text{Bu}$, $R_2=t\text{Bu}$

Figure S1. Chemical structures of BFD1, BFD2, and BFD3. In our previous study (*Angew. Chem. Int. Ed.* **2024**, 63, e202401465), the BFD2 compound had one tBu group at the R_1 position. In this work, BFD2 has tBu groups at both the R_1 and R_2 positions. Since the tBu groups serve as solubilizing groups and the compounds share the same backbone structure, the naming is the same in both studies.

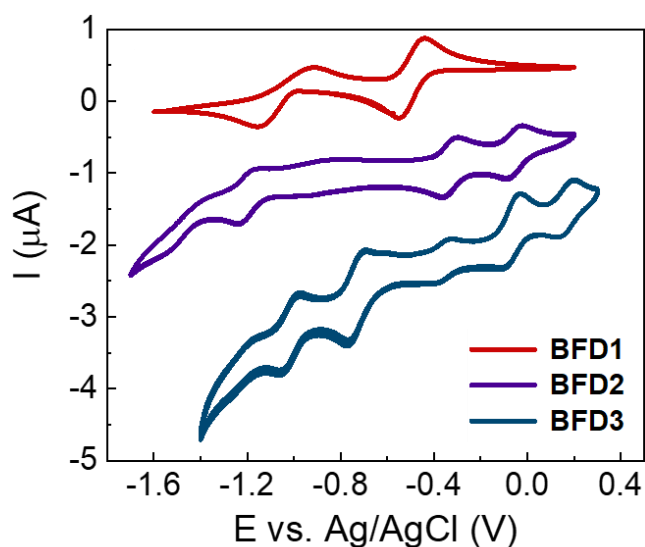


Figure S2. Cyclic voltammetry of model compounds in an electrolyte of 0.1 M TBAPF₆ in DCM.

Table S1. Photophysical and electrochemical properties of BFD1, BFD2, and BFD3.

	$\lambda_{\text{max}}^{\text{abs}}$ (nm) ^a	$\lambda_{\text{cut-off}}$ (nm)	$E_{\text{red}}^{\text{onset}}$ (V) ^b	HOMO (eV) ^c	LUMO (eV) ^c	E_{g} (eV) ^d
BFD1	401,458	546	-0.43	-6.25	-3.98	2.27
BFD2	458,572	655	-0.04	-6.26	-4.37	1.89
BFD3	474,630,670	738	0.22	-6.31	-4.63	1.68

a) Measured in dichloromethane. b) Cyclic voltammograms measured in 0.1M TBAPF₆ in CH₂Cl₂. c) LUMO = - e (4.8 + $E_{\text{red}}^{\text{onset}}$ - $E_{\text{Fc/Fc}^+}$), ferrocene = 0.388 eV, HOMO = LUMO - E_{g} . d) E_{g} is optical gap obtained from absorption threshold, $E_{\text{g}} = 1240/\lambda_{\text{cut-off}}$.

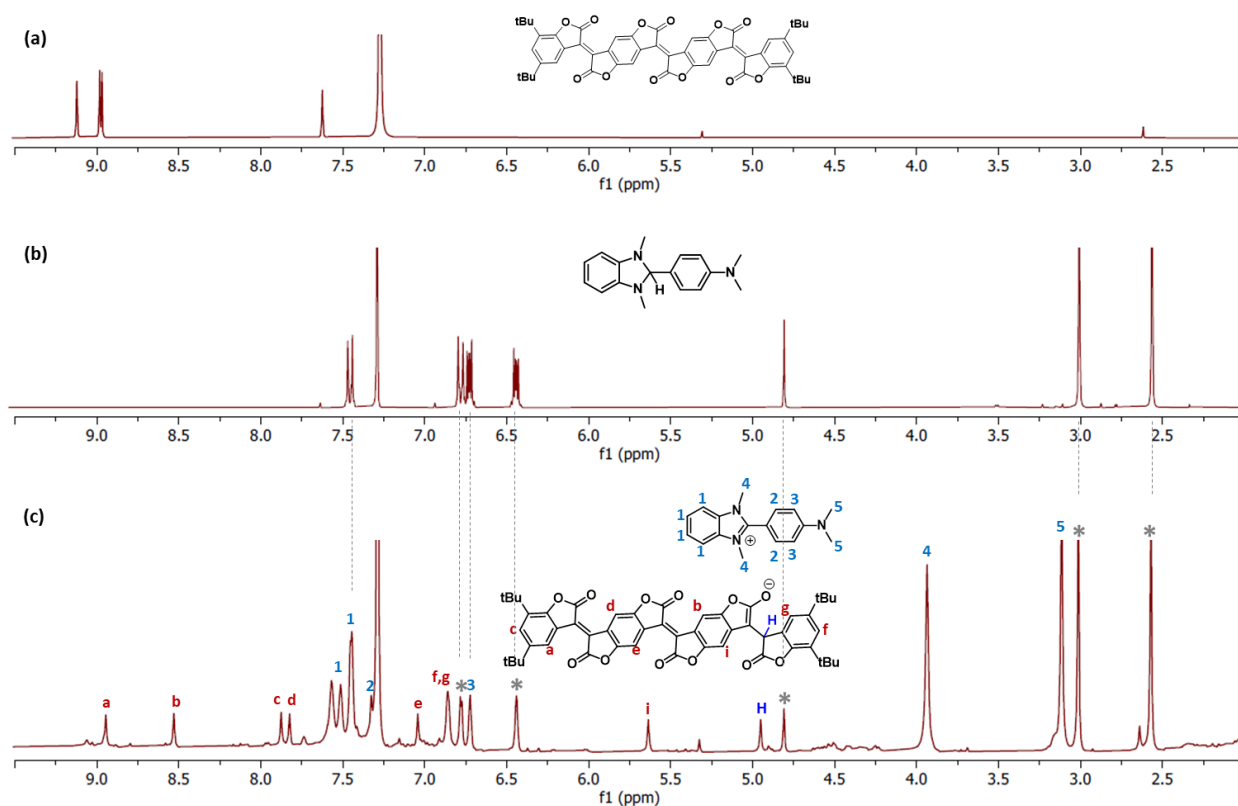


Figure S3. Stacked ¹H NMR spectrum of (a) BFD3, (b) N-DMBI, and (c) 1:2 mixture of BFD3:N-DMBI-H in CDCl₃ showing hydride transfer from N-DMBI to BFD3 occurring at the end group forming BFD3H⁻/N-DMBI⁺. The N-DMBI peak (gray star) demonstrates that BFD3H⁻/N-DMBI⁺ does not undergo further hydride transfer with excess N-DMBI.

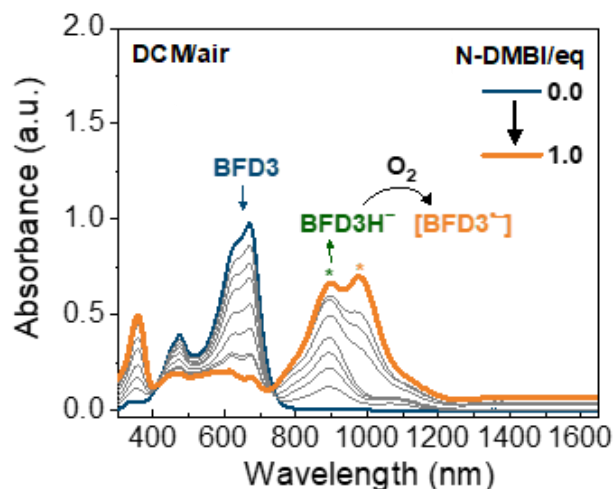


Figure S4. UV-Vis spectra of BFD3 reacting with N-DMBI under air.

Protonation of $\text{BFD3H}^-/\text{N-DMBI}^+$

$\text{BFD3H}^-/\text{N-DMBI}^+$ was found to undergo protonation in acidic conditions (Figure S5). The use of Amberlyst 15 enabled the replacement of N-DMBI^+ with a proton, shifting the absorption from 890 nm to 670 nm and changing the solution from colorless to purple, indicative of a decreased conjugation length (Figure S6). BFD3H_2 readily oxidizes to BFD3 upon air exposure in DCM and converts back to BFD3^{2-} with the protonated DMSO as a counter cation. Detailed structural characterization studies using BFD2 are provided in Figures S7-S11.

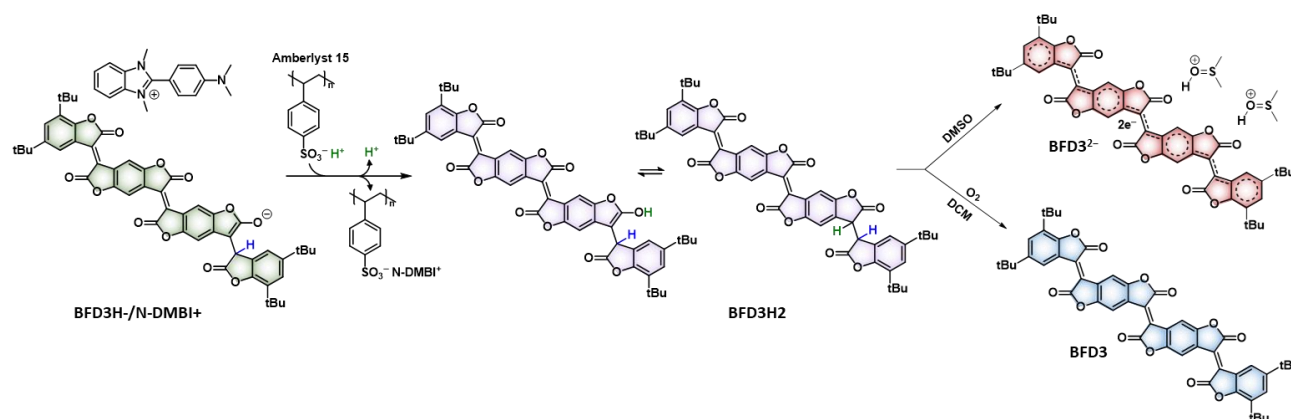


Figure S5. Schematic diagram showing the reaction between BFD3H^- and acid that generates BFD3H_2 . BFD3H_2 is oxidized to BFD3 by air in DCM and converts to BFD3^{2-} in DMSO.

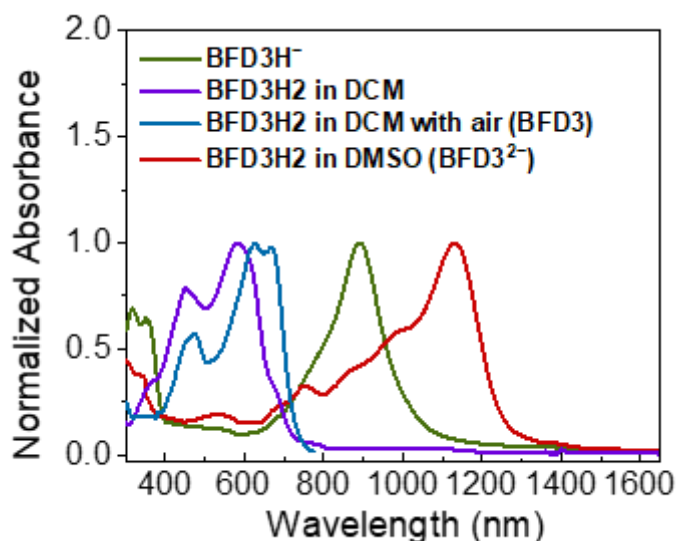


Figure S6. UV-Vis-NIR spectra of the protonation of BFD3H⁻/N-DMBI⁺ and the reactivity of BFD3H2.

Protonation of BFD2H⁻/N-DMBI⁺

To systematically study this process, we first tested the protonation using the BFD2 molecule (Figure S7-S11). In our previous work, we successfully isolated BFD2H⁻/N-DMBI⁺.² Therefore, starting from the relatively stable BFD2H⁻ provides a better understanding of the protonation reaction. The proton released by Amberlyst 15 interacts with the enolate on BFD2H⁻, forming an enol that immediately tautomerizes to a ketone, resulting in the formation of BFD2H2 (Figure S7). This transformation is accompanied by a shift in the absorption spectrum from 755 nm to 408 and 466 nm (Figure S8).

The cation exchange reaction between BFD2H⁻/N-DMBI⁺ and Amberlyst15 were investigated by using *in-situ* time dependent NMR spectra in CDCl₃ (Figure S9). Upon the addition of Amberlyst 15, protons were released, as indicated by a large broad peak around $\delta = 9.0$ -10.5 ppm. The N-DMBI⁺ was absorbed by the Amberlyst 15 resin, as evidenced by the gradual disappearance of its characteristic peaks (peaks 1, 2, 3, and 4). The two protons from the single bond of BFD2H2 appeared around $\delta = 4.5$ -4.6 ppm.

Adding hexane to the *in-situ* generated BFD2H2 in DCM solution results in the exclusive precipitation of the ketone form of BFD2H2 as a dark red solid (Figure S10a). After 1 hour of air

exposure, the aliphatic proton signals around $\delta = 4.5$ -4.6 ppm shows a mixture of keto-enol forms of BFD2H2 (Figure S10b). When BFD2H2 is added to DMSO- d_6 , it immediately produces a green solution, with the NMR spectrum corresponding to the hydride-transferred anion BFD2H $^-$ (Figure S10c). The UV-vis-NIR absorption spectrum of BFD2H2 in DMSO also confirmed the regeneration of BFD2H $^-$ (Figure S8). The NMR shows a sharp singlet peak around $\delta = 4.0$ ppm, indicating protonated DMSO, consistent with previous studies.^{3,4} The protonated DMSO was detected at m/z 79.0212 in ESI (+) mode (Figure S11).

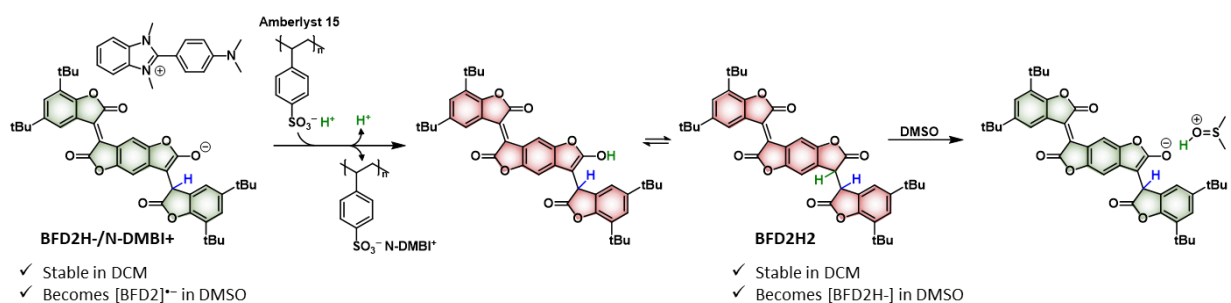


Figure S7. Schematic diagram of cation exchange of BFD2H $^-$ /N-DMBI $^+$ with Amberlyst 15 and deprotonation of BFD2H2 in DMSO.

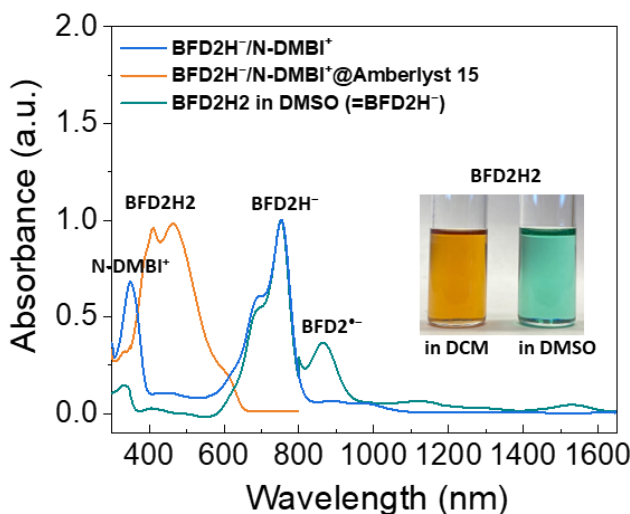


Figure S8. UV-vis-NIR spectrum of BFD2H $^-$ /N-DMBI $^+$ in DCM (blue). Adding Amberlyst 15 to BFD2H $^-$ /N-DMBI $^+$ generates BFD2H2. In DMSO solution, BFD2H2 immediately gets deprotonated and forms the BFD2H $^-$ salt with protonated DMSO. According to our previous work, BFD2H $^-$ easily oxidizes to BFD2 $^{2-}$ via ambient oxygen.²

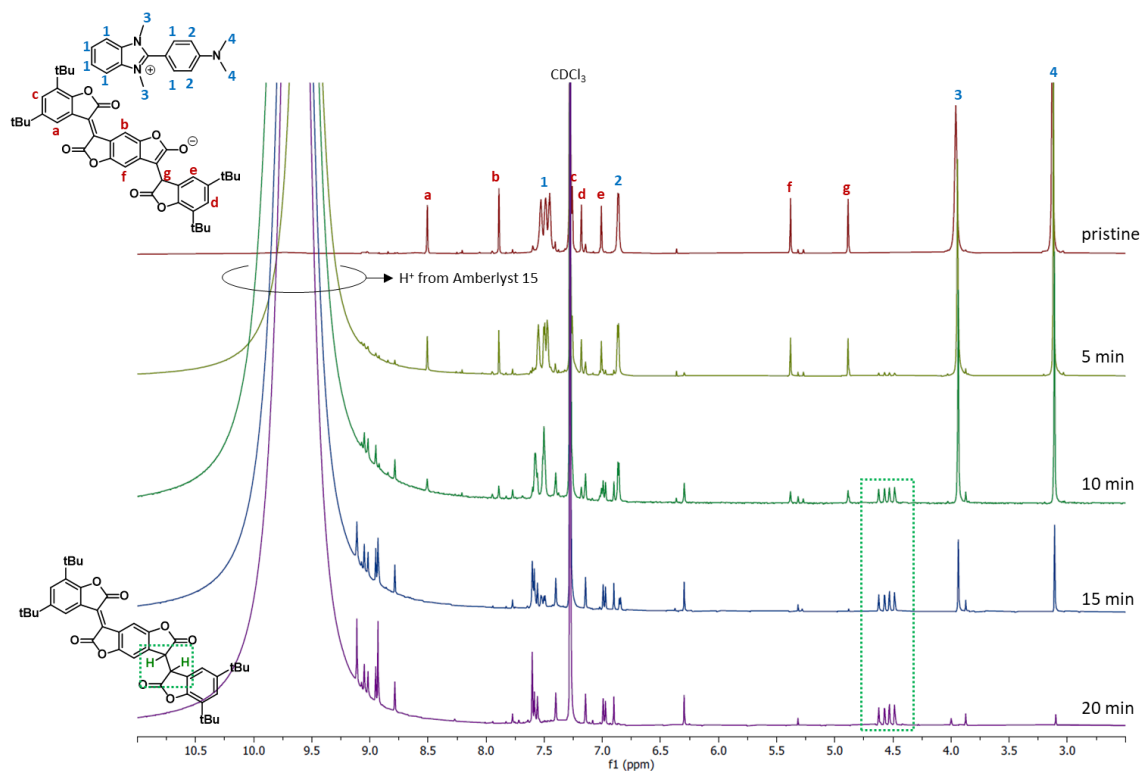


Figure S9. Time -dependent in-situ ^1H NMR spectrum of $\text{BFD2H}^-/\text{N-DMBI}^+$ with Amberlyst 15 in CDCl_3 .

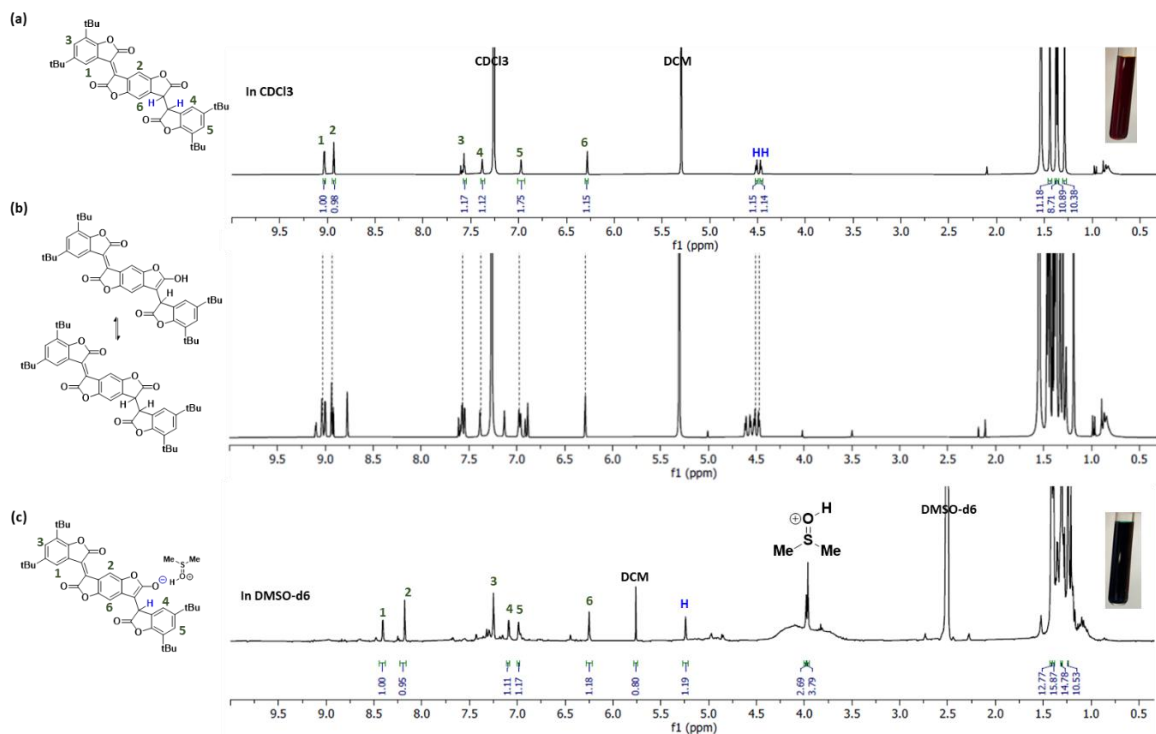


Figure S10. ^1H NMR spectra of (a) BFD2H_2 in CDCl_3 , (b) BFD2H_2 in CDCl_3 under air for 1 hour, and (c) BFD2H_2 in DMSO-d_6 .

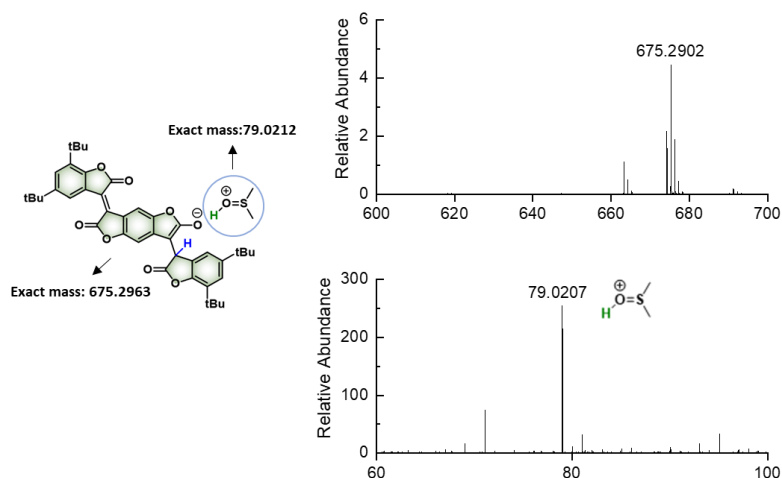


Figure S11. Negative ion ESI-MS spectrum showing BFD2H⁻ at m/z 675.2902 and the positive ion ESI-MS spectrum showing protonated DMSO at m/z 79.0207.

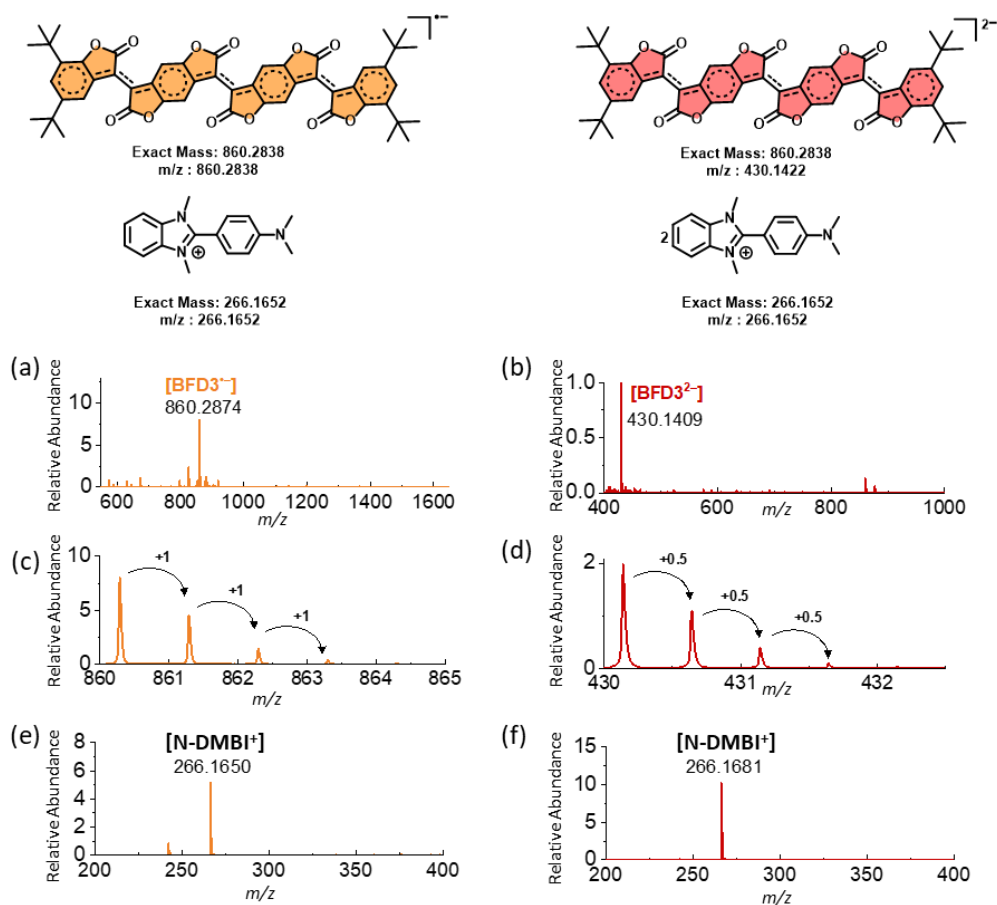


Figure S12. (a,b) Negative ion ESI-MS spectra of (a) BFD3⁻/N-DMBI⁺ and (b) BFD3²⁻/(N-DMBI⁺)₂ and (c,d) their zoom-ins in the region of interest of the mass spectra showing isotope spacing of (c) BFD3⁻/N-DMBI⁺ and (d) BFD3²⁻/(N-DMBI⁺)₂. (e,f) The positive ion ESI-MS spectra of (e) BFD3⁻/N-DMBI⁺ and (f) BFD3²⁻/(N-DMBI⁺)₂ showing N-DMBI⁺.

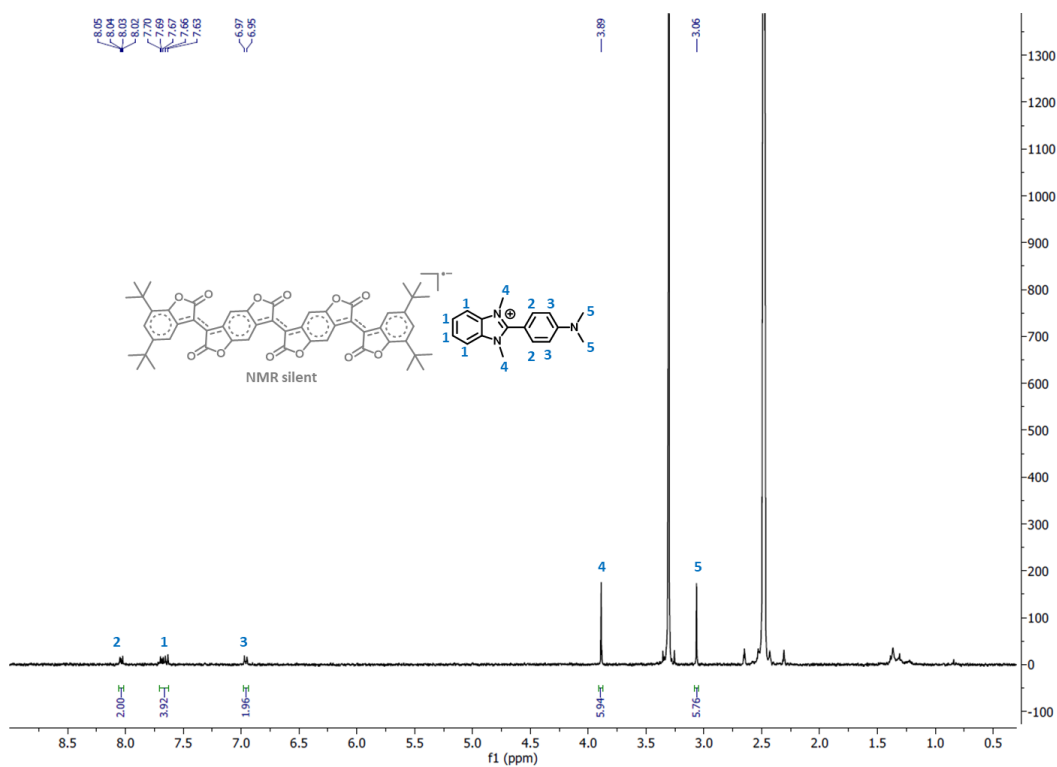


Figure S13. ^1H NMR Spectrum of $\text{BFD3}^{3-}/\text{N-DMBI}^+$ in DMSO-d_6 .

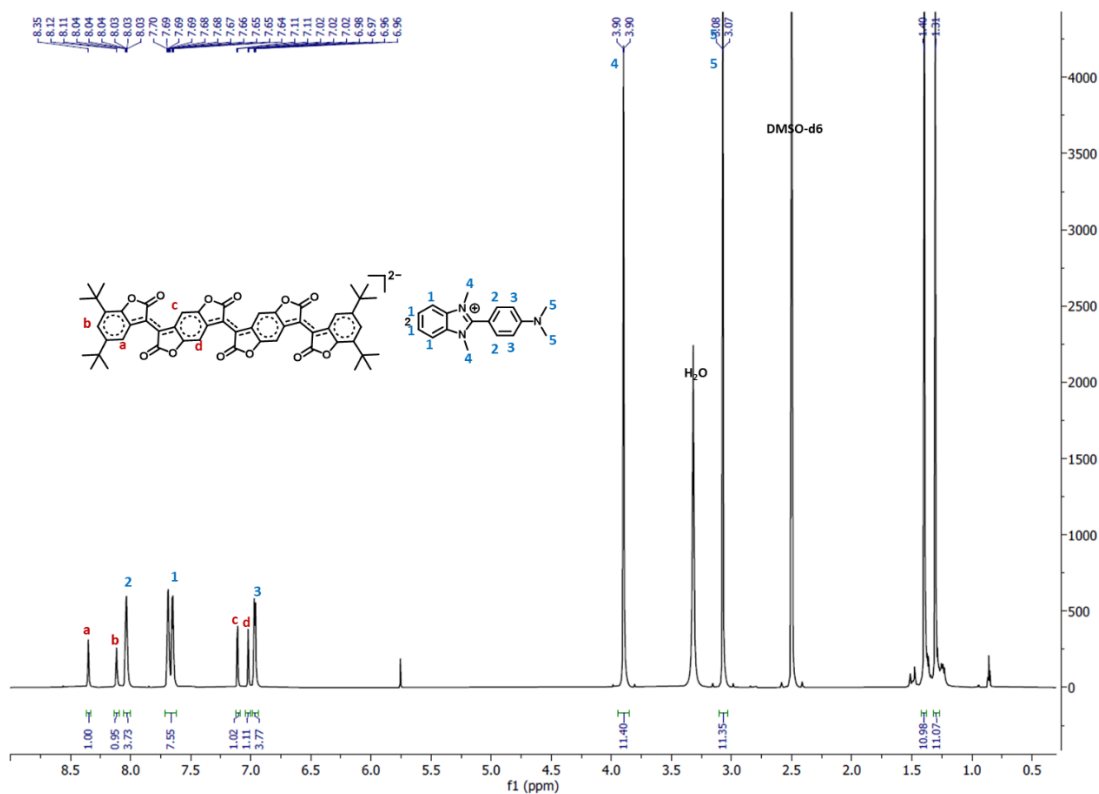


Figure S14. ^1H NMR Spectrum of $\text{BFD3}^{2-}/(\text{N-DMBI}^+)_2$ in DMSO-d_6 .

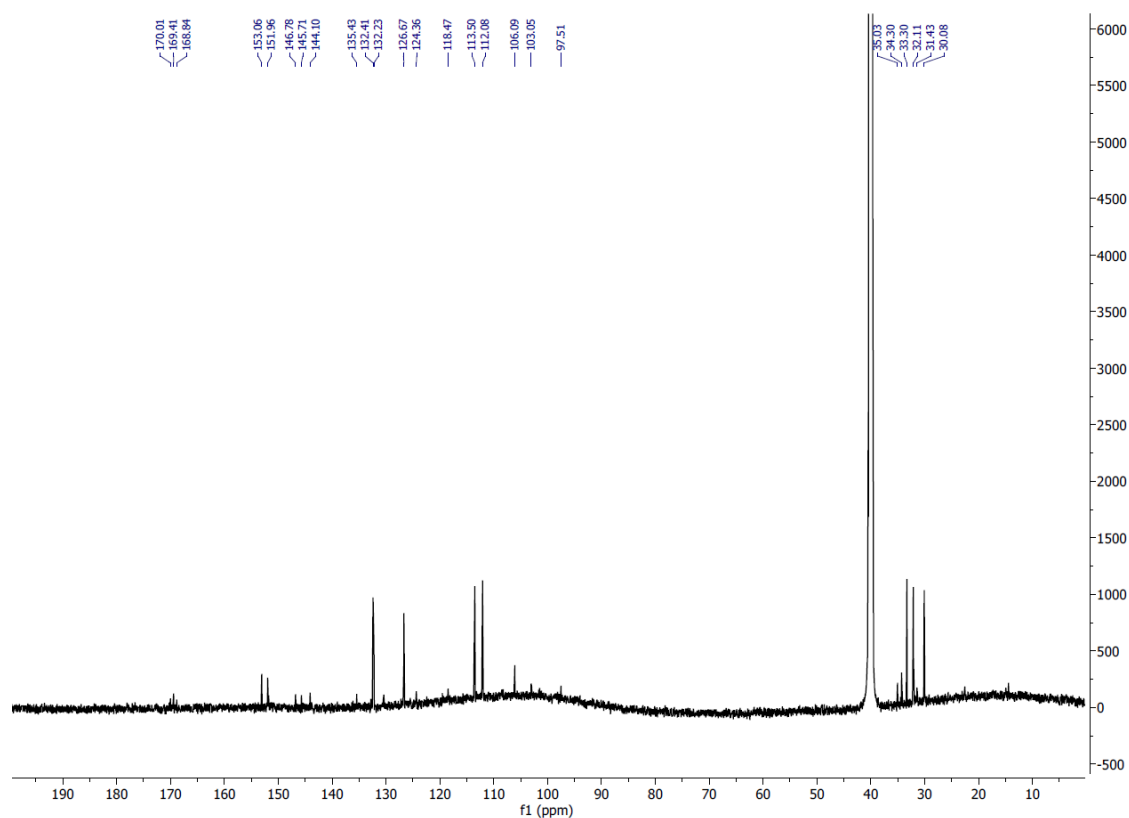


Figure S15. ^{13}C NMR Spectrum of $\text{BFD3}^{2-}/(\text{N-DMBI}^+)_2$ in DMSO-d_6 .

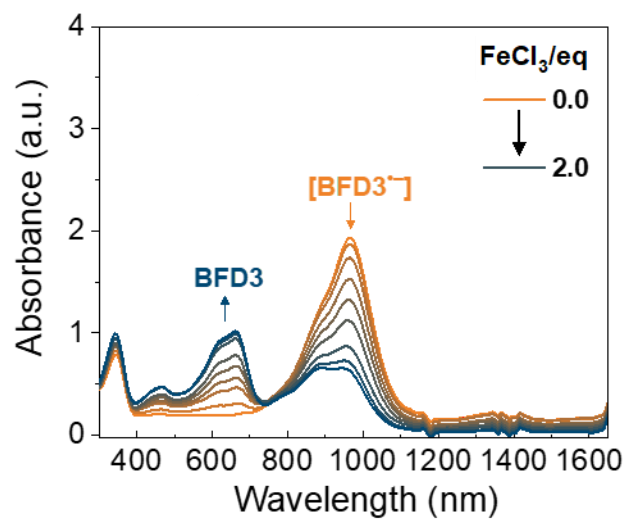


Figure S16. UV/Vis-NIR spectra of titrating 0.05 mM $\text{BFD3}^{2-}/\text{N-DMBI}^+$ with 1mM FeCl_3 in DMSO.

Crystal structures of neutral (BFD2), radical anion (BFD2^{•-}/N-DMBI⁺) and dianion (BFD3²⁻/(N-DMBI⁺)₂)

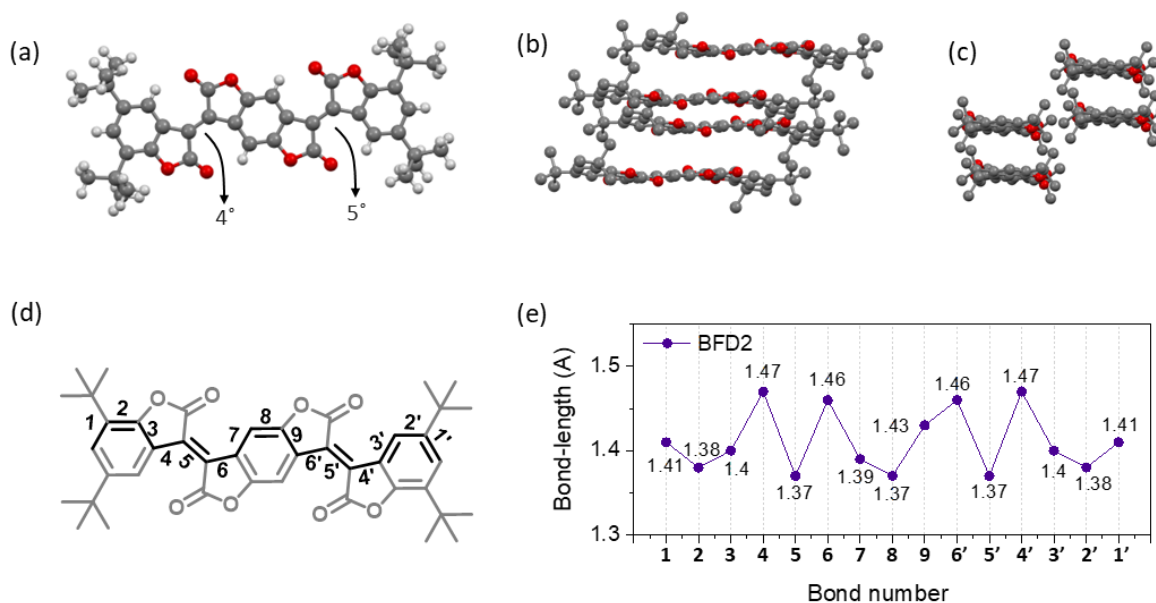


Figure S17. Crystal structure of BFD2: (a) Top view with illustration of twist angles and (b,c) side views. (d) Carbon–carbon bond-lengths of BFD2 in the crystal. The labels in the structure represent the bond indices. Selected bond lengths (Å): bond1 and 1' 1.402(2), bond2 and 2' 1.388(2), bond3 and 3' 1.399(2), bond4 and 4' 1.471(7), bond5 and 5' 1.371(8), bond6 and 6' 1.464(2), bond7 1.390(2), bond8 1.365(2), bond9 1.429(2).

Table S2. Crystal data and structure refinement for **BFD2**.**Crystal Data**

CCDC	2440628
Chemical Formula	C ₄₂ H ₄₂ O ₈
Moiety Formula	C ₄₂ H ₄₂ O ₈
<i>M_r</i>	674.75
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.1553(9), 9.5303(14), 15.397(2)
α , β , γ (°)	103.306(10), 99.922(9), 94.968(10)
<i>V</i> (Å ³)	858.3(2)
<i>Z</i>	1
Radiation Type	Mo <i>K</i> α
μ (mm ⁻¹)	0.090
Crystal Size (mm)	0.23 × 0.19 × 0.02

Data Collection

Diffractometer	Bruker AXS D8 Quest four circle diffractometer
Absorption Correction	multi-scan
<i>T_{min}</i> , <i>T_{max}</i>	0.629, 0.746
No. of measured, independent, and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11759, 4149, 2191
<i>R_{int}</i>	0.0933

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.1606, 0.2006, 1.025
No. of reflections	4149
No. of parameters	444
No. of restraints	827
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 0.9746P]$ where $P = (F_o^2 + 2F_c^2)/3$ 0.263, -0.251

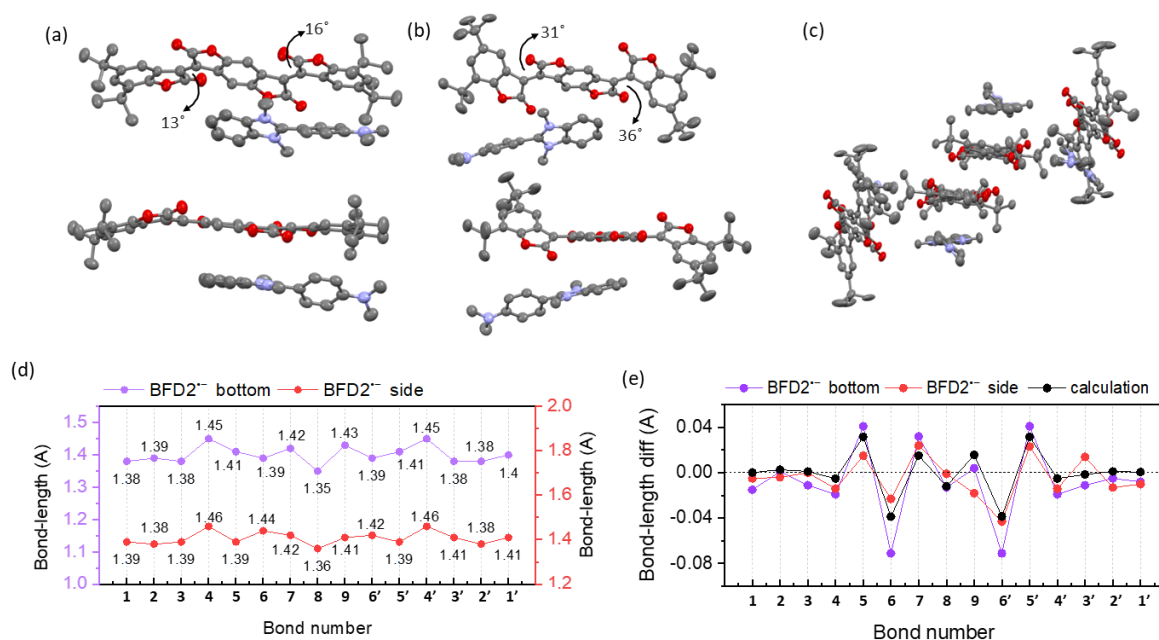


Figure S18. Crystal structure of the BFD2^{•-}/N-DMBI⁺ salt: (a) Top views with illustration of twist angles and (b,c) side views. (d) Carbon–carbon bond-lengths of BFD2^{•-} in the crystal. The labels in the structure represent the bond indices. Selected bond lengths (Å) for BFD2^{•-} bottom : bond1 and 1' 1.387(8), bond2 and 2' 1.388(7), bond3 and 3' 1.387(6), bond4 and 4' 1.452(5), bond5 and 5' 1.412(5), bond6 and 6' 1.392(6), bond7 1.424(6), bond8 1.352(6), bond9 1.430(5). BFD2^{•-} side : bond1 and 1' 1.397(7), bond2 and 2' 1.383(7), bond3 and 3' 1.398(5), bond4 and 4' 1.457(8), bond5 and 5' 1.386(7), bond6 and 6' 1.440(7), bond7 1.416(7), bond8 1.364(7), bond9 1.408(5). (e) Carbon–carbon bond-length differences with respect to neutral BDF2 for BFD2^{•-} from the crystal structure of its N-DMBI⁺ salt and from DFT calculations.

Table S3. Crystal data and structure refinement for BFD2⁺/N-DMBI⁺.**Crystal Data**

CCDC	2440627
Chemical Formula	C ₄₂ H ₄₂ O ₈ , C ₁₇ H ₂₀ N ₃
Moiety Formula	C ₄₂ H ₄₂ O ₈ , C ₁₇ H ₂₀ N ₃
<i>M_r</i>	3456.08
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8126(6), 19.8286(9), 23.2529(10)
α , β , γ (°)	107.530(3), 101.994(4), 96.590(3)
<i>V</i> (Å ³)	4565.3(4)
<i>Z</i>	1
Radiation Type	Cu <i>K</i> α
μ (mm ⁻¹)	1.778
Crystal Size (mm)	0.31 × 0.25 × 0.02

Data Collection

Diffractometer	Bruker AXS D8 Quest four circle diffractometer
Absorption Correction	multi-scan
<i>T_{min}</i> , <i>T_{max}</i>	0.580, 0.754
No. of measured, independent, and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	61219, 18719, 7835
<i>R_{int}</i>	0.1546

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.1922, 0.2811, 0.985
No. of reflections	18719
No. of parameters	1241
No. of restraints	318
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.1072P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.408, -0.514

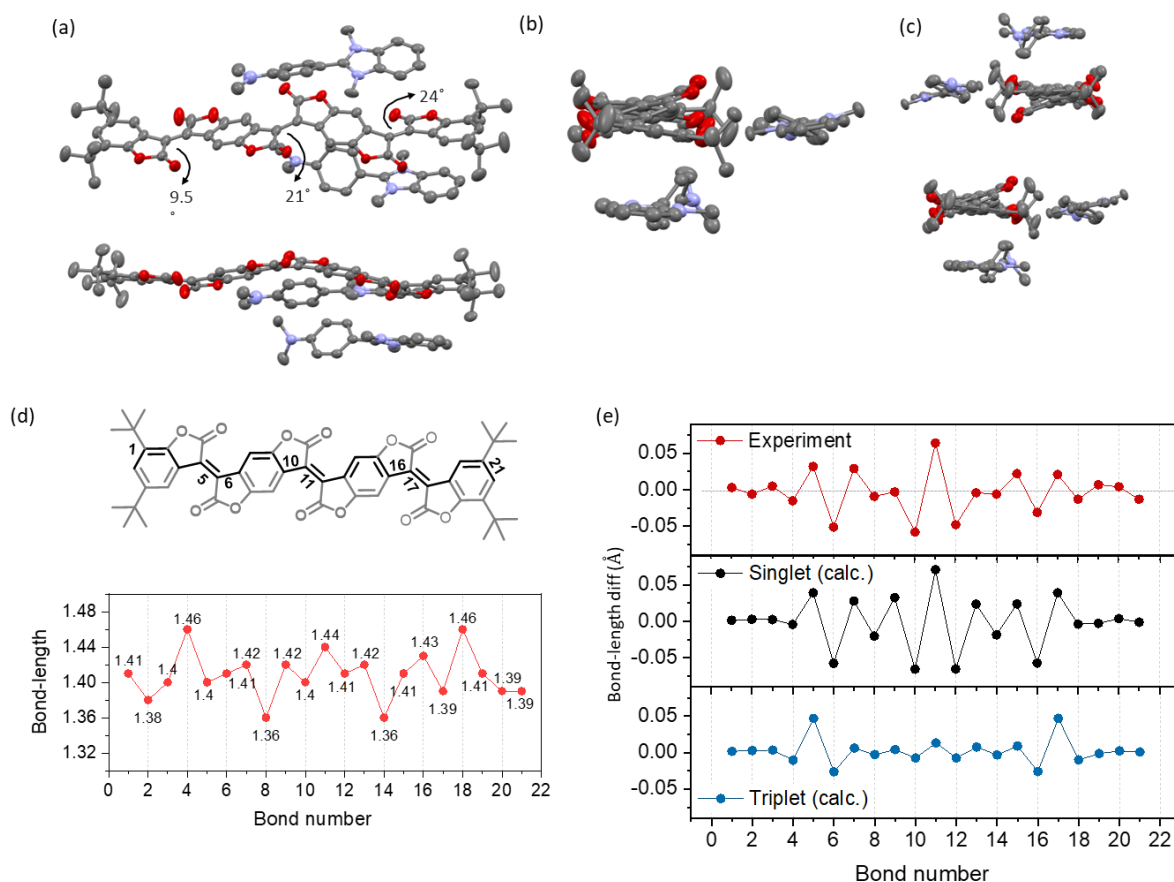


Figure S19. Crystal structure for BFD3²⁻/(N-DMBI⁺)₂: (a) Top views with illustration of the twist angles and (b,c) side views. (d) Carbon–carbon bond-length of BFD3²⁻ from the crystal structure of its N-DMBI⁺ salt. The labels in structure represent the bond indices. Selected bond lengths (Å) : bond1 1.405(2), bond2 1.381(3), bond3 1.403(3), bond4 1.456(2), bond5 1.403(2), bond6 1.412(2), bond7 1.421(2), bond8 1.356(3), bond9 1.423(3), bond10 1.405(2), bond11 1.435(3), bond12 1.412(3), bond13 1.422(3), bond14 1.359(3), bond15 1.414(3), bond16 1.432(3), bond17 1.392(3), bond18 1.458(3), bond19 1.405(3), bond20 1.391(3), bond21 1.389(2). (e) Carbon–carbon bond-length differences with respect to neutral BDF3 for BFD3²⁻ from the crystal structure of its N-DMBI⁺ salt (top) and from the DFT calculations of the singlet state (middle) and triplet state (bottom).

Computational modeling revealed that the electrons were delocalized across the backbone in the singlet dianion state, while the electrons were localized in two distinct regions in the triplet dianion state. Experimentally, bonds 5, 7, 15, 17, and especially 11 became longer, taking on more single-bond-like character, while bonds 6, 10, 12, and 16 shortened, showing more double-bond-like character. This suggests that the two electrons are delocalized across the entire backbone, which is consistent with the formation of the singlet state, where the electrons are coupled.

Table S4. Crystal data and structure refinement for BFD3²⁻/(N-DMBI⁺)₂.**Crystal Data**

CCDC	2440626
Chemical Formula	C ₅₂ H ₄₄ O ₁₂ , C ₁₇ H ₂₀ N ₃
Moiety Formula	C ₅₂ H ₄₄ O ₁₂ , C ₁₇ H ₂₀ N ₃
<i>M_r</i>	1527.41
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	150
<i>a, b, c</i> (Å)	9.7619(12), 16.5444(19), 25.822(4)
α, β, γ (°)	80.203(11), 89.727(8), 89.678(11)
<i>V</i> (Å ³)	4109.5(9)
<i>Z</i>	2
Radiation Type	Cu K α
μ (mm ⁻¹)	0.712
Crystal Size (mm)	0.17 × 0.14 × 0.04

Data Collection

Diffractometer	Bruker AXS D8 Quest four circle diffractometer
Absorption Correction	multi-scan
<i>T_{min}</i> , <i>T_{max}</i>	0.596, 0.754
No. of measured, independent, and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	60282, 17193, 12138
<i>R_{int}</i>	0.0655

Refinement

<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0754, 0.1611, 1.040
No. of reflections	17193
No. of parameters	1881
No. of restraints	3569
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2 + 0.3231 P]$ where $P = (F_o^2 + 2F_c^2)/3$ 0.325, -0.259

Doping induced degradation

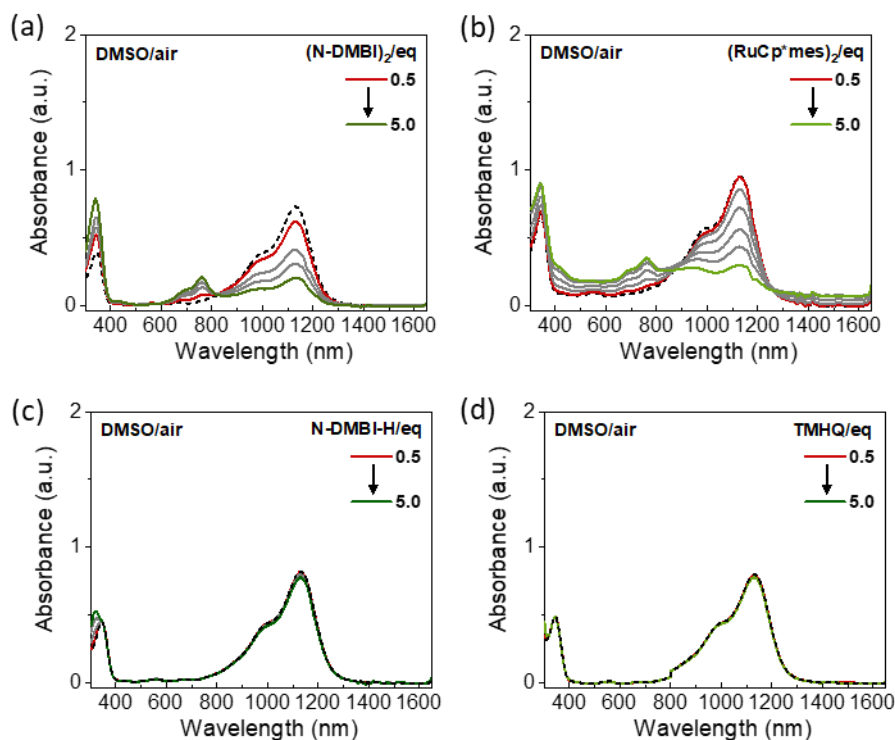


Figure S20. UV-vis-NIR spectrum when titrating $\text{BFD3}^{2-}/(\text{N-DMBI}^+)_2$ with (a) N-DMBI and (b) TMHQ.

Over-Reduction-Induced Degradation of BFD3^{2-}

To cross validate this degradation product, BFD1.5 was synthesized (Scheme S1). BFD1.5 can be deprotonated by DMSO, which exhibit an absorption spectrum matching with the degradation product (Figure S21). BFD1.5 was detected at m/z 431.1456 in ESI (–) mode (Figure S22). After 6 hours in DMSO, an additional peak at m/z 449.1547 appeared, indicating that BFD1.5 had undergone hydrolysis to hBFD1.5 (Figure S22).

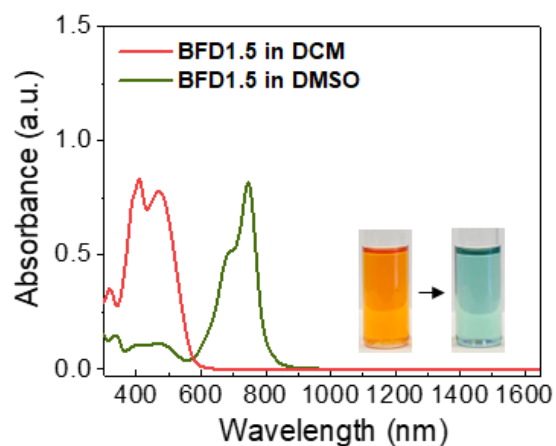


Figure S21. UV-vis-NIR spectra of BFD1.5 in DCM and in DMSO.

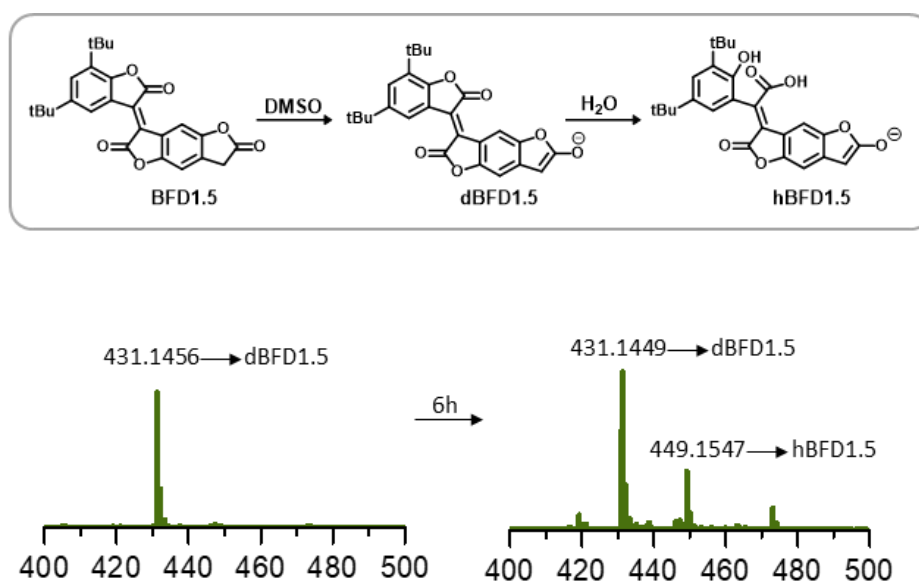


Figure S22. ESI-MS data showing BFD1.5 conversion to dBFD1.5 in DMSO and subsequent hydrolysis to hBFD1.5.

Degradation Pathway of n-PBDF at High Doping Levels

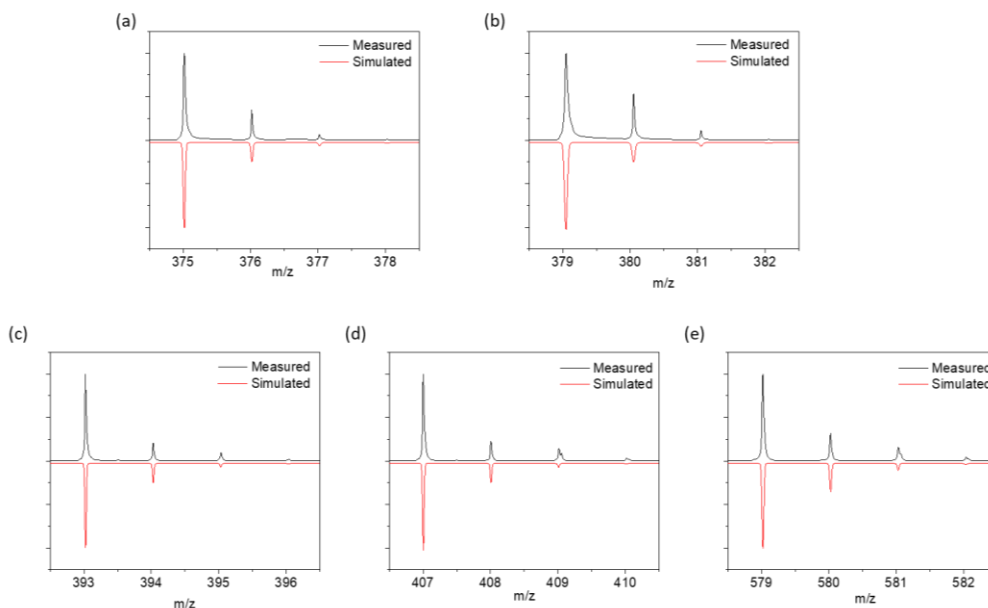


Figure S23. Zoomed-in spectra at m/z (a) 375, (b) 379, (c) 393, (d) 407, and (e) 579 (black: experimental; red: simulation).

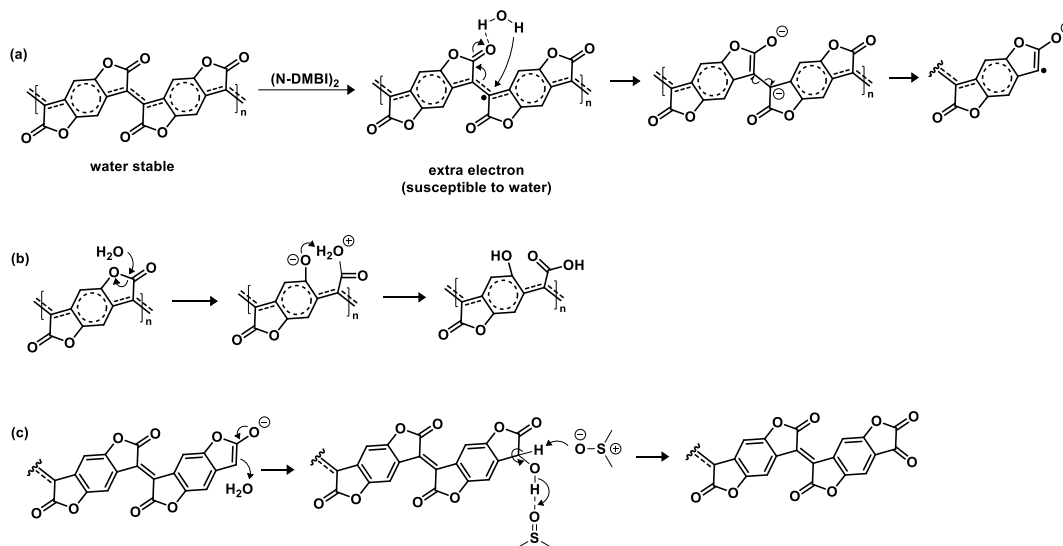
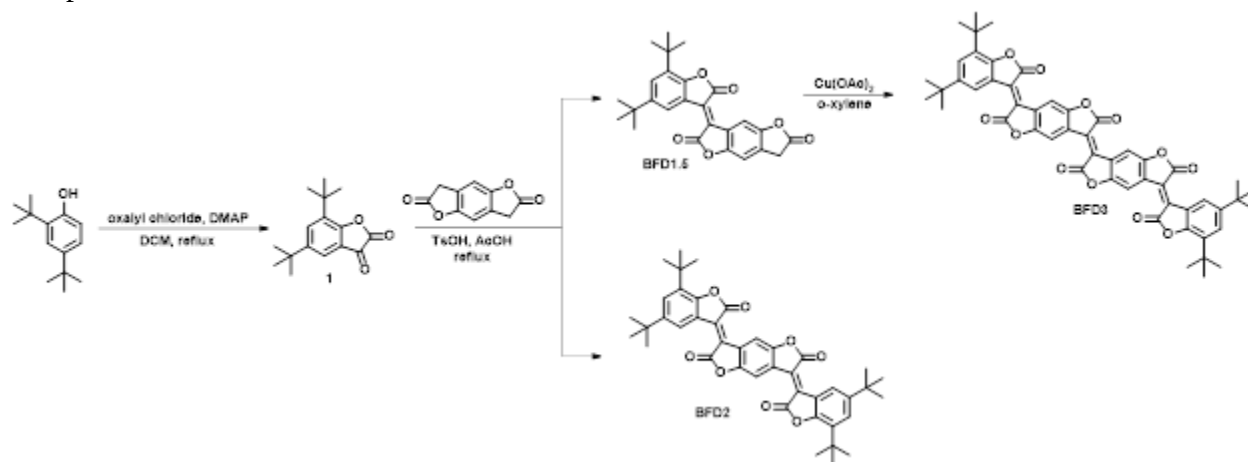


Figure S24. Proposed high doping induced degradation mechanism via (a) ring cleavage, (b) hydrolysis, and (c) oxidation.

Synthesis

All reagents were purchased from Sigma–Aldrich, TCI, and Fisher and used without purification. Dopants (N-DMBI)₂ and (RuCp*mes)₂, and compound 1 were synthesized via previously reported methods.^{5,6} The synthesis of BFD3 began with the conversion of phenol to benzofuran-2,3-dione via Lewis-acid catalyzed Friedel-Crafts acylation. This was followed by an acid-catalyzed aldol condensation and a copper-catalyzed oxidative dimerization, resulting in the final model compound, BFD3.



Scheme S1. Synthesis of BFD3.

Synthesis of compound 1

In a 100 mL round bottom flask, 2,4-di-*tert*-butyl phenol (5g, 24 mmol) were dissolved in DCM (100 mL), then oxalyl chloride (4.2 mL, 48 mmol) and DMAP (878 mg, 7.2 mmol) were added. The solution was refluxed for 3 h and the completion of the reaction was monitored by TLC. Solvent and oxalyl chloride was removed by rotary evaporation. Afterward that the obtained product was dissolved in DCM (100 mL), AlCl₃ (6.4 g, 48 mmol) was added in 30 min at room temperature, accompanied by additional stirring for 30 min at room temperature. Then the reaction mixture was poured into ice carefully for hydrolysis. The color turned from dark to yellow, then the organic phase was separated. The aqueous layer was extracted with DCM and the combined organic phase was washed with water, brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure to obtain the crude product. The crude products were recrystallized to afford compound 1 as bright yellow crystals. ¹H NMR (CDCl₃, 300 MHz): δ 7.76 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 1.44 (s, 9H), 1.34 (s, 9H). ¹³C NMR (CDCl₃, 125 MHz): δ 29.3, 31.1, 34.4, 34.8, 118.9, 119.5, 135.1, 135.9, 148.7, 156.3, 160.2, 178.1.

Synthesis of BFD1.5 and BFD2

Compound 1 (860 mg, 2 mmol), 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (380 mg, 2 mmol), and toluenesulfonic acid (TsOH) (344 mg, 2 mmol) were stirred in acetic acid (15 mL) at 115 °C under nitrogen for 17 h. The reaction mixture was then cooled to room temperature, evaporated, and 25 mL of hexane was added, cooled down in a –20 °C freezer for 3 h and filtered. The solid was washed with hexane. The filtrate was purified through column chromatography on silica gel (dichloromethane: hexane 1:1, v:v) to yield 40 mg (4.6 %) of **BFD1.5** as a red solid and 520 mg (47 %) of **BFD2** as a dark purple solid.

BFD1.5; ^1H NMR (CDCl_3 , 300 MHz): δ 9.05 (d, J = 2.0 Hz, 1H), 8.90 (s, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.13 (d, J = 1.2 Hz, 1H), 3.85 (s, 2H), 1.45 (s, 9H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 125 MHz): δ 172.6, 166.9, 166.4, 152.3, 150.9, 147.1, 132.9, 131.3, 130.2, 129.0, 127.2, 124.2, 122.6, 122.3, 111.1, 107.3, 35.1, 34.4, 33.8, 31.4, 29.5. HRMS (ESI) m/z : $[\text{M}]^-$ Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ 260.1412; Found 260.1408. TLC (ethyl acetate/hexane = 1/1) Rf: 0.21.

BFD2; ^1H NMR (CDCl_3 , 800 MHz): δ 9.10 (d, J = 2.0 Hz, 1H), 8.92 (s, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.13 (d, J = 1.2 Hz, 1H), 1.46 (s, 9H), 1.40 (s, 9H). ^{13}C NMR (none, 126 MHz): δ 167.0, 165.5, 151.5, 146.6, 134.6, 133.0, 130.4, 126.6, 124.7, 122.4, 110.0, 95.7, 34.9, 32.9, 31.6, 29.7. HRMS (ESI) m/z : $[\text{M}]^-$ Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ 260.1412; Found 260.1408. TLC (ethyl acetate/hexane = 1/1) Rf: 0.21.

Synthesis of BFD3

Under an air atmosphere, compound 2 (20 mg, 0.05 mmol) and $\text{Cu}(\text{OAc})_2$ (3 mg, 0.015 mmol) were added to o-xylene (5 mL), and the mixture was stirred at 100 °C for 2 h. After the reaction was complete, the reaction mixture was evaporated, and the crude product was purified via silica-gel column chromatography (hexane:DCM= 1:1 v/v) to obtain 13 mg BFD3 (60%), which was a blue solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 9.12 (d, J = 2.0 Hz, 1H), 8.97 (d, J = 5.8 Hz, 2H), 7.63 (d, J = 2.0 Hz, 1H), 1.48 (s, 9H), 1.41 (s, 9H). ^{13}C NMR (none, 126 MHz) δ 167.8, 165.8, 164.3, 152.5, 149.4, 134.2, 132.6, 129.0, 126.1, 122.5, 111.9, 110.1, 36.3, 34.9, 32.2, 29.9. HRMS (ESI) m/z : $[\text{M}]^-$ Calcd for $\text{C}_{52}\text{H}_{44}\text{O}_{12}$ 860.2838; Found 860.2799. UV-Vis (0.05 mM in DCM, nm): 474, 630, 670. TLC (hexane/dichloromethane = 1/1) Rf: 0.1.

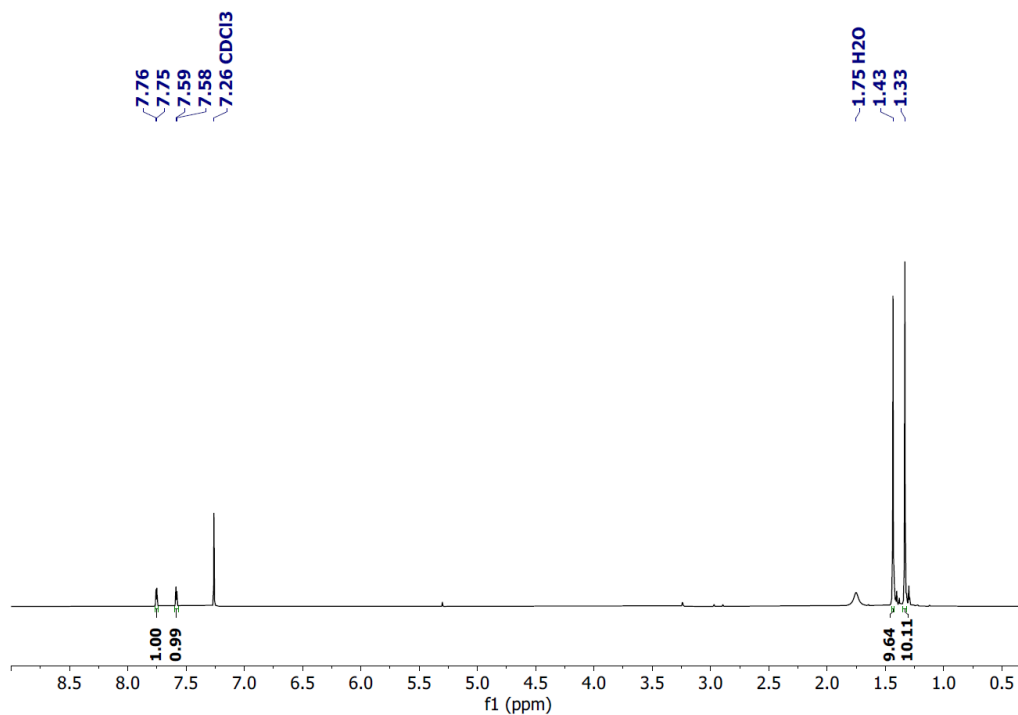


Figure S25. ¹H NMR of Compound 1

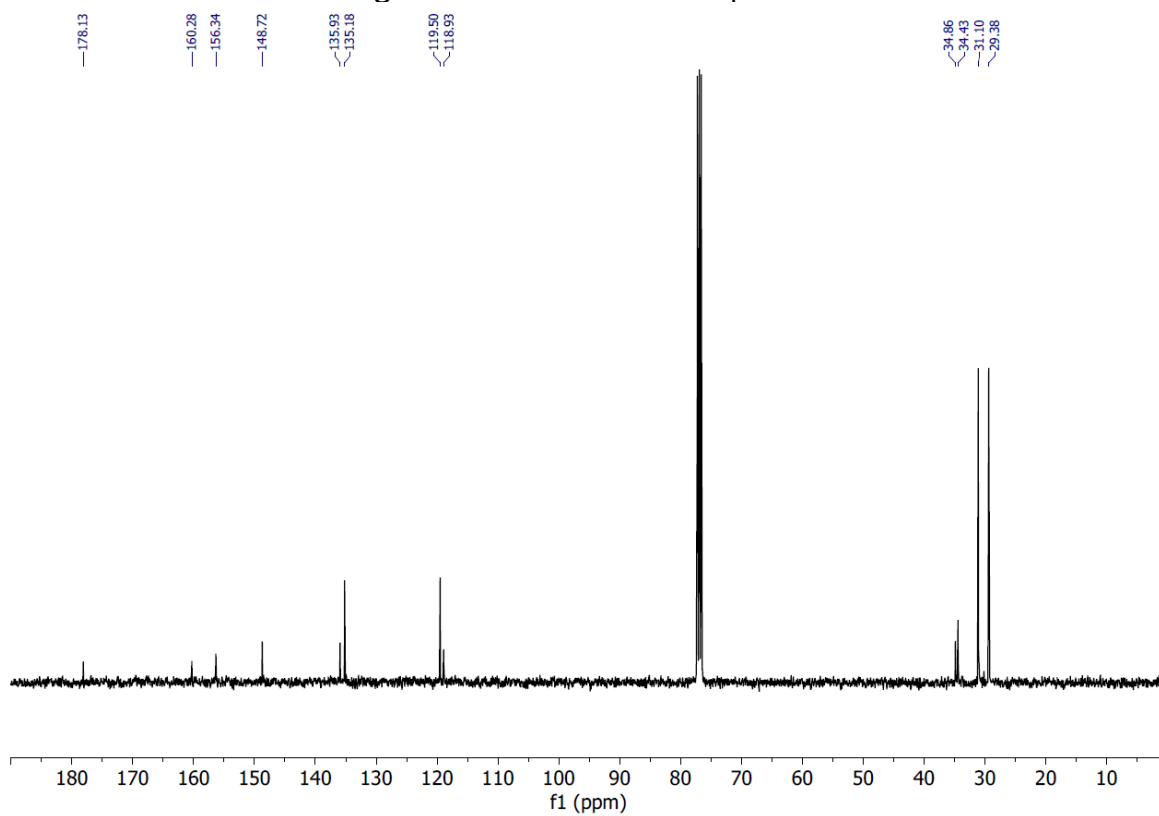


Figure S26. ¹³C NMR of Compound 1.

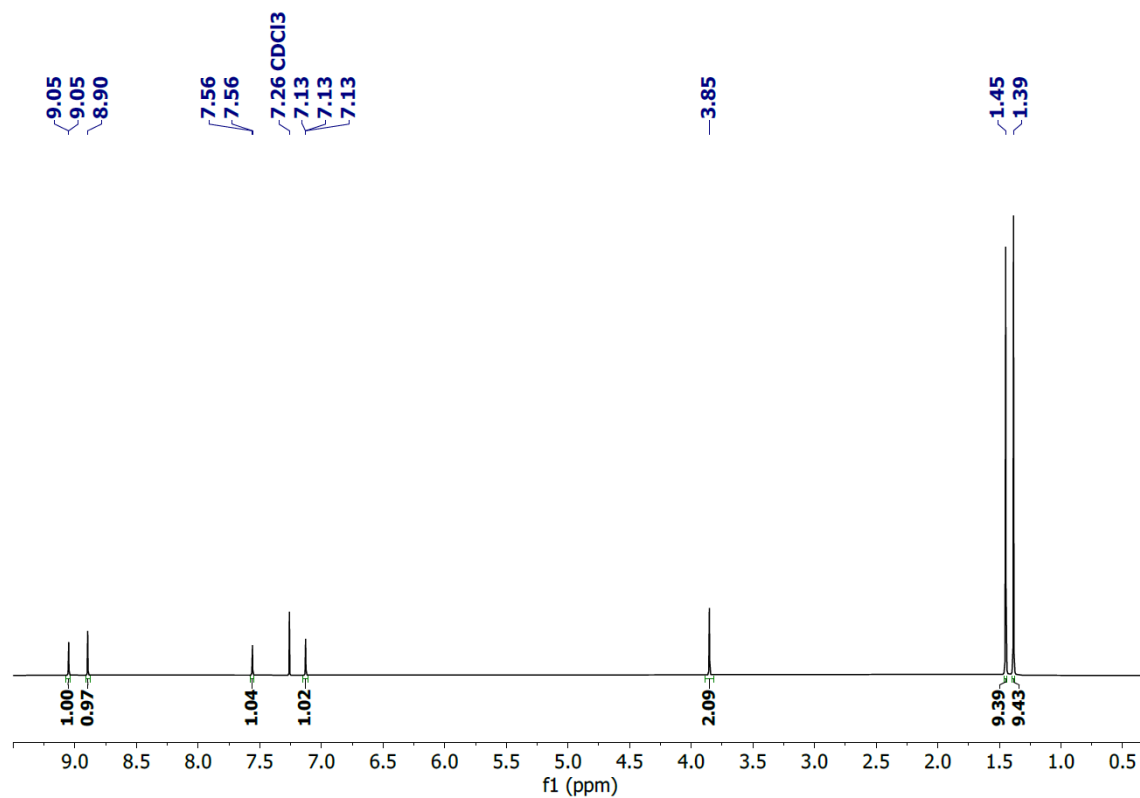


Figure S27. ¹H NMR of Compound **BFD1.5**

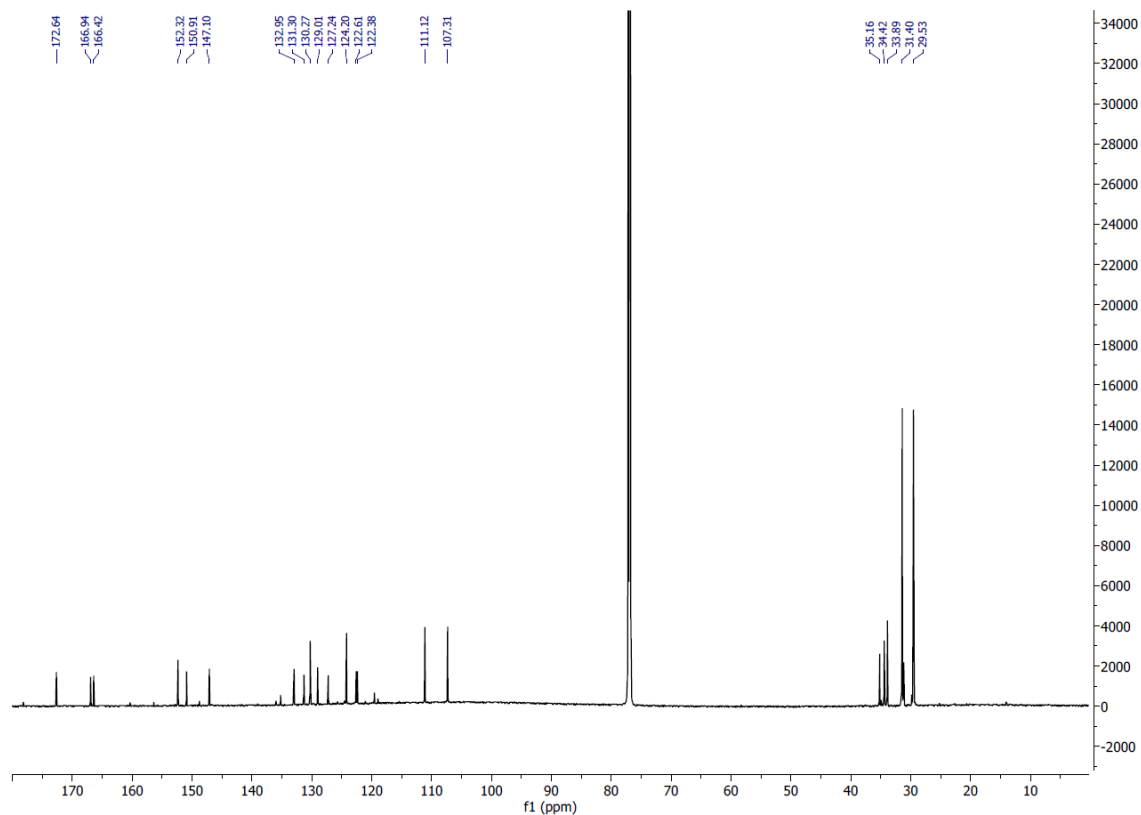
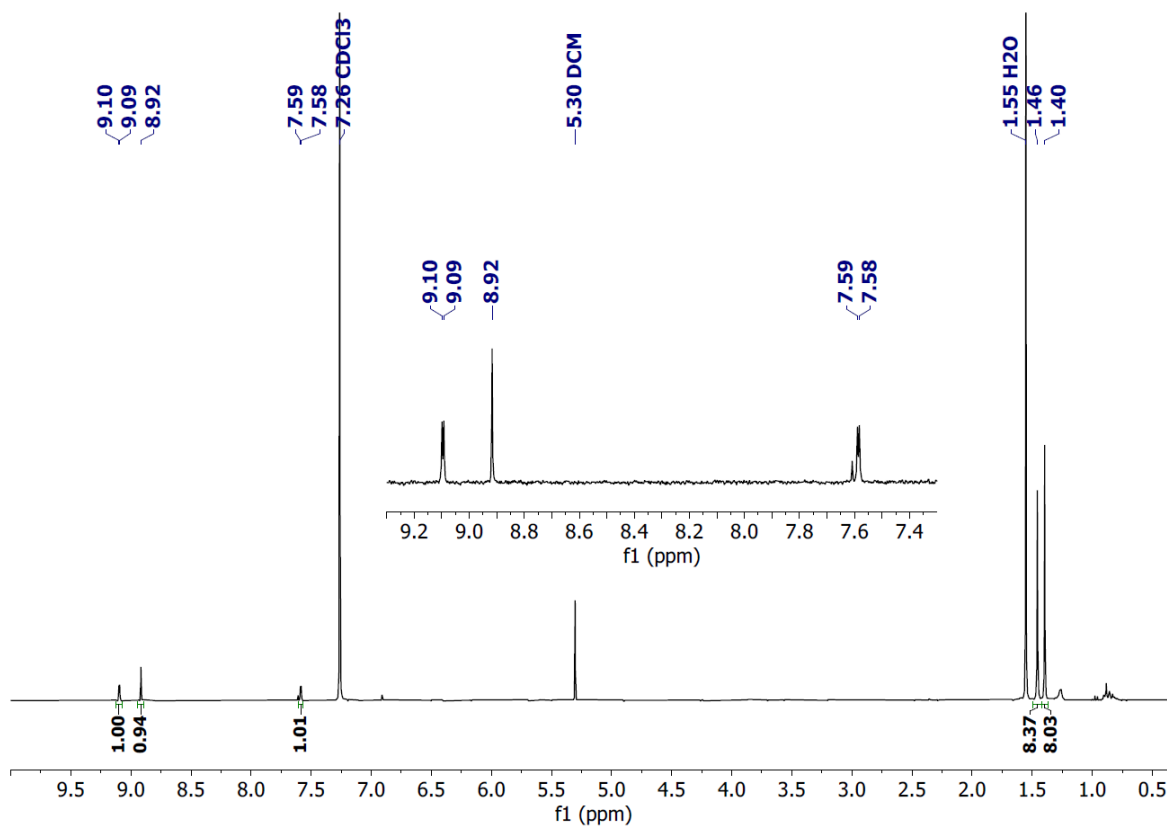
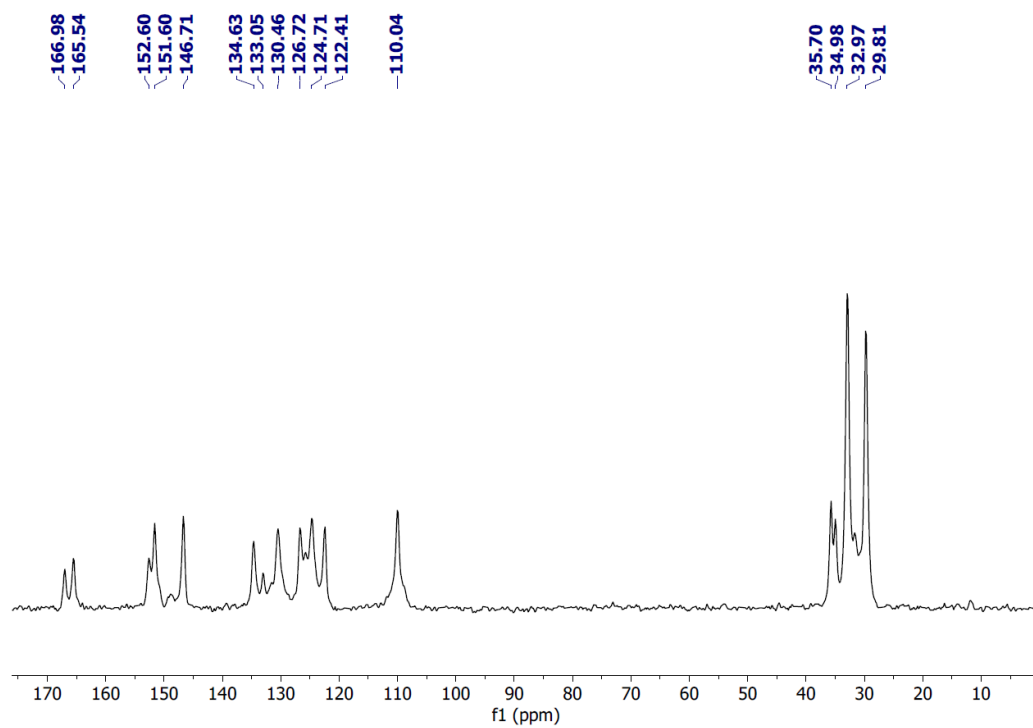


Figure S28. ¹³C NMR of Compound **BFD1.5**



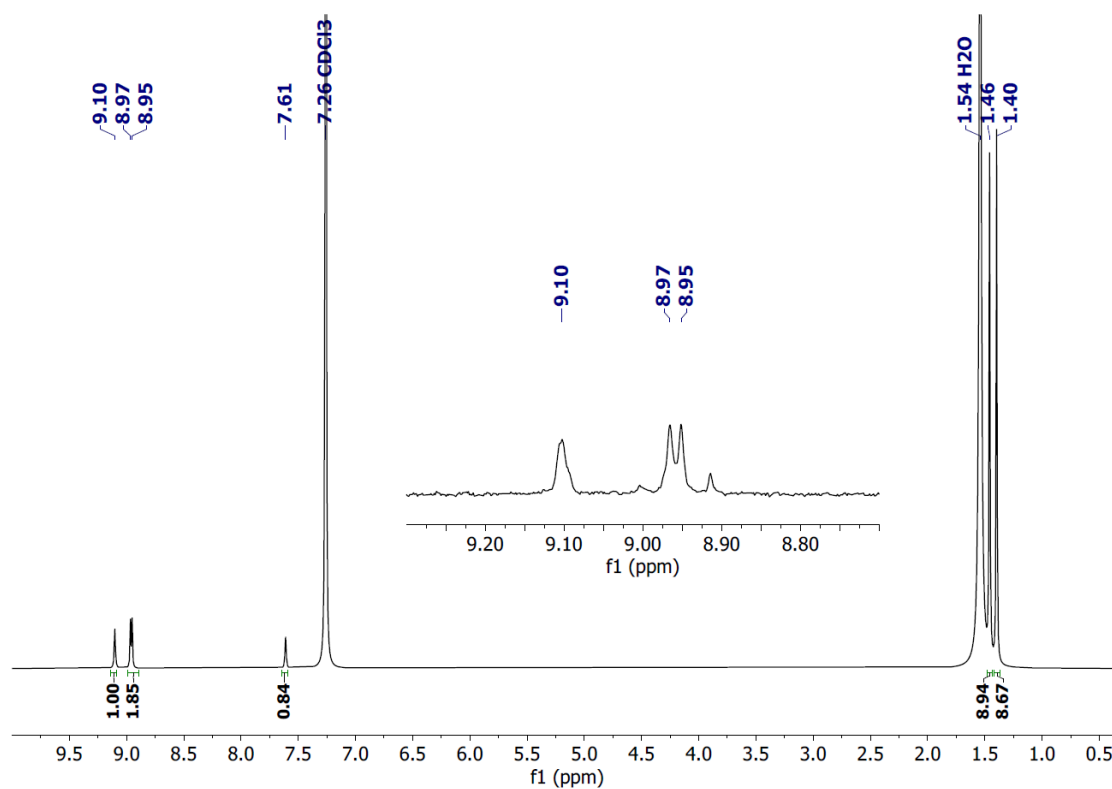


Figure S31. ¹H NMR of BFD3

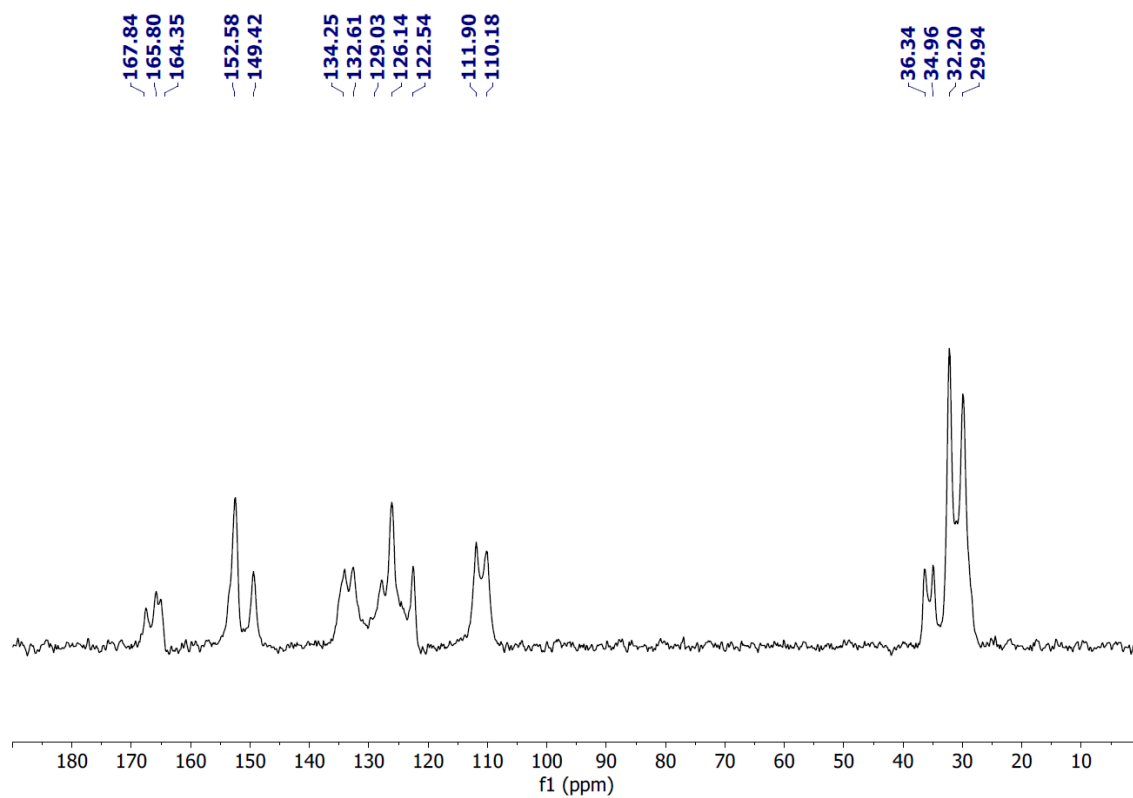


Figure S32. Solid state ¹³C NMR of BFD3

References

- (1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian16, Revision C.01. Gaussian Inc. Wallingford CT 2016.
- (2) Hwang, J.; Zhao, Q.; Ahmed, M.; Yakisan, A. C.; Espenship, M. F.; Laskin, J.; Savoie, B. M.; Mei, J. Reductive Doping Inhibits the Formation of Isomerization-Derived Structural Defects in N-Doped Poly(Benzodifurandione) (n-PBDF). *Angew. Chem. Int. Ed.* **2024**, 63, e202401465.
- (3) Tang, H.; Liang, Y.; Liu, C.; Hu, Z.; Deng, Y.; Guo, H.; Yu, Z.; Song, A.; Zhao, H.; Zhao, D.; Zhang, Y.; Guo, X.; Pei, J.; Ma, Y.; Cao, Y.; Huang, F. A Solution-Processed n-Type Conducting Polymer with Ultrahigh Conductivity. *Nature* **2022**, 611, 271–277.
- (4) Tang, H.; Cai, H.; Zhao, H.; Liu, Z.; Tan, R.; Huang, F. A Solution-Processed n-Type Conducting Polymer Without Side Chains Formed via Nonmetal-Participated Polymerization and in Situ n-Doping. *CCS Chem.* **2023**, 5, 2534–2544.
- (5) Naab, B. D.; Zhang, S.; Vandewal, K.; Salleo, A.; Barlow, S.; Marder, S. R.; Bao, Z. Effective Solution- and Vacuum-Processed n-Doping by Dimers of Benzimidazoline Radicals. *Adv. Mater.* **2014**, 26, 4268–4272.
- (6) Guo, S.; Kim, S. B.; Mohapatra, S. K.; Qi, Y.; Sajoto, T.; Kahn, A.; Marder, S. R.; Barlow, S. N-Doping of Organic Electronic Materials Using Air-Stable Organometallics. *Adv. Mater.* **2012**, 24, 699–703.