



## Supporting Information

### **Reductive Doping Inhibits the Formation of Isomerization-Derived Structural Defects in N-doped Poly(benzodifurandione) (n-PBDF)**

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## **Reductive Doping Inhibits the Formation of Isomerization-Derived Structural Defects in N-doped Poly(benzodifurandione) (n-PBDF)**

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## 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 (TBAPF<sub>6</sub>) 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<sup>+</sup>) was used as an external standard to calculate the  $E_{\text{LUMO}}$ . Cyclic voltammetry was performed at a scan rate of 20 mV s<sup>-1</sup>, 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 (TBAPF<sub>6</sub>) 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.

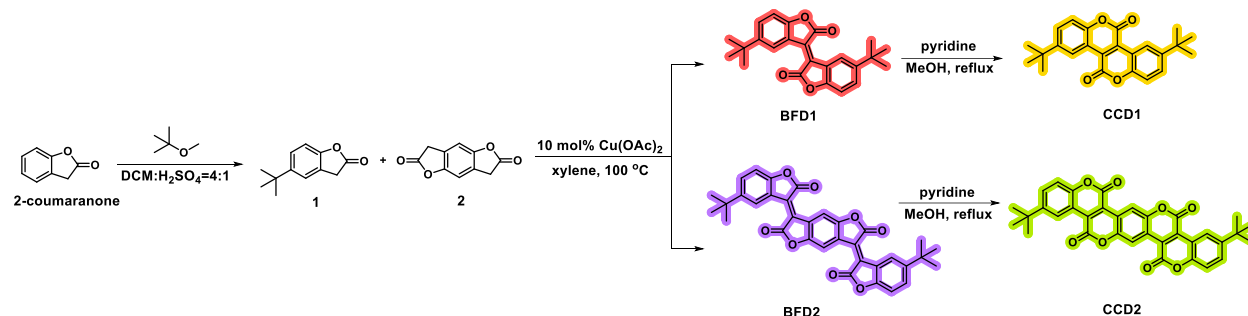
*ESI-Mass spectrometric measurements:* ESI-MS were acquired using an Agilent 6560 ion mobility quadrupole time-of-flight (IM Q-TOF) mass spectrometer (Santa Clara, CA, USA) fitted with a custom-designed electrospray ionization (ESI) source. A 1000  $\mu$ M solution of sample species was infused into the inlet of the instrument via a fused-silica capillary (50 $\mu$ m ID, 150 $\mu$ m OD) at a flow rate of 1 $\mu$ L/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:* YARP v2.0 package was utilized to explore the isomerization pathway,<sup>1</sup> employing GFN2-xTB<sup>2</sup> for pre-exploring the transition states and B3LYP-D3/TZVP<sup>3,4</sup> with Conductor-like Polarizable Continuum Model (CPCM, using DMSO as solvent)<sup>5,6</sup> as a more accurate DFT level of theory to quantitatively describe the reaction properties. A bi-directional search was conducted by YARP, which has been extensively described for potential energy surface exploration,<sup>1,7</sup> and a modified Dijkstra algorithm as the reaction network exploration policy.<sup>8</sup> The bi-directional search was initiated from BDF and CCD to identify a low-barrier isomerization pathway between these two isomers. The first step reaction explorations initiated from BDF and CCD considered both unimolecular reactions and bimolecular reactions with H<sub>2</sub>O, while the remaining explorations starting from other intermediates solely considered unimolecular reactions. A conditional break three bonds and form three bonds (Cb3f3) elementary reaction step was employed to enumerate possible reactions,<sup>1</sup> which included all b2f2 reactions and a subset of b3f3 reactions with at least one  $\pi$ -bond breaking and forming during the reaction. For each enumerated reaction, both a non-catalyzed mechanism and a H<sub>2</sub>O-catalyzed mechanism where an additional H<sub>2</sub>O molecule served as a proton shuttle were tested. The mechanism with the lower  $\Delta G^\ddagger$  was selected. After each step of the exploration, the modified Dijkstra algorithm was used to select the five intermediates with the lowest overall barrier ( $\Delta G^\ddagger$  of the rate-limiting step) as the active intermediates for seeding further explorations. To avoid exploring reactions with high energy-barriers, we implemented a threshold for the free energy of activation ( $\Delta G^\ddagger$ ). Specifically, we excluded reactions with  $\Delta G^\ddagger$  computed by GFN2-xTB larger than 50 kcal/mol from DFT characterizations. Moreover, we excluded reactions with  $\Delta G^\ddagger$  computed by DFT larger than 40 kcal/mol from further characterization via intrinsic reaction coordinate (IRC) calculations. We direct readers to our previous studies for more details.<sup>1,7-10</sup>

## Synthesis

All reagents were purchased from Sigma–Aldrich, TCI, and Fisher and used without purification. Compound **2** was synthesized via previously reported methods.<sup>11</sup>



**Scheme S1.** Synthesis of BFD1, CCD1, BFD2, and CCD2.

As shown in Scheme S1, the *tert*-butyl groups were introduced onto 2-coumaranone under acidic conditions to give **1**. Next, oxidative coupling of **1** with **2** mediated by copper(II) acetate in *o*-xylenes selectively gave a mixture of the BFD1 and BFD2. The same oxidative coupling conditions (10 mol% Cu(OAc)<sub>2</sub>, 100 °C) in DMSO exclusively resulted in CCD1. The isomerization of BFD2 to CCD2 is not seen in DMSO because BFD2 is readily doped in this condition, preventing isomerization. Refluxing BFD1 or BFD2 in a mixture of pyridine and methanol results in CCD1 or CCD2, respectively.

### Synthesis of compound 1

To a stirred solution of 2-coumaranone (1.52 g, 11.3 mmol) in DCM:H<sub>2</sub>SO<sub>4</sub> (4:1 v/v, 50 mL) was added methyl *tert*-butyl ether (1.6 mL, 13.5 mmol) and heated in an oil bath at 40 °C for 14 h. Stirring was stopped when two phases separated in red (top) and brown (bottom). The brown phase was discarded and red phase was purified via flash column chromatography (Hexane:DCM=2:1) and recrystallized from hexane and placed into a –20 °C freezer to give **1** as white crystals in 55% yield (1.18 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.37 – 7.29 (m, 2H), 7.02 (d, *J* = 9.2 Hz, 1H), 3.72 (s, 2H), 1.32 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 174.4, 152.4, 147.2, 125.5, 122.5, 121.5, 109.9, 34.5, 33.1, 31.4

### Synthesis of BFD1 and BFD2

In the air, compound **2** (BDF, 0.19 g, 1.0 mmol), compound **1** (1.9 g, 10 mmol, 10 eq), Cu(OAc)<sub>2</sub> (54 mg, 0.3 mmol, 0.33 eq), and dried molecular sieves were added to an anhydrous *o*-xylene (25 mL) in a round bottom flask (100 mL), and the mixture was stirred in an oil bath at 100 °C for 14 h. After the reaction mixture was cooled to room temperature, hexane (25 mL) was added. The flask was stored in a freezer (~ –20 °C) for 3 h. The precipitate (BFD2) was filtered. The obtained solid from the Büchner funnel was further purified via silica gel column chromatography (hexane:DCM=1:2). It was then recrystallized in hot hexane to yield BFD2 as a purple solid in 48% yield (280 mg). From the filtrate, we can recover BFD1 as a red solid in 84% yield (0.89 g) after the silica gel column chromatography purification and (hexane:DCM=1:1) and recrystallization from hexane. BFD1; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.21 (d, *J* = 2.1 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.09 (dd, *J* = 8.5, 0.5 Hz, 1H), 1.39 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 167.2, 153.7, 147.4, 131.6, 129.1, 126.5, 122.1, 109.8, 34.9, 31.3. HRMS (APCI–) *m/z*: Calculated for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>: 376.1753; Found 376.1767.

BFD2;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 9.25 (s, 2H), 8.94 (s, 2H), 7.64 (d,  $J = 8.3$  Hz, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz) 167.1, 166.6, 154.8, 152.3, 148.3, 133.6, 132.2, 127.5, 126.8, 122.3, 110.9, 110.4, 35.3, 31.5. HRMS (APCI-)  $m/z$ : Calculated for  $\text{C}_{34}\text{H}_{26}\text{O}_8$ : 563.1706; Found 563.1713.

#### Synthesis of CCD1

**BFD1** (300 mg, 0.80 mmol) was added to a mixture of pyridine:MeOH (1:10 v/v, 11 mL), and the reaction was refluxed for 10 h. After cooling the reaction mixture to room temperature, the reaction mixture was extracted with DCM and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the crude product was purified via silica gel column chromatography (hexane:DCM=1:1) and recrystallized in MeOH to obtain CCD1 as a yellow solid (87%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.32 (d,  $J = 2.3$  Hz, 1H), 7.68 (dd,  $J = 8.7, 2.3$  Hz, 1H), 7.36 (d,  $J = 8.7$  Hz, 1H), 1.42 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  158.1, 150.4, 148.3, 129.7, 126.3, 124.5, 115.8, 115.1, 34.9, 31.3. HRMS (APCI-)  $m/z$ : Calculated for  $\text{C}_{24}\text{H}_{24}\text{O}_4$ : 376.1753; Found 376.1769.

#### Synthesis of CCD2

**BFD2** (30 mg, 0.05 mmol) were added to pyridine:MeOH (1:10 v/v, 11 mL), and the mixture was refluxed for 10 h. After cooling the reaction mixture to room temperature, the reaction mixture was extracted with DCM and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the crude product was purified via silica gel column chromatography (hexane:DCM=1:2) and recrystallized in hexane. The reaction product CCD2 was obtained as a yellow solid (76%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.25 (s, 2H), 8.94 (s, 2H), 7.64 (d,  $J = 8.3$  Hz, 2H), 7.11 (d,  $J = 8.4$  Hz, 2H), 1.40 (s, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  160.7, 148.7, 124.9, 116.1, 115.2, 31.3, 25.5. HRMS (APCI-)  $m/z$ : Calculated for  $\text{C}_{34}\text{H}_{26}\text{O}_8$ : 563.1706; Found 563.1703.

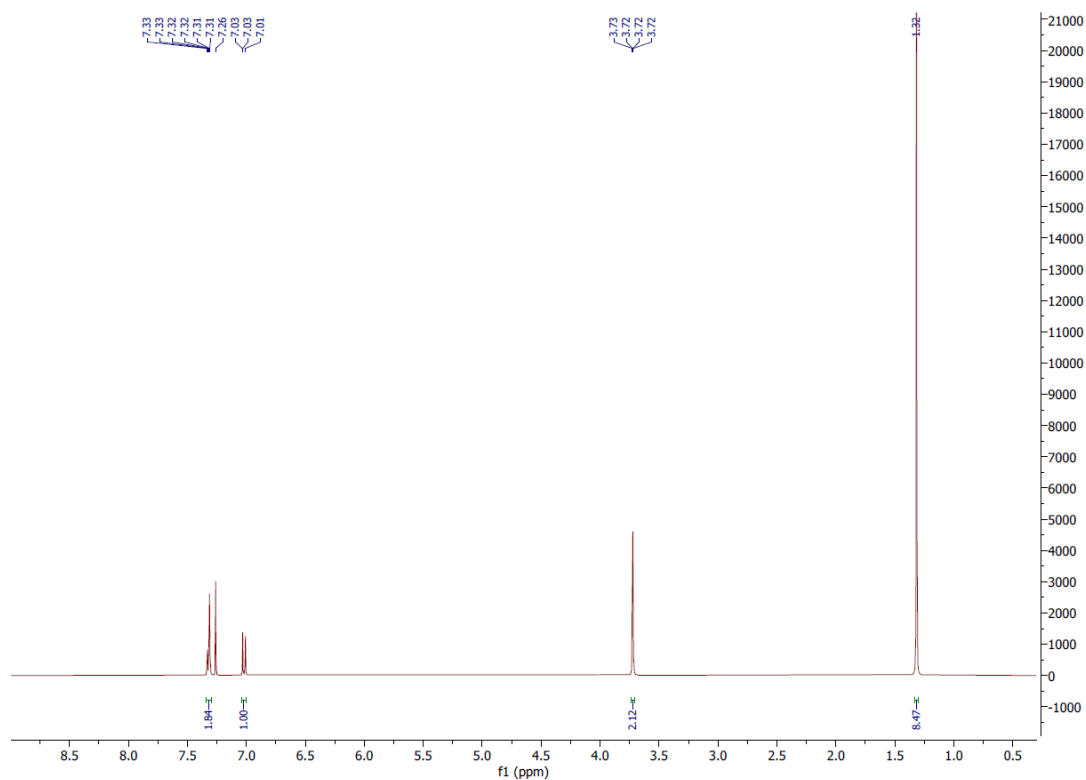


Figure S1. <sup>1</sup>H NMR of Compound 1

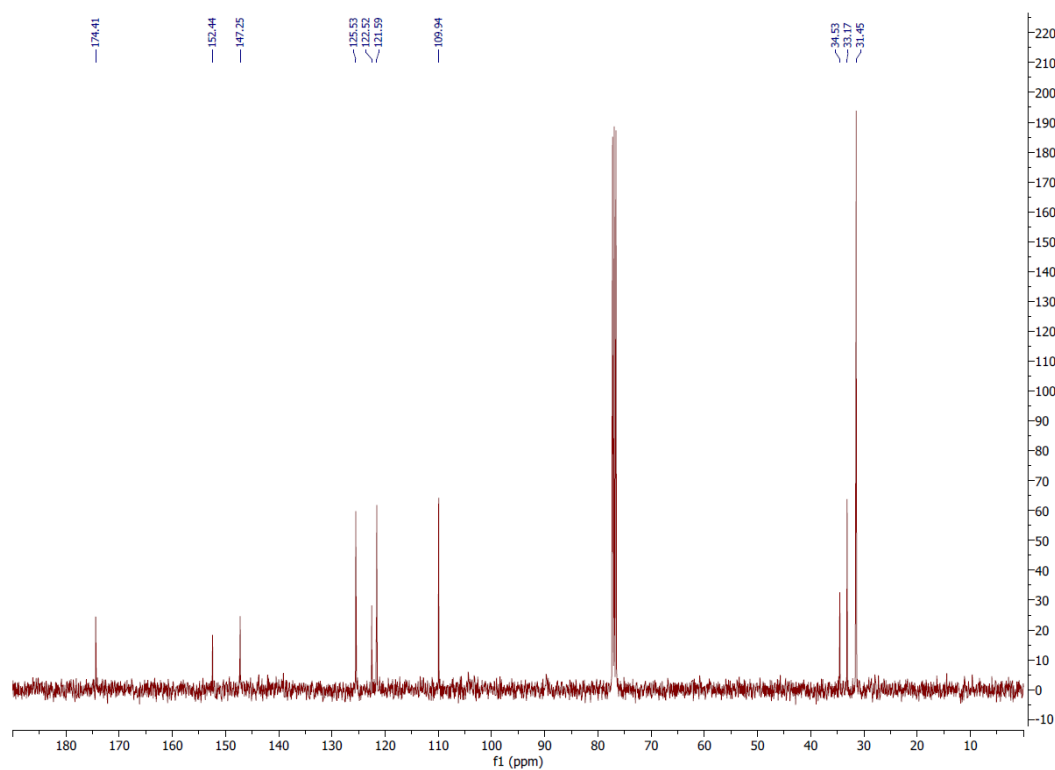


Figure S2. <sup>13</sup>C NMR of Compound 1

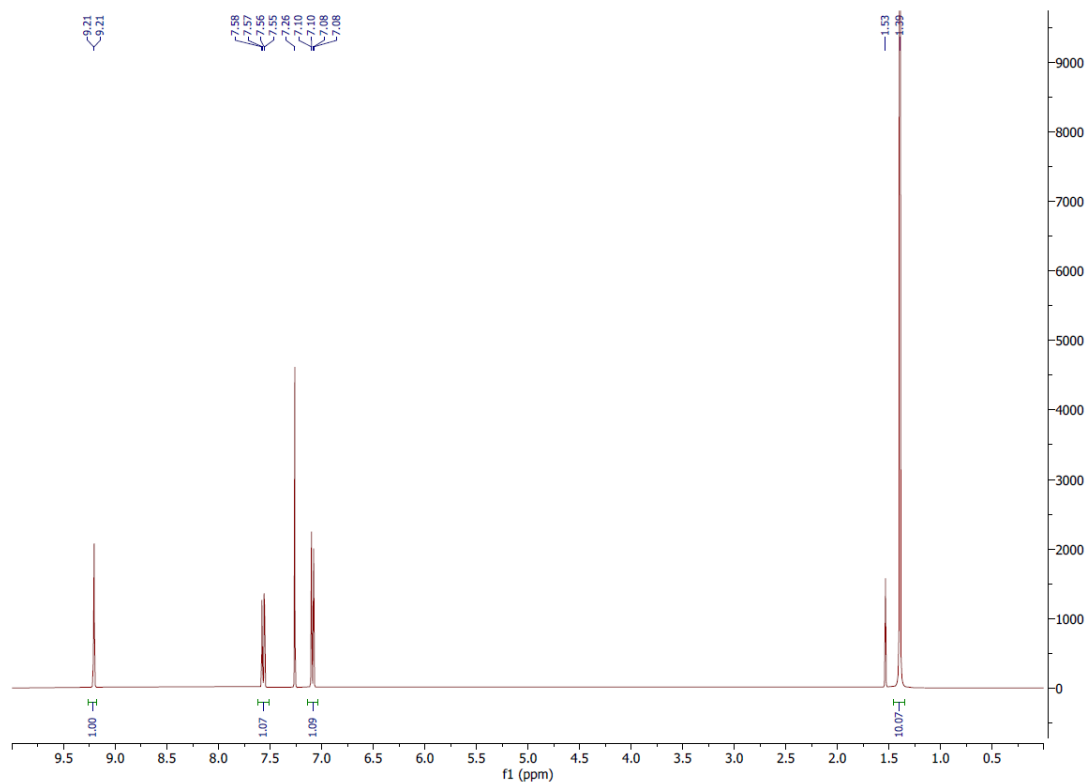


Figure S3. <sup>1</sup>H NMR of BFD1

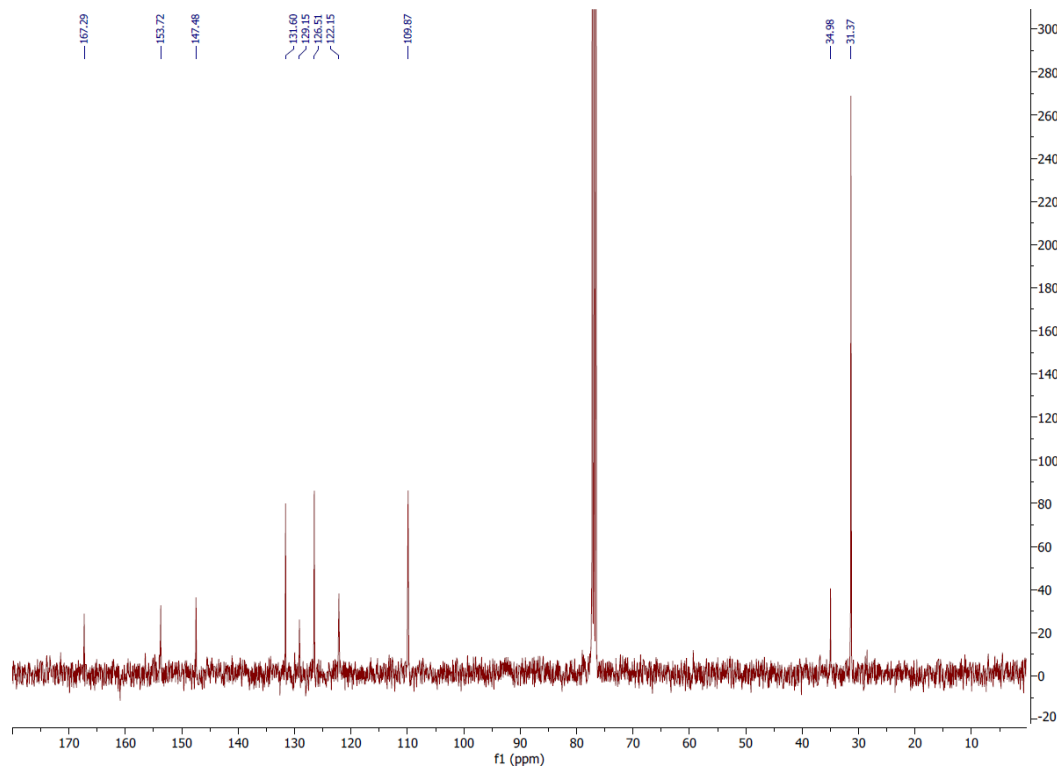


Figure S4. <sup>13</sup>C NMR of BFD1

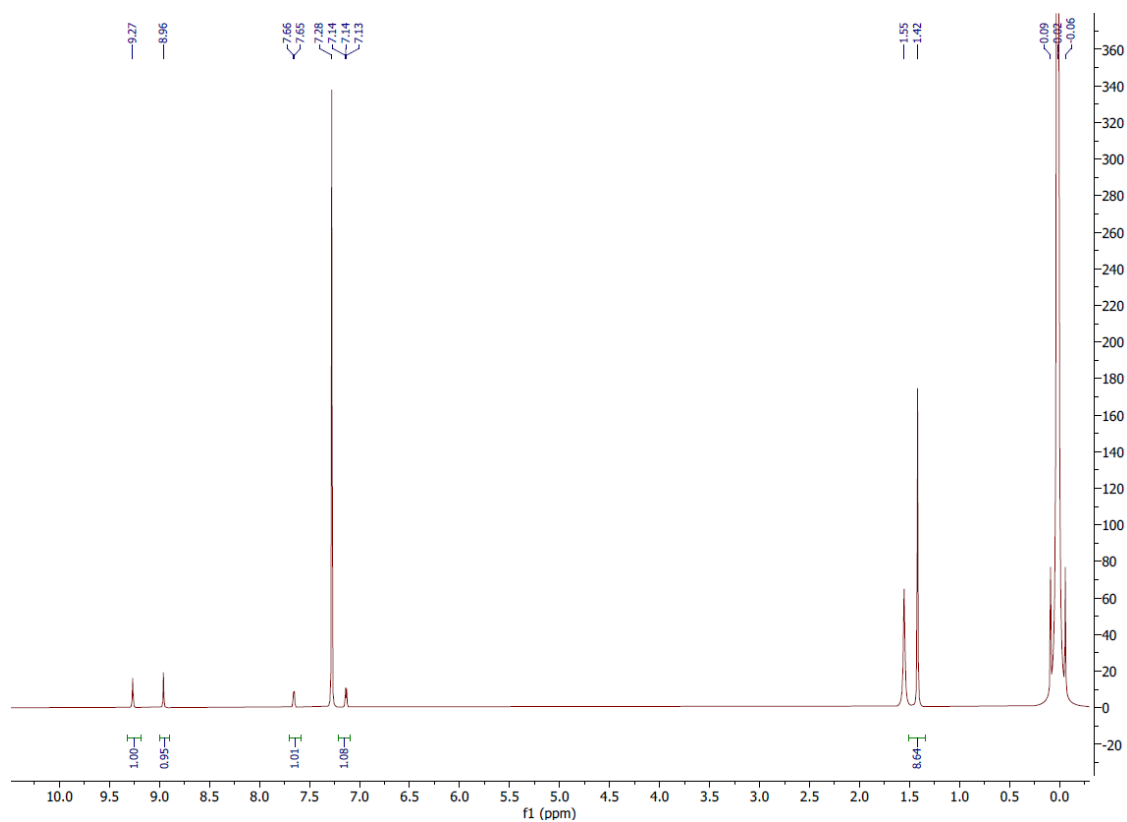


Figure S5. <sup>1</sup>H NMR of BFD2

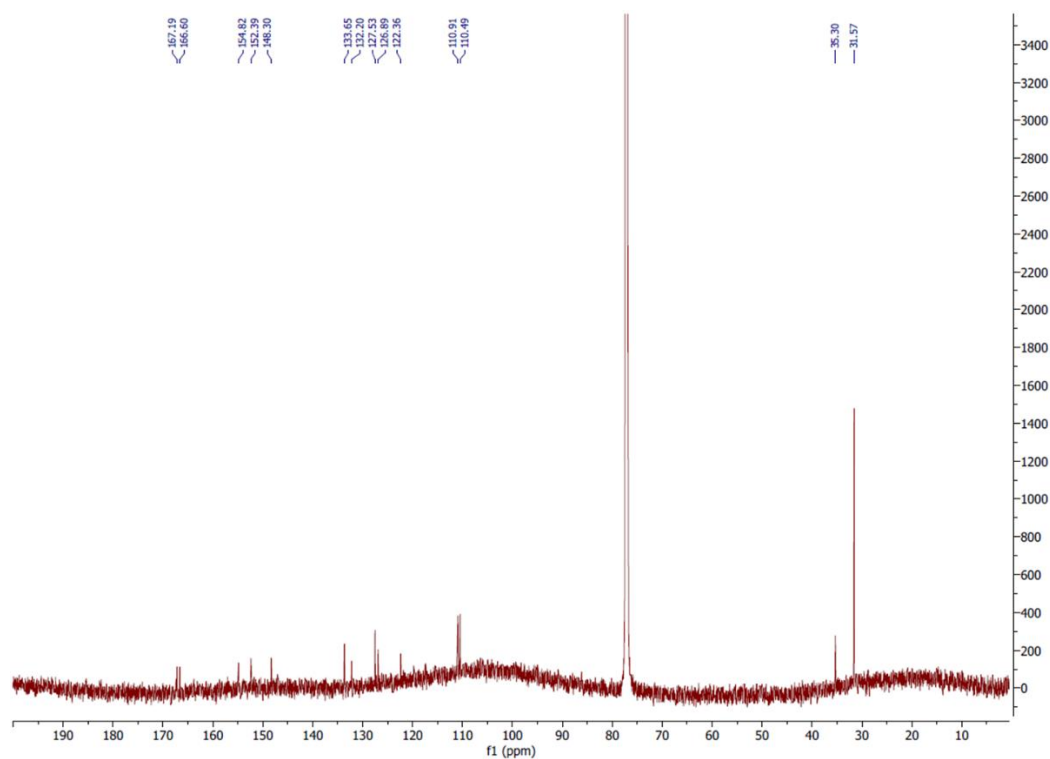


Figure S6. <sup>13</sup>C NMR of BFD2

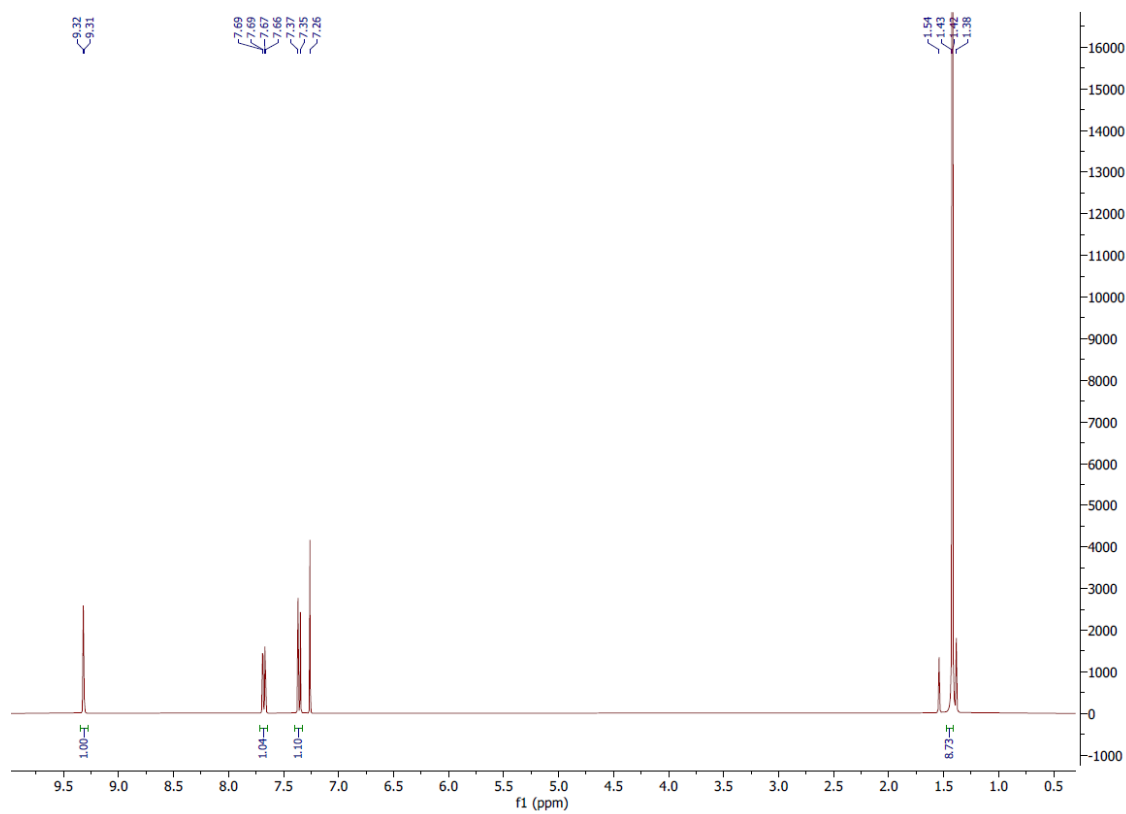


Figure S7. <sup>1</sup>H NMR of CCD1

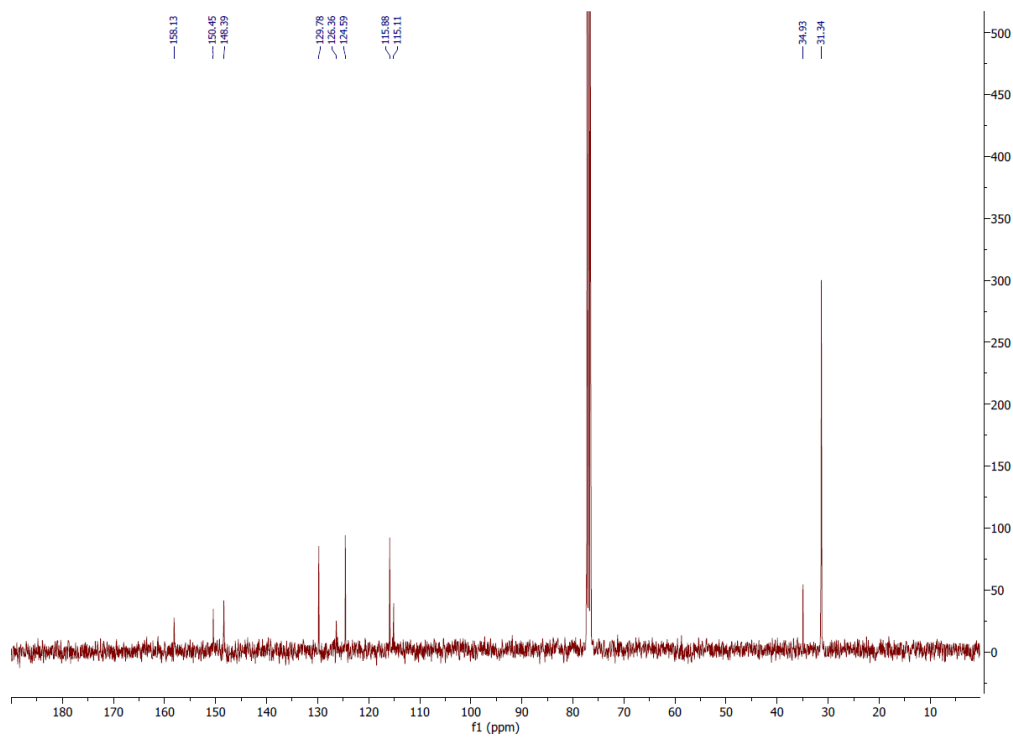


Figure S8. <sup>13</sup>C NMR of CCD1

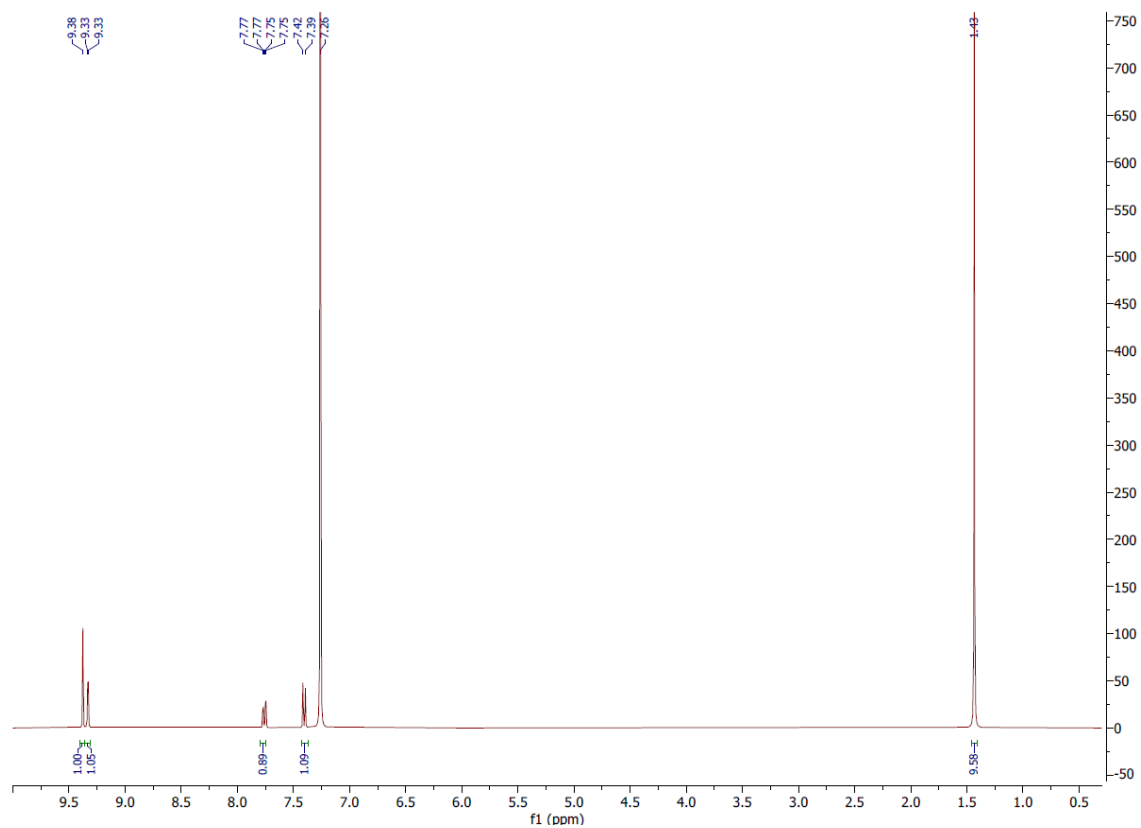


Figure S9. <sup>1</sup>H NMR of CCD2

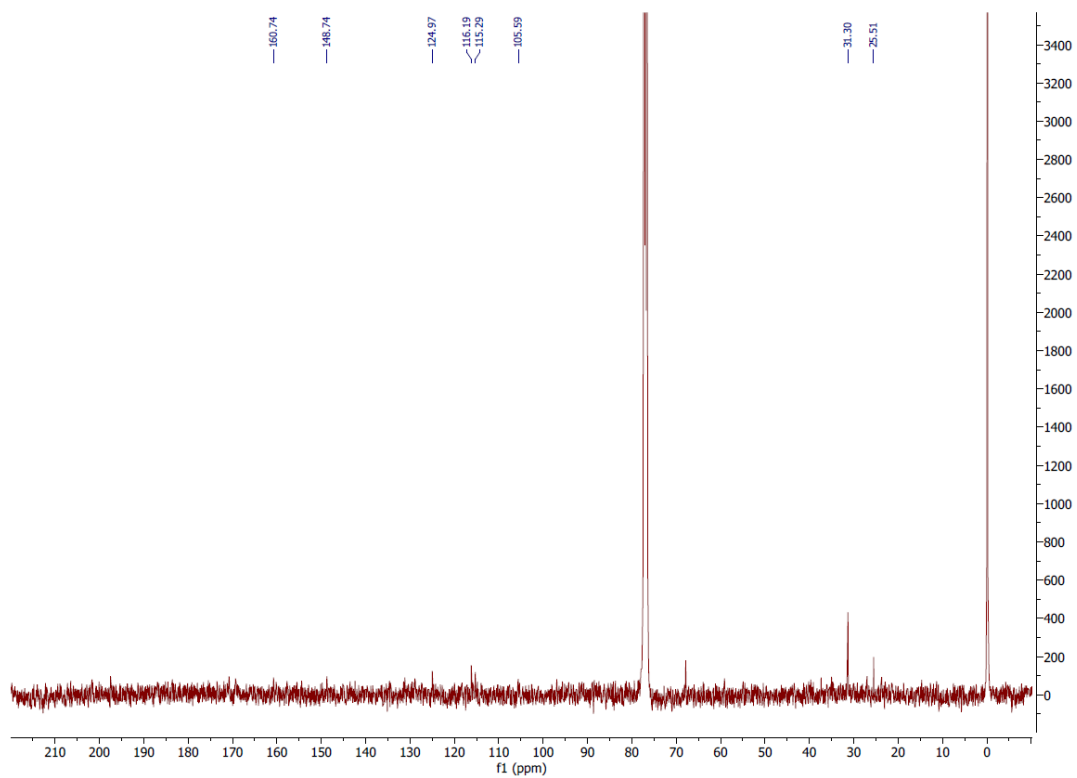


Figure S10. <sup>13</sup>C NMR of CCD2

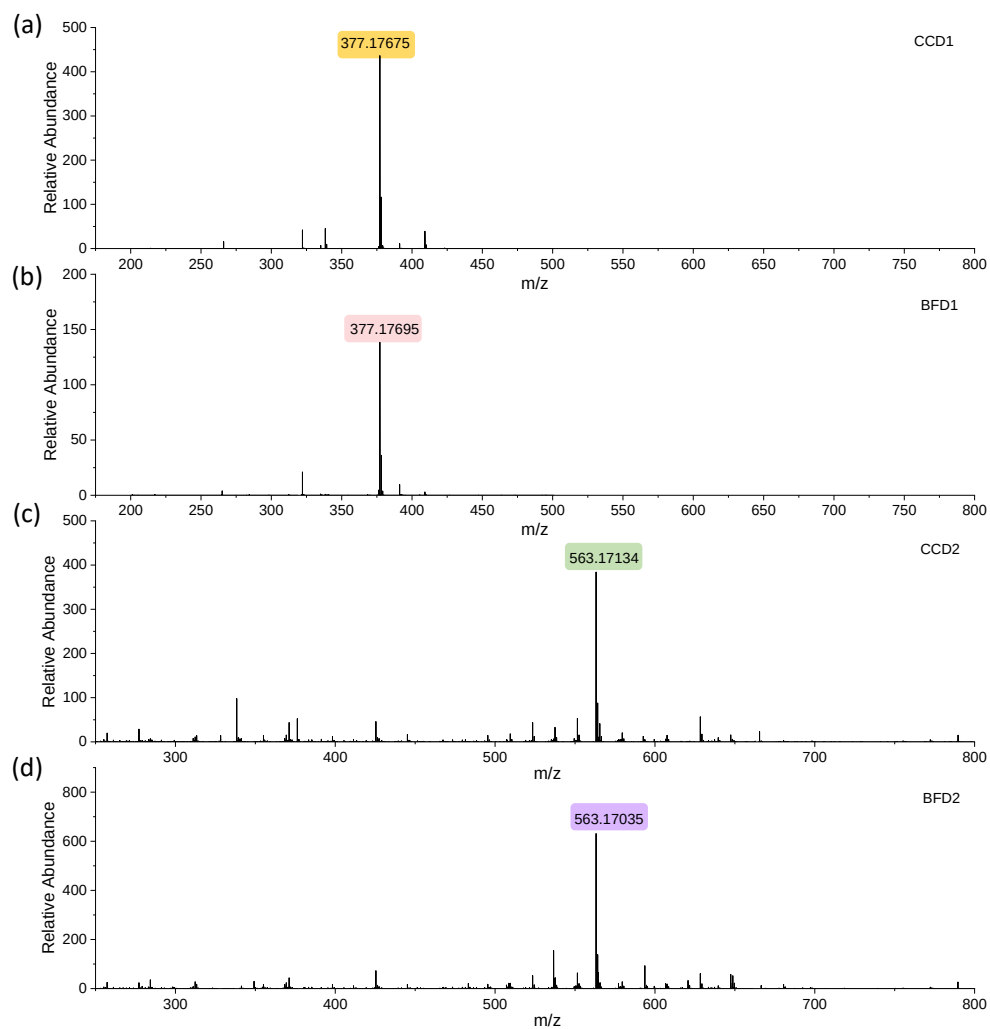


**Figure S11.** APCI+ full scan mass spectrum of (a) CCD1, (b) BFD1, (c) CCD2, and (d) BFD2.

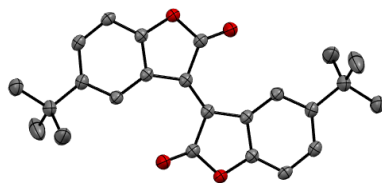


**Table S1.** Crystal data and structure refinement for BFD1.

|                                                                                                                |                                                                                   |
|----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|
| Chemical Formula                                                                                               | C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>                                    |
| Moiety Formula                                                                                                 | C <sub>14</sub> H <sub>24</sub> O <sub>4</sub>                                    |
| <i>M<sub>r</sub></i>                                                                                           | 376.43                                                                            |
| Crystal system, space group                                                                                    | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>                                    |
| Temperature (K)                                                                                                | 150                                                                               |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)                                                                             | 12.6231(7), 6.4963(4), 13.0310(7)                                                 |
| α, β, γ(°)                                                                                                     | 90, 109.682(3), 90                                                                |
| <i>V</i> (Å <sup>3</sup> )                                                                                     | 1006.16                                                                           |
| <i>Z</i>                                                                                                       | 2                                                                                 |
| Radiation Type                                                                                                 | Mo <i>K</i> α                                                                     |
| μ (mm <sup>-1</sup> )                                                                                          | 0.084                                                                             |
| Crystal Size (mm)                                                                                              | 0.50 × 0.21 0.06                                                                  |
| <b>Data Collection</b>                                                                                         |                                                                                   |
| Diffractometer                                                                                                 | Bruker AXS D8 Quest three circle diffractometer                                   |
| Absorption Correction                                                                                          | multi-scan                                                                        |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>                                                                | 0.979, 0.995                                                                      |
| No. of measured, independent, and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                            | 19493, 3083, 2324                                                                 |
| <i>R<sub>int</sub></i>                                                                                         | 0.0668                                                                            |
| <b>Refinement</b>                                                                                              |                                                                                   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.0657, 0.1342, 1.033                                                             |
| No. of reflections                                                                                             | 3083                                                                              |
| No. of parameters                                                                                              | 130                                                                               |
| No. of restraints                                                                                              | 0                                                                                 |
| H-atom treatment                                                                                               | Geom                                                                              |
|                                                                                                                | $w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.23971P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )                                                     | 0.386, -0.211                                                                     |

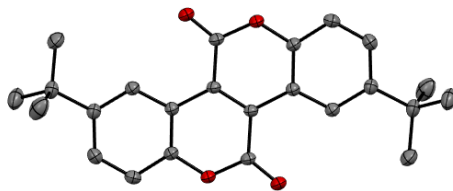


Table S2. Crystal data and structure refinement for CCD1.

### Crystal Data

|                                    |                                                |
|------------------------------------|------------------------------------------------|
| Chemical Formula                   | C <sub>24</sub> H <sub>24</sub> O <sub>4</sub> |
| Moiety Formula                     | C <sub>24</sub> H <sub>24</sub> O <sub>4</sub> |
| <i>M<sub>r</sub></i>               | 376.43                                         |
| Crystal system, space group        | Triclinic, <i>P</i> $\bar{1}$                  |
| Temperature (K)                    | 150                                            |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 5.8300(6), 6.2105(6), 13.9651(16)              |
| $\alpha$ , $\beta$ , $\gamma$ (°)  | 78.927(5), 85.139(5), 87.708(5)                |
| <i>V</i> (Å <sup>3</sup> )         | 494.29(9)                                      |
| <i>Z</i>                           | 1                                              |
| Radiation Type                     | Mo <i>K</i> α                                  |
| $\mu$ (mm <sup>-1</sup> )          | 0.085                                          |
| Crystal Size (mm)                  | 0.55 × 0.10 × 0.07                             |

### Data Collection

|                                                                                     |                                                 |
|-------------------------------------------------------------------------------------|-------------------------------------------------|
| Diffractometer                                                                      | Bruker AXS D8 Quest three circle diffractometer |
| Absorption Correction                                                               | multi-scan                                      |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>                                     | 0.955, 0.994                                    |
| No. of measured, independent, and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections | 13493, 2994, 2252                               |

|                        |        |
|------------------------|--------|
| <i>R<sub>int</sub></i> | 0.0455 |
|------------------------|--------|

### Refinement

|                                                                                                                |                                                                                                   |
|----------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.0725, 0.1514, 1.036                                                                             |
| No. of reflections                                                                                             | 2994                                                                                              |
| No. of parameters                                                                                              | 130                                                                                               |
| No. of restraints                                                                                              | 0                                                                                                 |
| H-atom treatment                                                                                               | Constr                                                                                            |
| $\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )                                                 | $w = 1/[\sigma^2(F_o^2) + (0.0788P)^2 + 0.1285P]$ where $P = (F_o^2 + 2F_c^2)/3$<br>0.437, -0.213 |

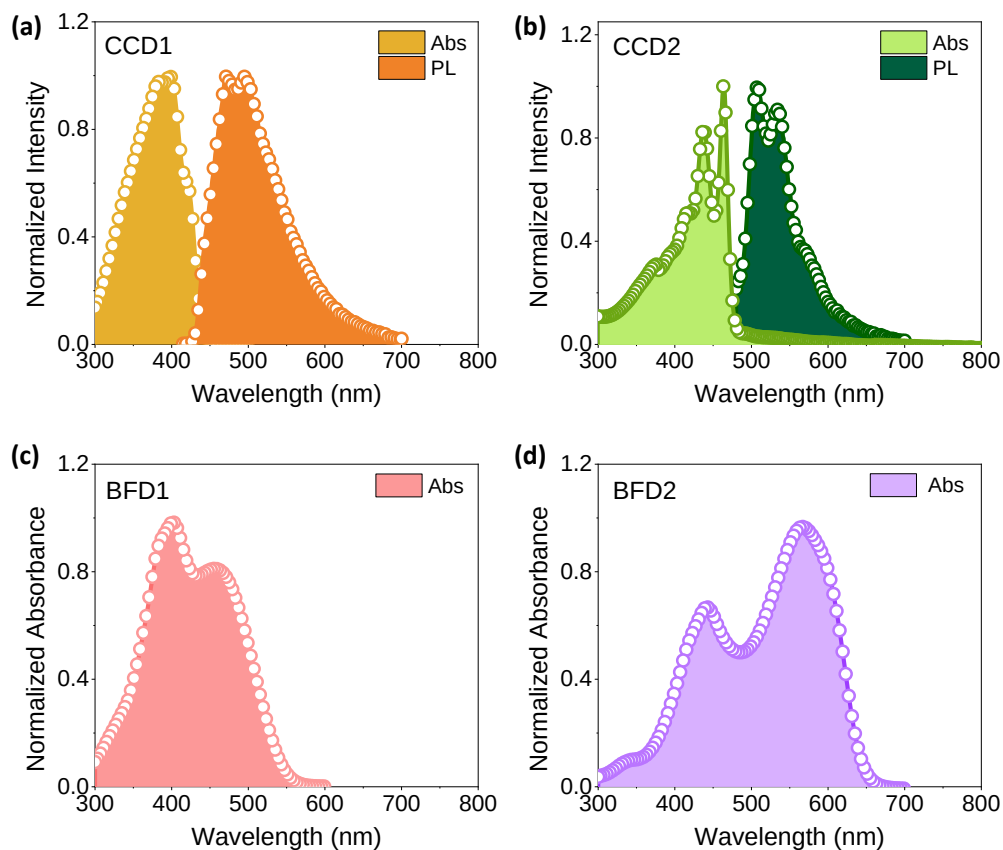


**Figure S12.** Normalized UV-vis absorption and photoluminescence spectra of (a) CCD1 and (b) CCD2, (c) BFD1 and (d) BFD2. (Sample: 0.05 mM in dichloromethane)

The normalized absorption spectra of model compounds in DCM solution (0.05 mM) are shown in Figure S12 and Table S3. The UV-Vis absorption of CCD1 exhibited a high-energy band at 382 nm and 400 nm. As the conjugation length increases, the absorption maximum undergoes a red shift around 50 nm at 436 nm and 463 nm for CCD2. Absorption maxima of BFD1 appeared at 401 nm and 458 nm. Compared to BFD1, BFD2 remarkably red-shifted around 100 nm upon increasing the number of aromatic units, absorption maxima at 443 nm and 562 nm. Out of the four model compounds studied, CCD1 and CCD2 were fluorescent, which is in a good agreement with previous work.<sup>12</sup> The emission maximum was 474 nm for CCD1 and 508 nm for CCD2 (Table S3).

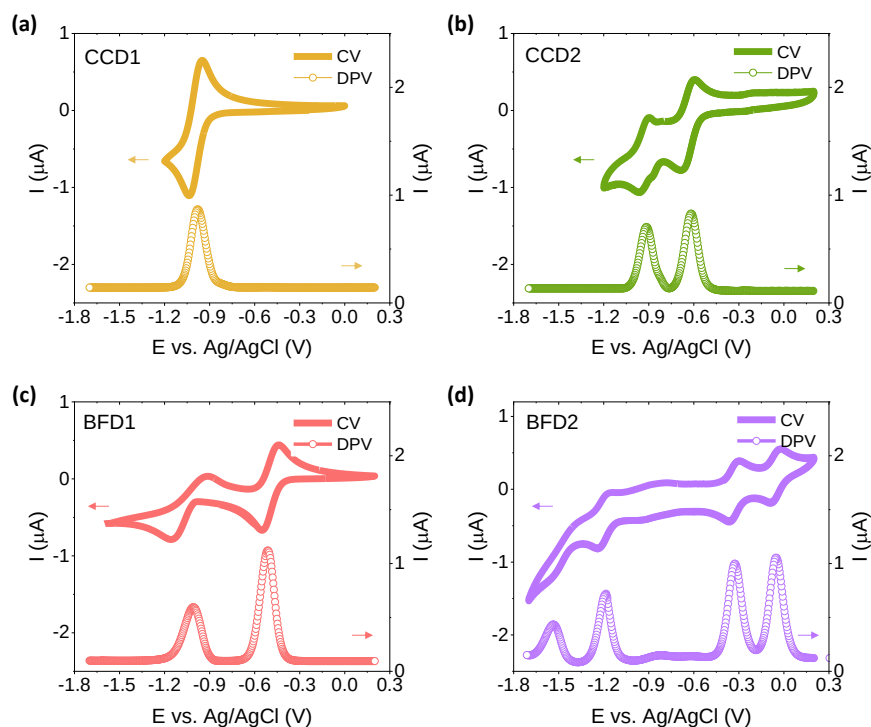


**Figure S13.** Cyclic voltammetry and differential pulse voltammetry of (a) CCD1 and (b) CCD2, (c) BFD1 and (d) BFD2. (Sample: 0.5 mM solutions of model compounds dissolved in an electrolyte of 0.1 M TBAPF<sub>6</sub> in DCM)

The redox behavior and molecular orbital energy levels (HOMO and LUMO) of model compounds were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in 0.1 M TBAPF<sub>6</sub> in DCM (Figure S13 and Table S3). The first onset of reduction potentials could be estimated from CV: -0.92 V for CCD1, -0.57 V for CCD2, -0.43 V for BFD1, and +0.02 V for BFD2. The LUMO level values were further calculated to be -3.49, -3.84, -3.98, and -4.43 eV, respectively. We then estimated the HOMO level by subtracting the optical bandgaps ( $E_g^{\text{opt}}$ ) from the LUMO levels, leading to -6.27 eV for CCD1, -6.44 V for CCD2, -6.25 eV for BFD1, and -6.28 eV for BFD2. Overall, the results show that the highly electron-deficient nature of the isoxindigo with respect to BFD1 and BFD2 leads to the low-lying LUMO among these model compounds. The LUMO level value of CCD1 and CCD2 is slightly higher, due to the relatively weaker electron-donating ability of dibenzonaphthyrone. The DPV experiments revealed similar results compared with the CV measurements. The DPV spectrum of CCD1 showed a single reduction potential at -0.43 V and that of CCD2 showed first reduction potential at -0.57 V and -0.80 V for CCD2. For BFD1, the first reduction potential was detected at -0.43 V and second reduction potential was detected at -0.99 V, and BFD2 undergoes a first reduction at a potential of +0.02 V, the second reduction occurs at a potential of -0.24 V the third reduction at -1.13 V, and the fourth at -1.51 V versus Fc/Fc<sup>+</sup>.

**Table S3.** Photophysical and electrochemical properties of CCD1, CCD2, BFD1, and BFD2.

|      | $\lambda_{\max}^{\text{abs}}$ (nm) <sup>a</sup> | $\lambda_{\max}^{\text{PL}}$ (nm) <sup>a</sup> | $\lambda_{\text{cut-off}}$ (nm) | $E_{\text{red}}^{\text{onset}}$ (V) <sup>b</sup> | HOMO (eV) <sup>c</sup> | LUMO (eV) <sup>c</sup> | $E_g$ (eV) <sup>d</sup> |
|------|-------------------------------------------------|------------------------------------------------|---------------------------------|--------------------------------------------------|------------------------|------------------------|-------------------------|
| CCD1 | 382,400                                         | 474,496                                        | 445                             | -0.92                                            | -6.27                  | -3.49                  | 2.79                    |
| CCD2 | 436,463                                         | 508,534                                        | 476                             | -0.57                                            | -6.44                  | -3.84                  | 2.61                    |
| BFD1 | 401,458                                         | -                                              | 546                             | -0.43                                            | -6.25                  | -3.98                  | 2.27                    |
| BFD2 | 443,562                                         | -                                              | 646                             | 0.02                                             | -6.28                  | -4.43                  | 1.92                    |

a) Measured in dichloromethane. b) Cyclic voltammograms measured in 0.1M TBAPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. c) LUMO =  $-e(4.8 + E_{\text{red}}^{\text{onset}} - E_{\text{Fc/Fc}^+})$ , ferrocene = 0.388 eV, HOMO = LUMO – E<sub>g</sub>. d) E<sub>g</sub> is optical bandgap obtained from absorption threshold,  $E_g = 1240/\lambda_{\text{cut-off}}$ .

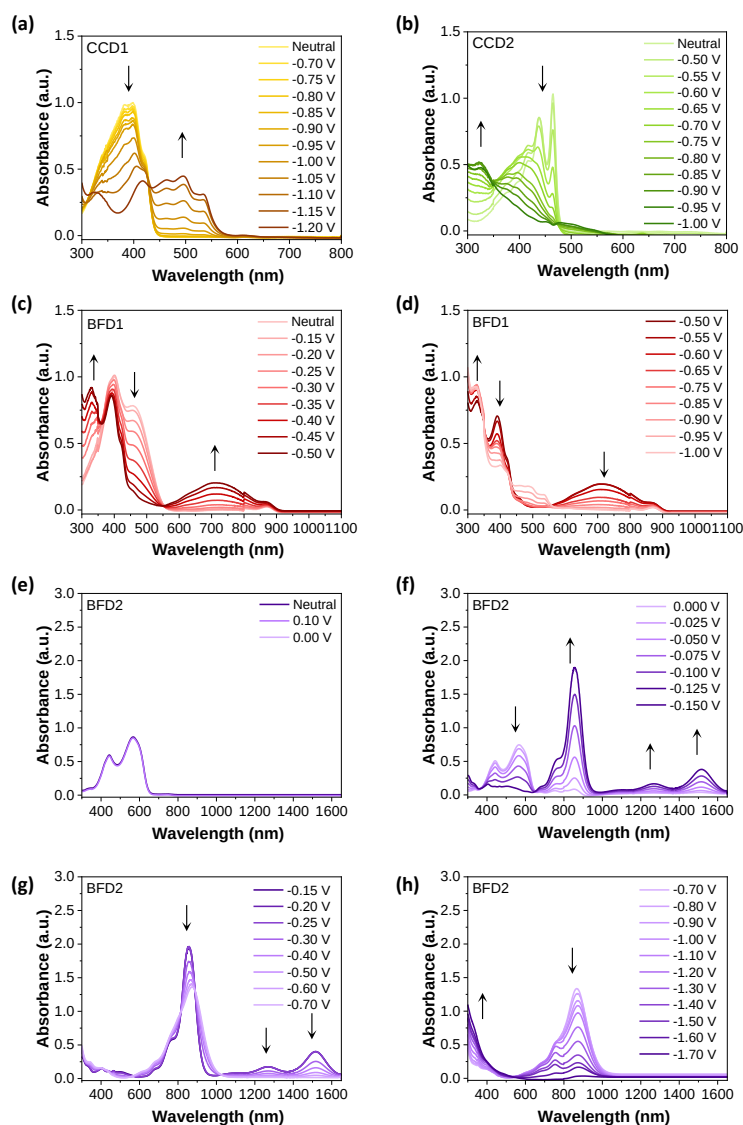


**Figure S14.** Results of spectroelectrochemistry experiments, recorded in a honey-comb setup using 0.05 mM solutions of the (a) CCD1, (b) CCD2, (c,d) BFD1, and (e,f,g,h) BFD2 dissolved in 0.1 M TBAPF<sub>6</sub> in dichloromethane.

UV-vis-NIR spectro-electrochemistry was performed to monitor the reduction behavior of model compounds (0.05mM) upon application of electrochemical potential in 0.1 M TBAPF<sub>6</sub> in dichloromethane (Figure S14). The decreasing potentials range from -0.7 to -1.2 V for CCD1, -0.5 to -1.0 V for CCD2, -0.15 to -1.0 V for BFD1, and +0.1 to -1.7 V for BFD2. For CCD1, as the potential magnitude increases, the neutral absorption at 382 nm and 400 nm begins to decrease in intensity, while new absorption features appear at 467 nm, 496 nm, and 534 nm (Figure S14a). No clear and gradual increase in intensity of the polaronic absorption features with increasing potential was observed for CCD2 (Figure S14b), which indicates rapid decomposition of the reduced species during the experiment.

BFD1, in the neutral state, exhibited strong absorption in the visible light region with an absorption maximum at 401 nm and 458 nm. When the applied potential was decreased to -0.5 V, there were one new strong absorption band with the appearance of absorption maxima at 719 nm, indicating the formation of BFD1 radical anions (Figure S14c). Further, the spectrogram continued to transform to a more negative potential at -1.0 V. With this more negative potential, the new weak absorption band with a maximum of 331 nm, 497 nm, and 539 nm appeared and the absorption at 719 nm decreased (Figure S14d). BFD2 exhibits the biggest changes in absorbance at the lowest electrochemical potential, in agreement with its low  $E_{\text{red}}$  and LUMO level (Figure S14e-h). In-situ spectroelectrochemical experiments on the BFD2 reveal the characteristic absorption signatures of the radical anion and the dianion. Figure S14e shows the corresponding neutral absorption recorded during the forward scan in a potential window of 0.10 V and 0.00 V. During the first reduction process (0.00 V to -0.15 V) new signals at 856, 1274, and 1524 nm occur, while the absorption intensities of the neutral bands at 443 and 562 nm decrease. The reduction process between -0.15 V and -1.70 V results in the disappearance of polaron bands and a short wavelength peak at 300 nm increase, indicating the decomposition of doped BFD2.

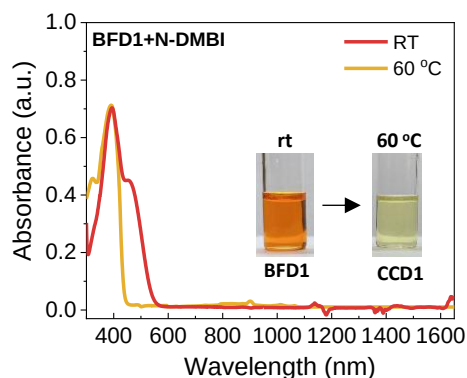


**Figure S15.** UV-vis absorption spectra of BFD1 with N-DMBI at room temperature and 60 °C. (inset: color change of BFD1 (orange) to CCD1 (yellow)).

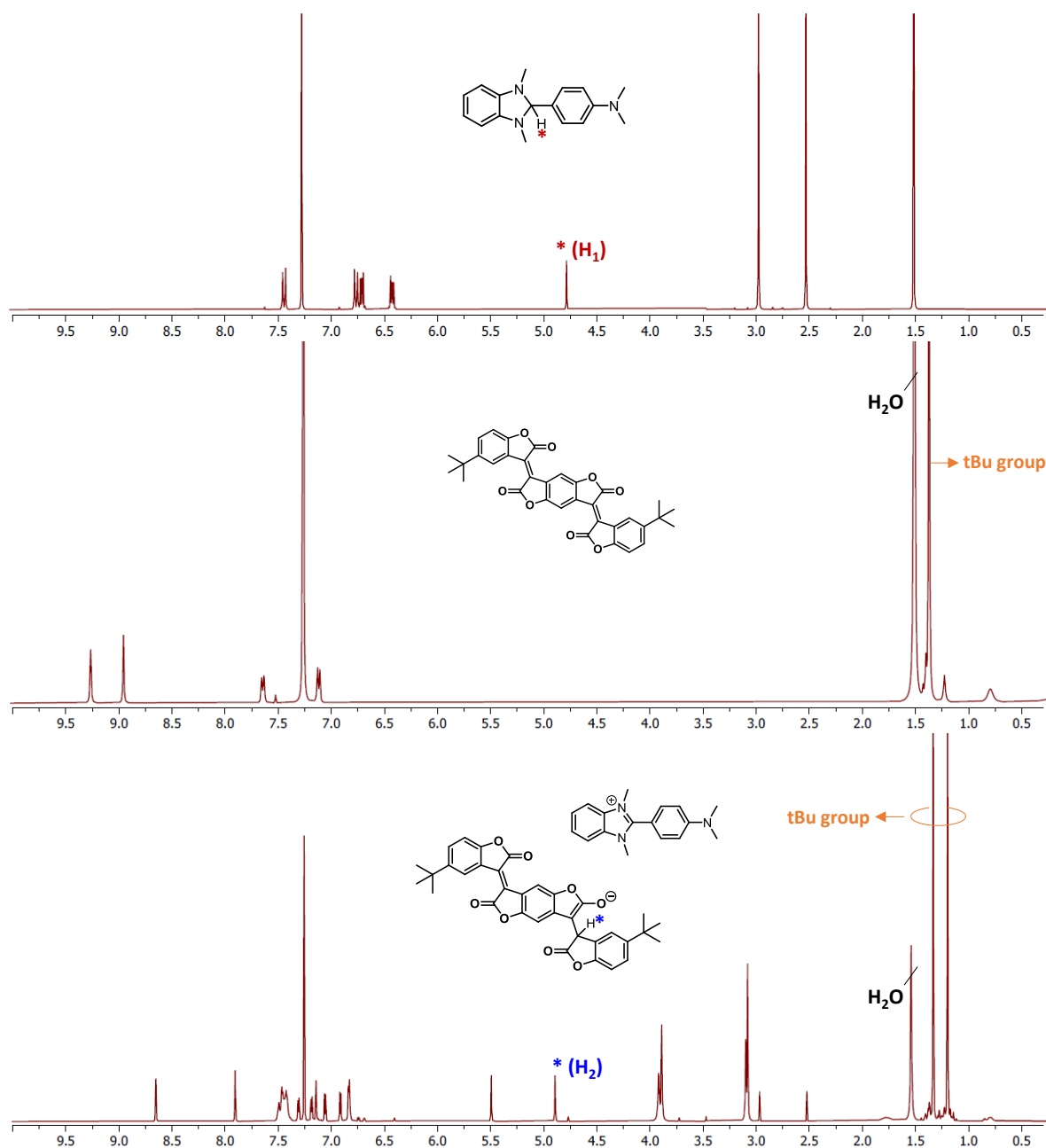


**Figure S16.** Stacked  $^1\text{H}$  NMR spectrum of N-DMBI-H (top), BFD2 (middle) and BFD2H $^+$ /N-DMBI $^+$  (bottom) in  $\text{CDCl}_3$ . The reaction was carried out between 1:1.2 mixture of BFD2 and N-DMBI-H in  $\text{CDCl}_3$ . The NMR spectra indicates complete hydride transfer from N-DMBI-H to BFD2. The hydride present in N-DMBI-H ( $\text{H}_1$ ,  $\delta = 4.78$ ) disappeared and transferred to BFD2 ( $\text{H}_2$ ,  $\delta = 4.91$ ). The single tert-butyl peak of BFD2 (middle,  $\delta = 1.40$ ) due to the symmetric structure is split to two singlet peaks at  $\delta = 1.36$  and  $\delta = 1.23$  (bottom), indicating the broken symmetry.

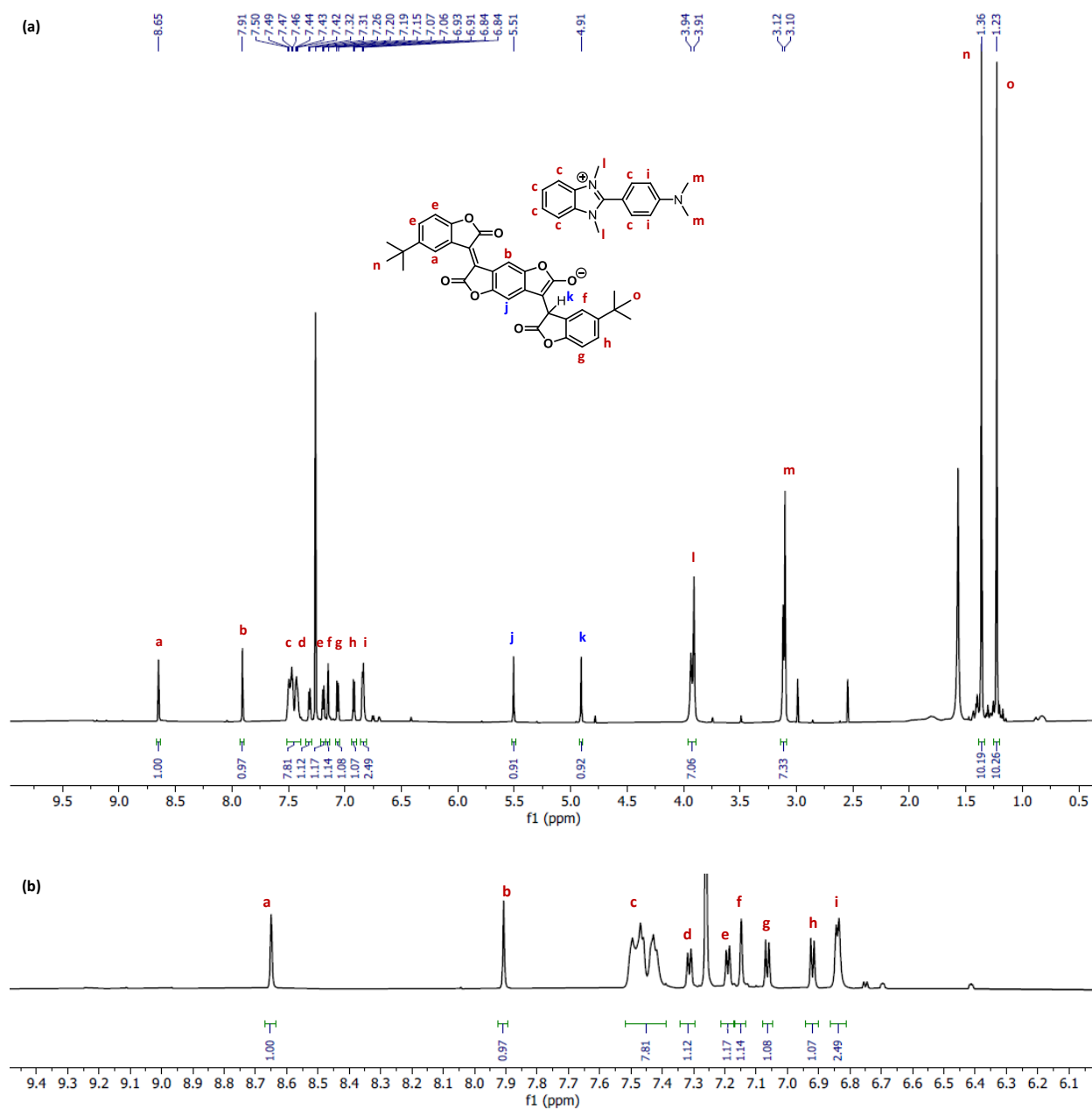


**Figure S17.** (a)  $^1\text{H}$  NMR Spectrum of BFD2H<sup>+</sup>/N-DMBI<sup>+</sup> in  $\text{CDCl}_3$  and (b) detailed zoom between 9.5 and 6.0 ppm.

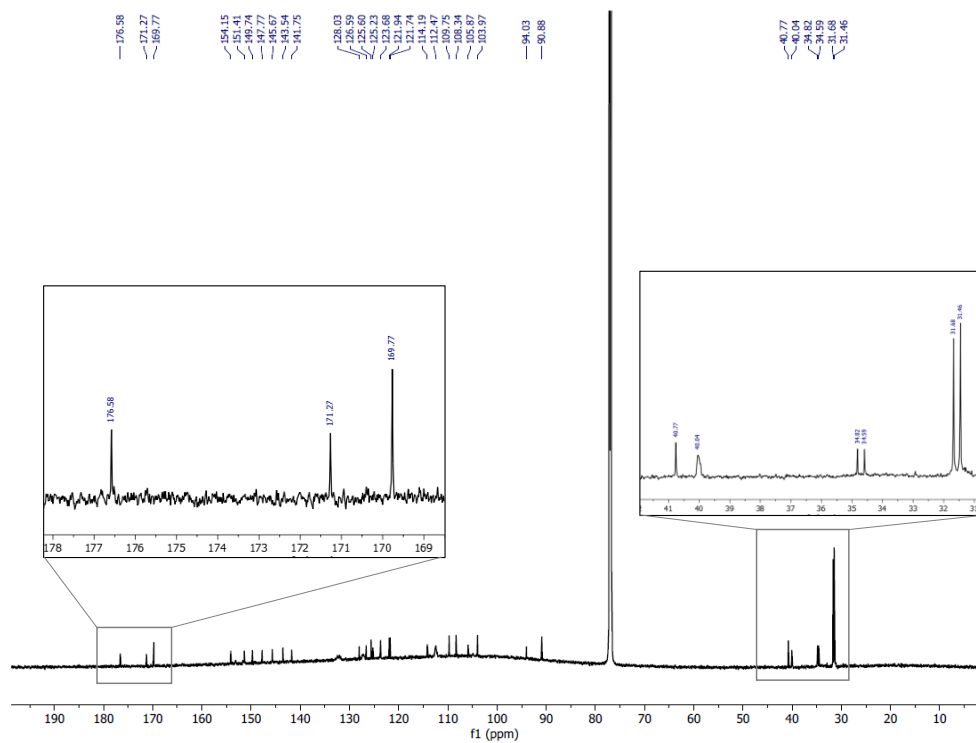


**Figure S18.**  $^{13}\text{C}$  NMR Spectrum of  $\text{BFD2H}^+/\text{N-DMBI}^+$  in  $\text{CDCl}_3$ . The left inset presence of three inequivalent  $\text{C=O}$  resonances, consistent with the broken symmetry and emphasizing the generated cabanion is transferred to oxygen anion, which means the carbonyl form changes to enol form.

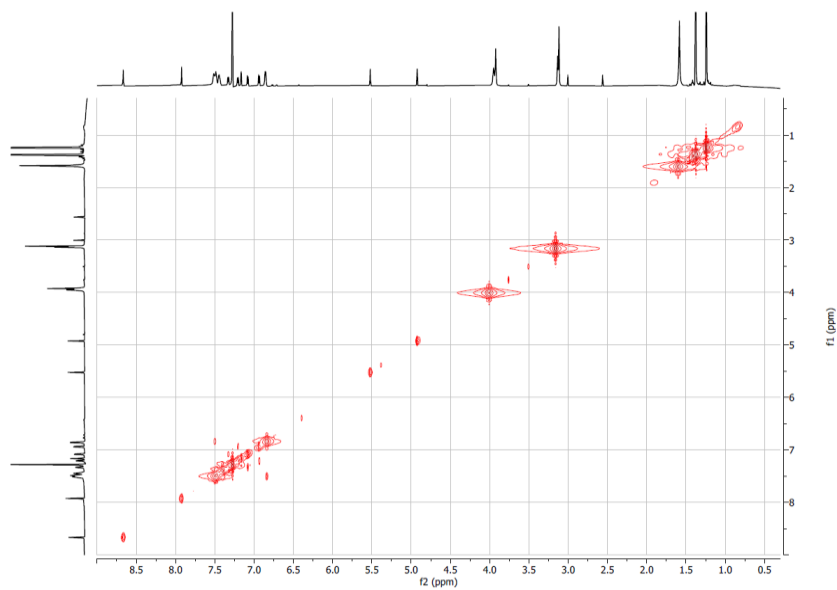


**Figure S19.** COSY NMR Spectrum of  $\text{BFD2H}^+/\text{N-DMBI}^+$  in  $\text{CDCl}_3$ .

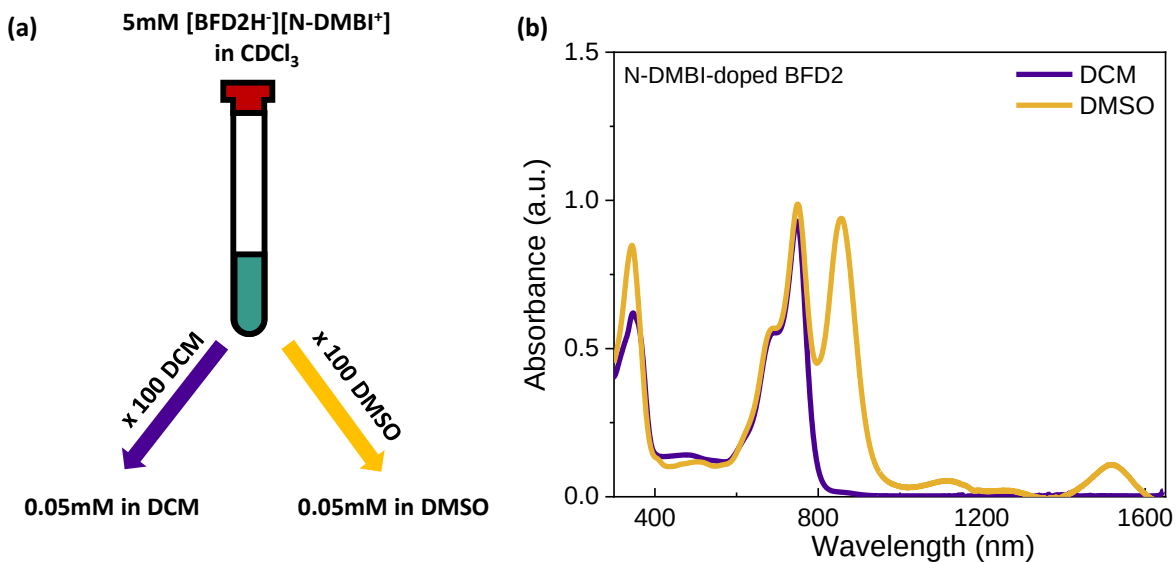


**Figure S20.** (a) Schematic diagram of sample preparation. The 5 mM BFD2 and N-DMBI-H was reacted together in  $CDCl_3$ . The NMR spectrum shows exclusively  $BFD2H^+/N-DMBI^+$  in the NMR sample (Figure S16-S18). The UV-Vis-NIR spectrum was measured after diluting the NMR sample to 0.05 mM, either in DCM (non-polar solvent) or DMSO (polar solvent). (b) UV-vis-NIR spectrum showing  $BFD2H^+$  peak was exclusively observed in DCM solution, while the mixture of  $BFD2H^+$  and  $BFD2^{\cdot-}$  was observed after redissolving in DMSO solution.

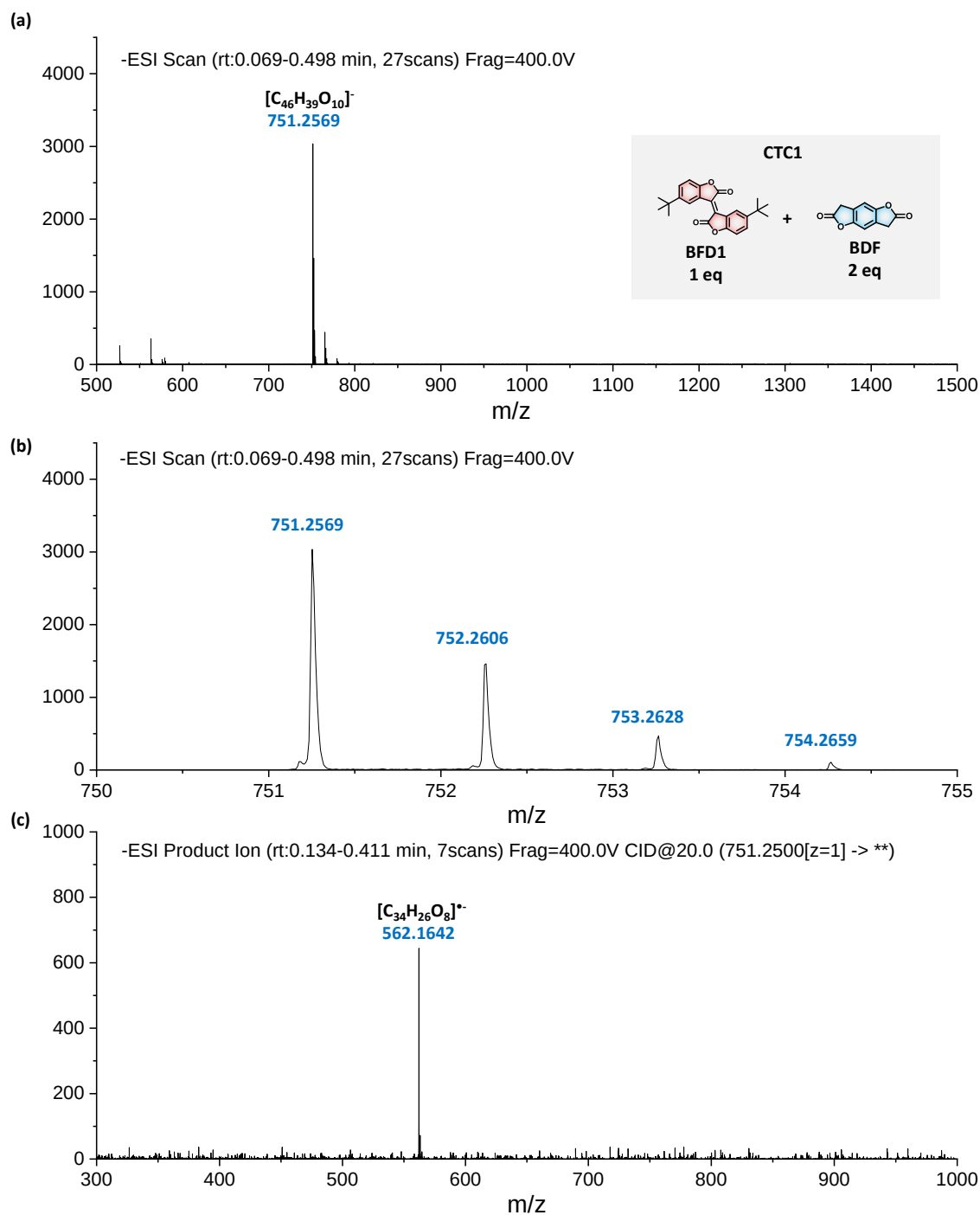
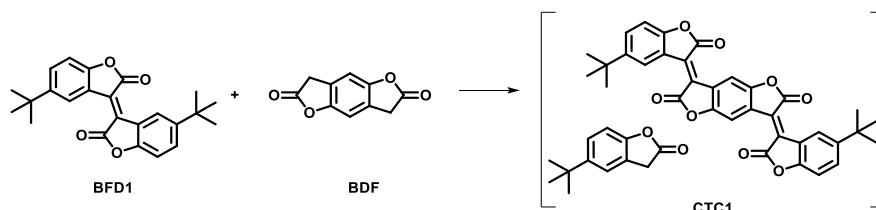


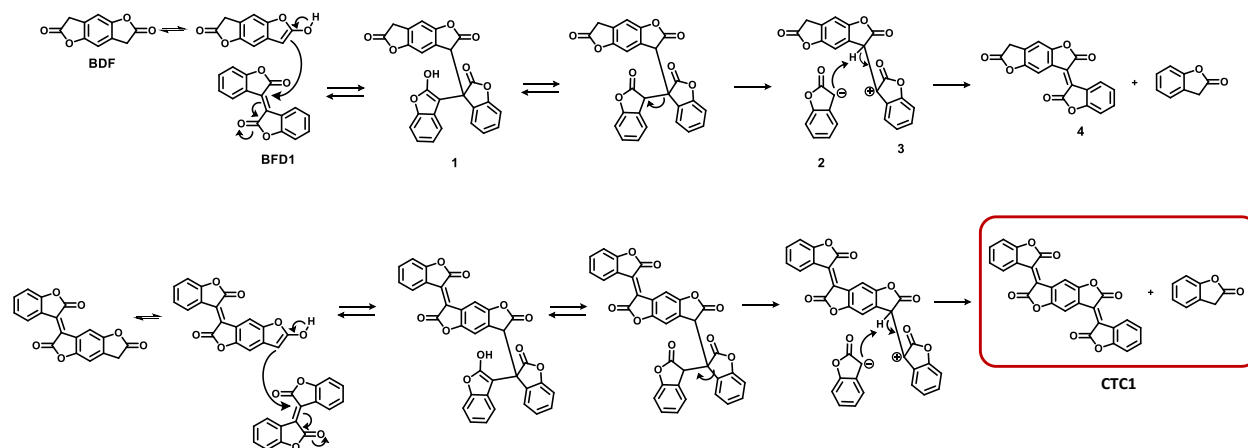
**Figure S21.** (a) ESI-MS mass spectrum of CTC1 and (b) zoomed ESI-MS mass spectrum in negative ionization mode. (c) The CID spectra of the precursor ion  $m/z$  751.

High-resolution mass spectra in negative ionization mode showed abundant species at  $m/z$  751.2569, which corresponds to the elemental formula  $[C_{46}H_{39}O_{10}]^-$  (Figure S21a and S21b). Using the collision-induced dissociation (CID) technique, the compound will be further ionized to give a signal at  $m/z$  562, matching BFD2 with the elemental formula  $[C_{34}H_{26}O_8]^-$  (Figure S21c). Since the nominal mass of both BDF and BF is  $m/z$  190, it makes several candidates of structures corresponding to the assigned nominal mass of  $m/z$  751 as shown in Figure S22. From mass spectrometry measurement, we proposed CTC1 structure as follows.



**Scheme S2.** Charge transfer complex, CTC1, formed between BFD1 and BDF.

The proposed reaction mechanism for the formation of CTC1 is as follows. In DMSO, an enol lactone form of BDF is formed, which reacts with BFD1 via a Michael addition. The formed adduct 1 can further undergo reversible bond cleavage and generate enolate 2, which dehydrogenate the  $\alpha$  proton from 3 followed by elimination to give the final intra-molecular fragment exchanged product 4. The second fragment exchange reaction between BFD1 and 4 can generate charge transfer complex, CTC1.



**Scheme S3.** The proposed mechanism of the olefin metathesis.

To further validate this reaction mechanism, we designed and compared BFD derivatives with no tertbutyl, two tertbutyl, and four tertbutyl group. The obtained HRMS results show corresponding charge transfer complexes with olefin metathesis in  $m/z$  583,  $m/z$  751, and  $m/z$  919, respectively, as shown in Figure S22.

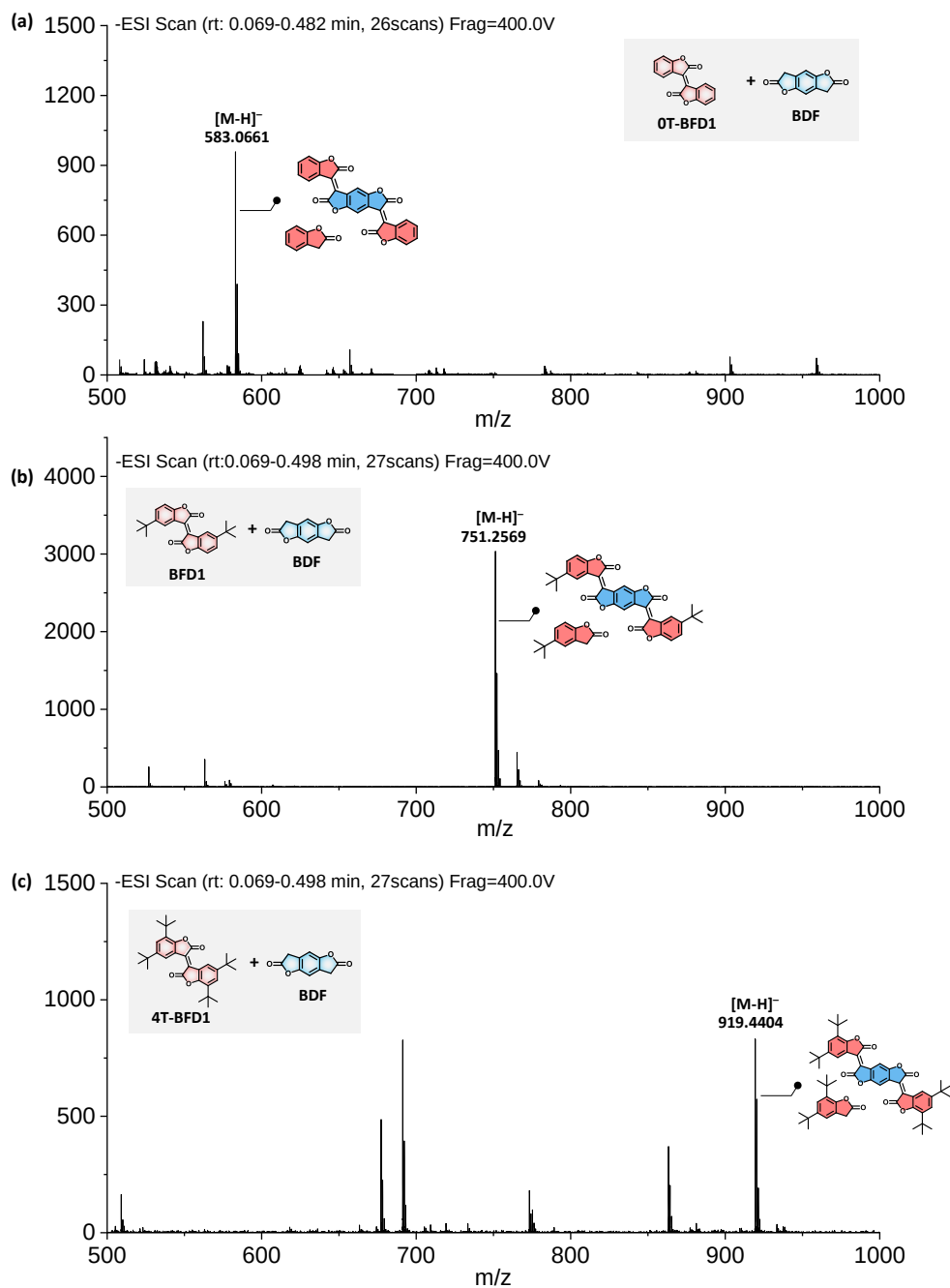


**Figure S22.** Negative mode ESI-MS mass spectra of reaction between BDF monomer and (a) no tert-butyl BFD, (b) two tert-butyl BFD (BFD1), and (c) four tert-butyl BFD in negative ionization mode.

We also noticed that these three pairs of compounds showed distinct reaction rates. The color change from orange (BFD derivatives) to green (CTC derivatives) took about 3, 20 and 720 mins with increasing steric hindrance, in the order of OT-BFD1, 2T-BFD1 (BFD1 in main text) and 4T-BFD1 (sample:20mM in DMSO).

Similarly, CTC2 is formed through charge transfer complex between BFD2 and BDF (Figure S23 and S24).

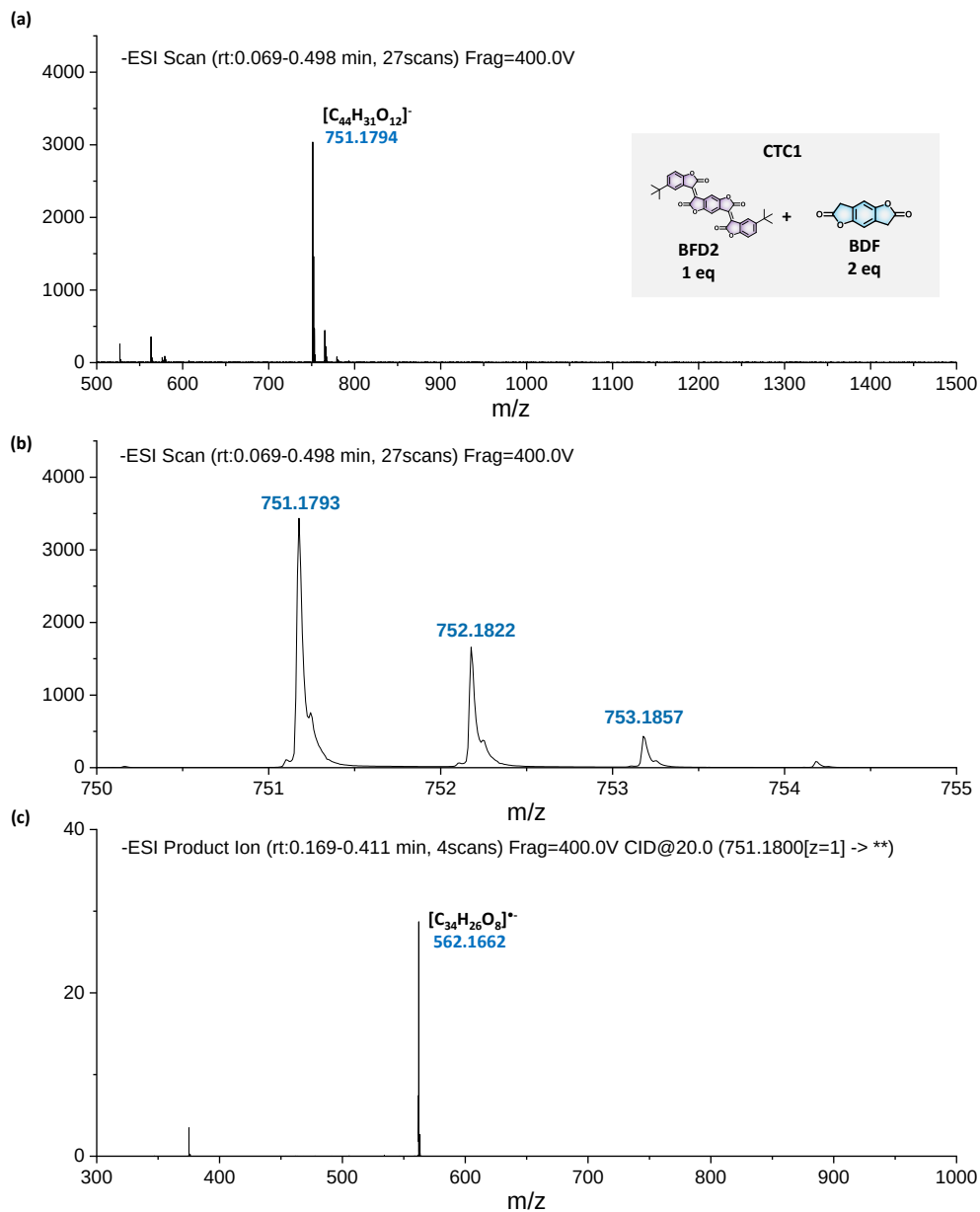


**Figure S23.** (a) ESI-MS mass spectrum of CTC2 and (b) zoomed ESI-MS mass spectrum in negative ionization mode. (c) The CID spectra of the precursor ion  $m/z$  751.

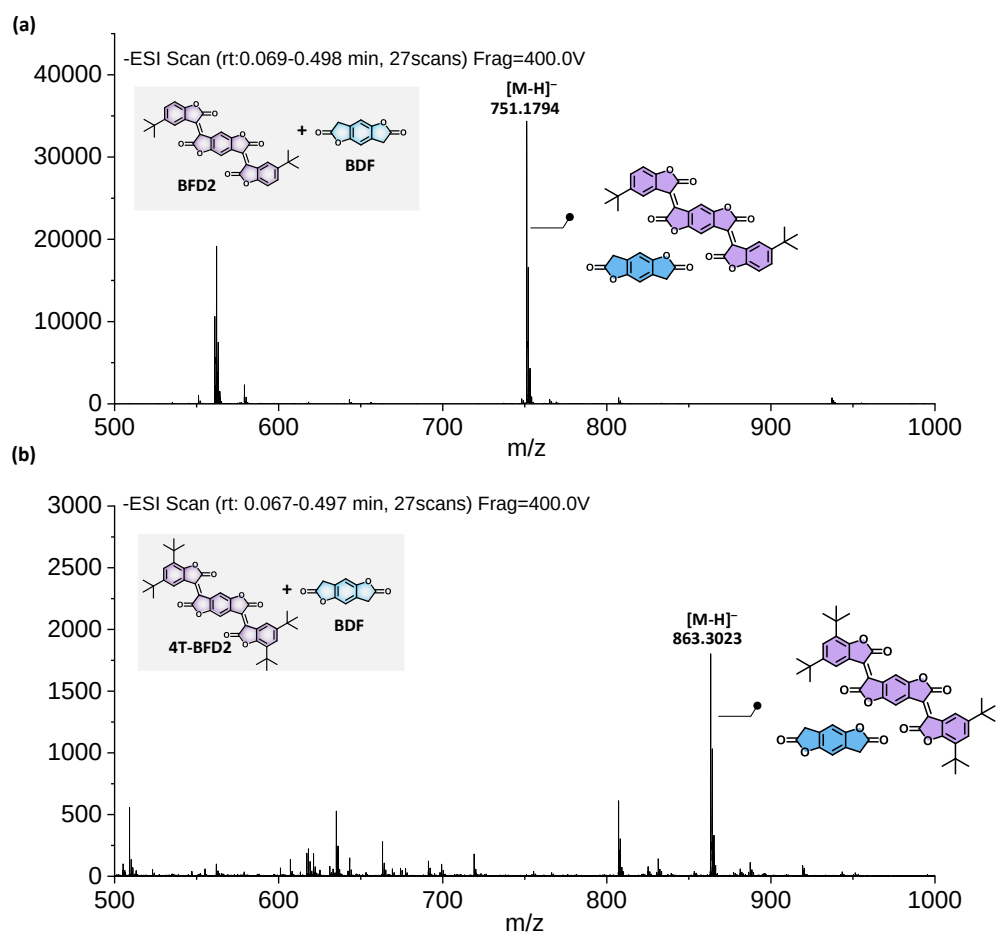


**Figure S24.** Negative mode ESI-MS mass spectra of reaction between BDF monomer and (a) two tert-butyl BFD (BFD2), and (c) four tert-butyl BFD in negative ionization mode.

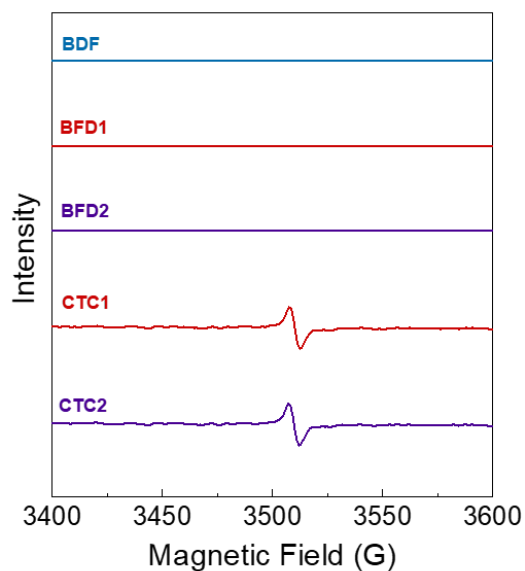


**Figure S25.** Stacked EPR spectra of BDF precursors and charge transfer complexes.

Weak charge transfer complex has been identified in previous literatures, featuring the active EPR/ESR signal.<sup>14–16</sup> However, free charge is not immediately generated by the molecular dopant for CTC1 and CTC2, showing lack of an EPR signal, indicating that the number of unpaired electrons is low (Figure S25).

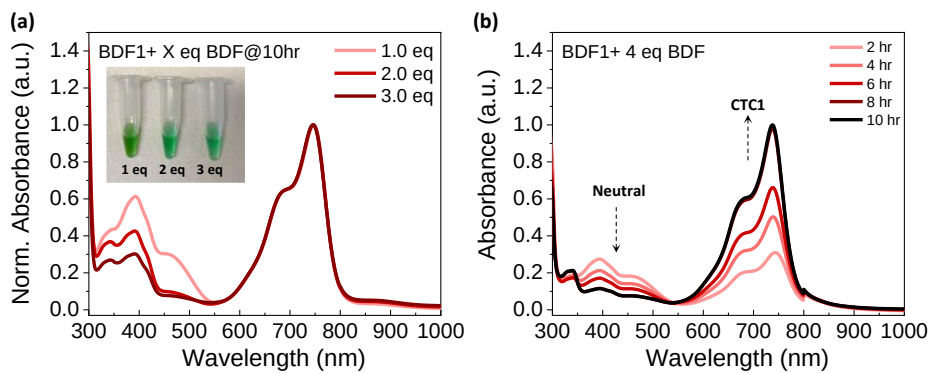


**Figure S26.** UV-vis absorption spectra of BFD1 (a) upon addition of various equivalents of BDF in after 10 hour and (b) with 4 equivalents of BDF reacted with different time intervals showing CTC1 formation in DMSO (sample: 0.05 mM in DMSO).

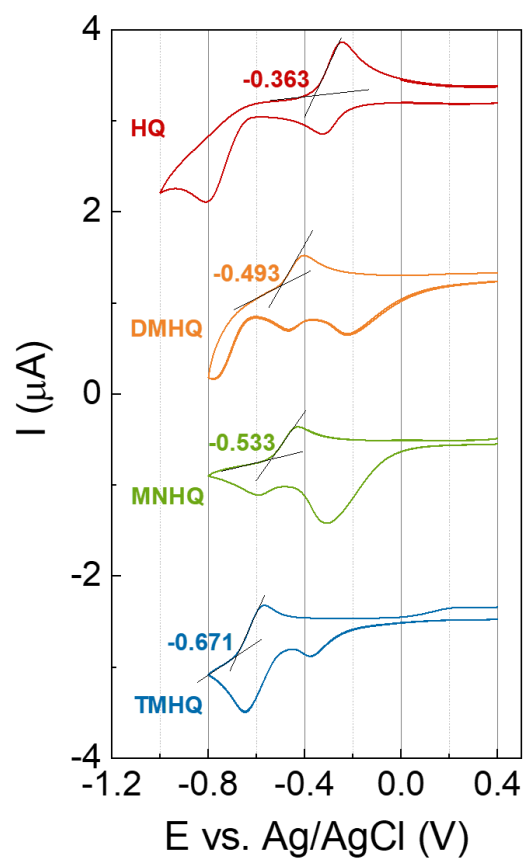


**Figure S27.** Cyclic voltammetry of 0.5 mM solutions of hydroquinone derivatives dissolved in an electrolyte of 0.1 M TBAPF<sub>6</sub> prepared in DMSO.

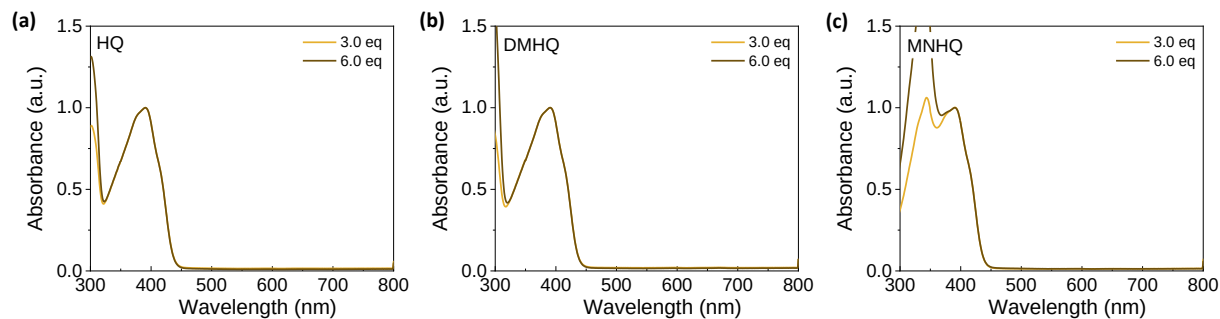


**Figure S28.** UV/Vis-NIR spectra obtained by titrating CCD1 with (a) HQ, (b) DMHQ and (c) MNHQ. The absorption spectrum shows there is no reaction between HQ, DMHQ, and MNHQ with CCD1.

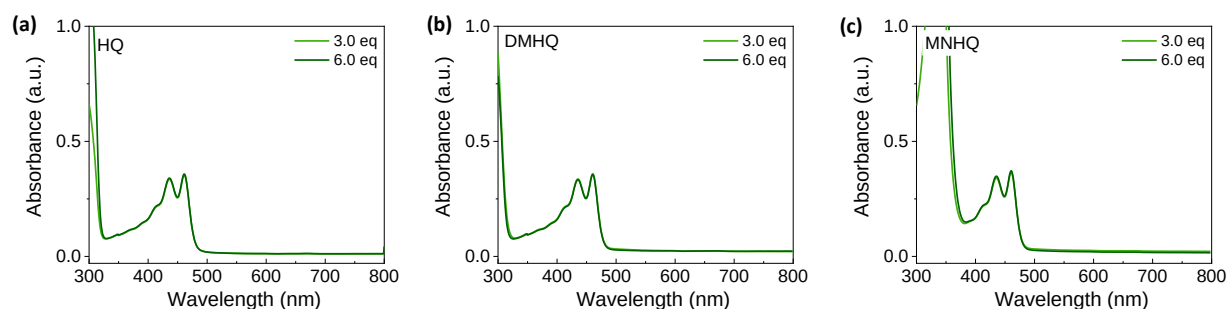


**Figure S29.** UV/Vis-NIR spectra obtained by titrating CCD2 with (a) HQ, (b) DMHQ and (c) MNHQ. The absorption spectrum shows there is no reaction between HQ, DMHQ, and MNHQ with CCD2.

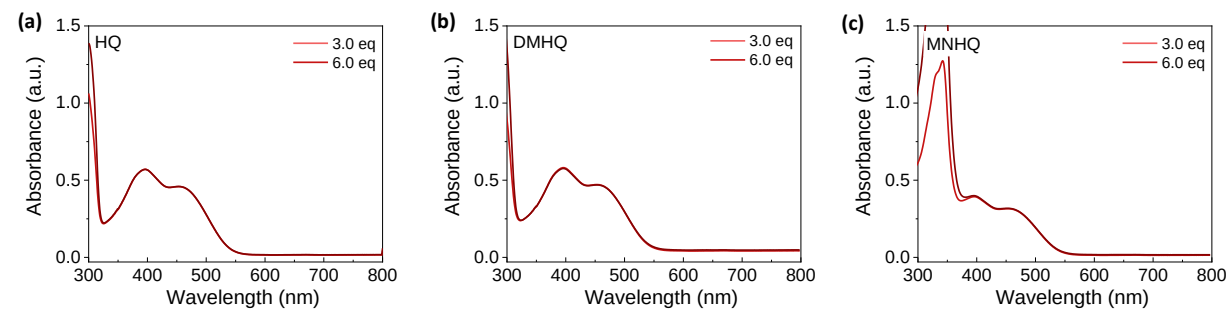


**Figure S30.** UV/Vis-NIR spectra obtained by titrating BFD1 with (a) HQ, (b) DMHQ and (c) MNHQ. The absorption spectrum shows there is no reaction between HQ, DMHQ, and MNHQ with BFD1.

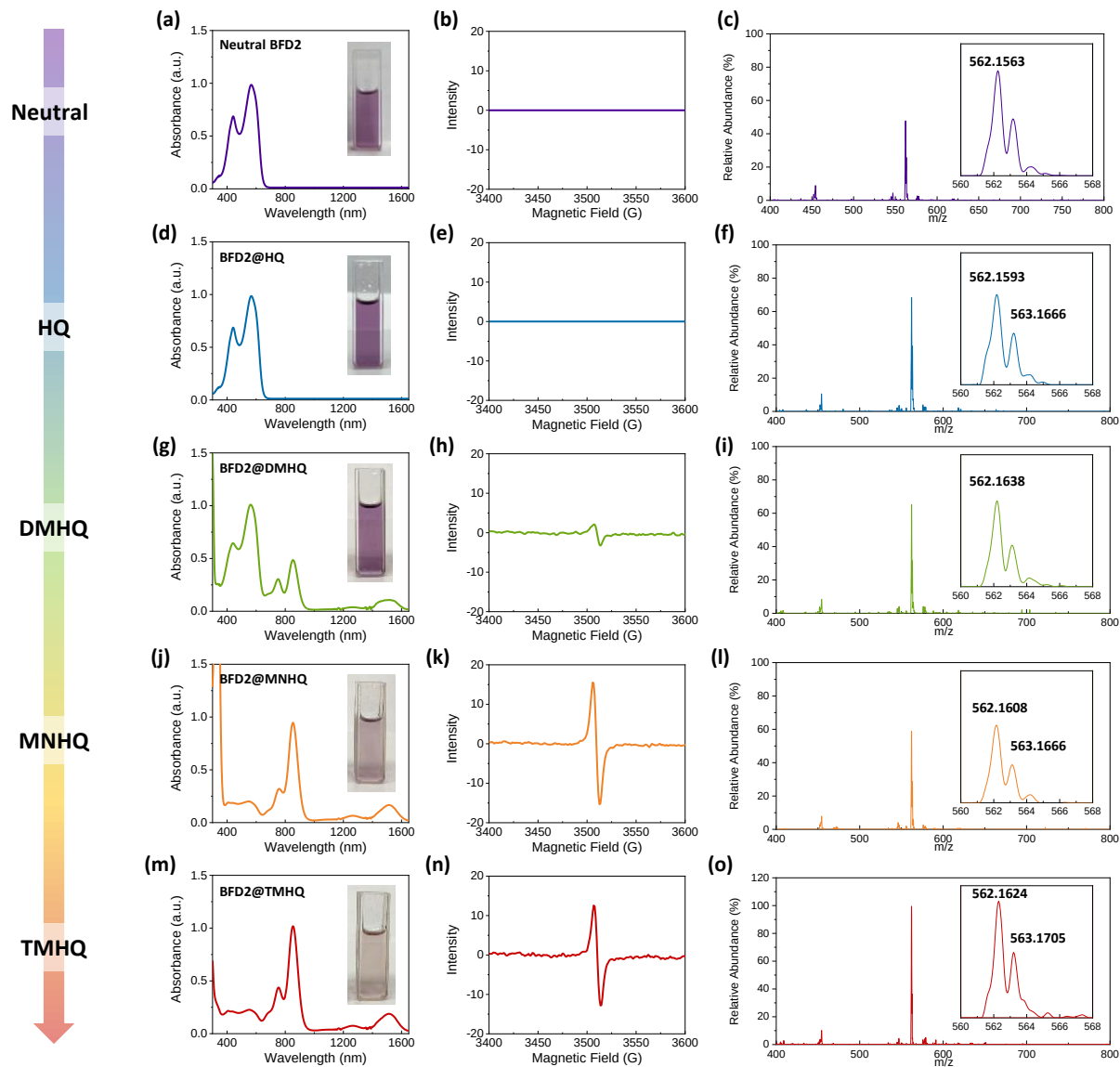
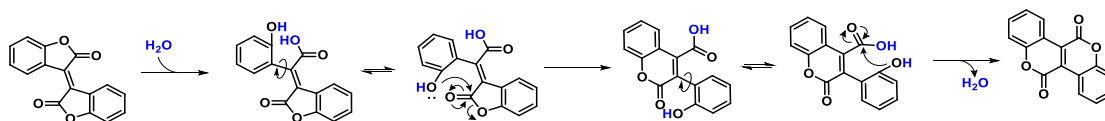


**Figure S31.** UV/Vis-NIR spectra (a,d,g,j,m), EPR spectra (b,e,h,k,n), APCI-mass spectra of neutral (purple;a,b,c), HQ-doped (blue;d,e,f), DMHQ-doped (green;g,h,i), MNHQ-doped (orange;j,k,l), and TMHQ-doped (red;m,n,o) BFD2.



**Scheme S4.** Water catalyzed isomerization from BFD1 to CCD1.

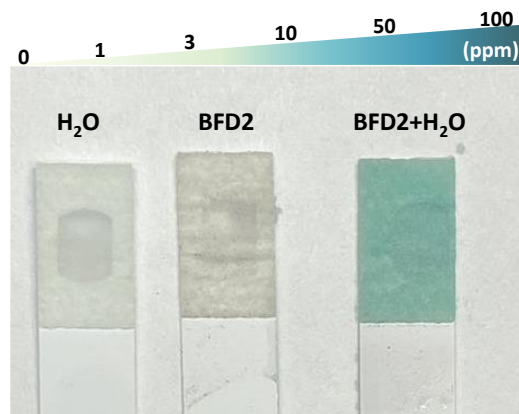


**Figure S32.** Image of  $\text{H}_2\text{O}_2$  test strips showing  $\text{H}_2\text{O}_2$  formation on BDF2. From left to right, water, neutral BFD2, and doped BFD2.

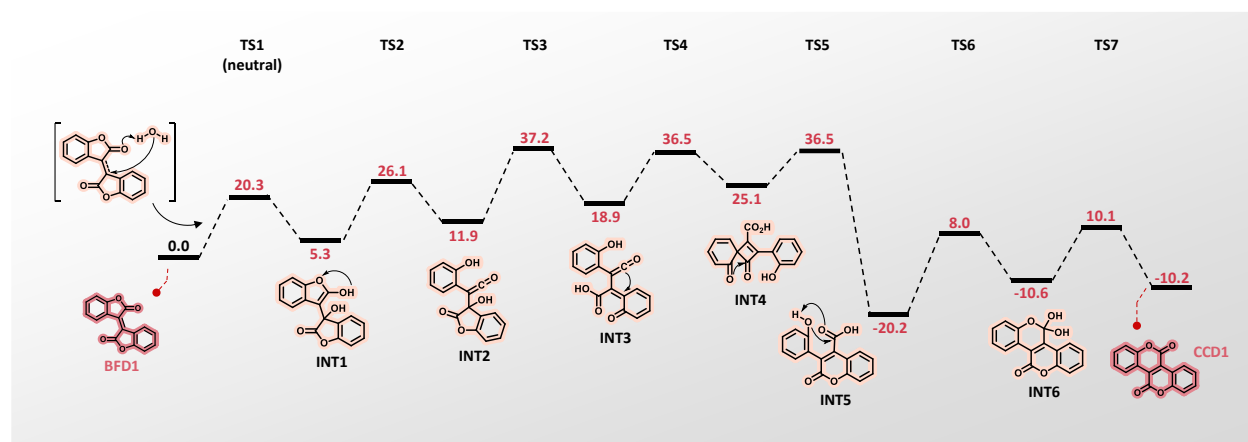


**Figure S33.** A comparison of the barriers for the seven-step isomerization mechanism explored in a neutral, closed-shell condition.

**Isomerization Mechanism.** The YARP methodology was used to discover a reaction pathway for the isomerization of BFD1 to CCD1 (Figure S33). In the first step, Michael addition occurs on BFD1', with an external  $\text{H}_2\text{O}$  molecule acting as a proton shuttle to produce INT1. The second step involves a ring-opening process of INT1, with a proton transfer between two oxygens, known as reverse Korcek cyclization, to form INT2 that contains a ketene group.<sup>17</sup> Unexpectedly, in the third step, the five-membered ring on the opposite side opens through a C–O bond cleavage and the hydroxyl group transfers, resulting in the formation of a carboxylic group in INT3, which is a crucial part of the overall isomerization. The fourth step involves a conformational change of INT3, wherein the ketene group rotates  $180^\circ$  away from the carboxyl group and forms a four-membered ring through  $\pi$ -bond rearrangements, leading to the formation of INT4. This intermediate is the most energetically unfavorable intermediate along the isomerization pathway and readily transforms into the more stable INT5 through a low-barrier ring rearrangement (free energy of activation [ $\Delta G^\ddagger$ ] of 11.4 kcal/mol), which is both kinetically and thermodynamically favorable (free energy of reaction [ $\Delta G_r$ ] of -56.7 kcal/mol). In the sixth step, a  $\text{H}_2\text{O}$ -catalyzed Korcek cyclization facilitates ring closure, which is likely to be the rate-limiting step with a  $\Delta G^\ddagger$  of 28.2 kcal/mol. Finally, INT6 undergoes a  $\text{H}_2\text{O}$ -catalyzed  $\beta$ -H elimination to produce CCD1'. This isomerization pathway automatically identified by YARP exhibits an overall barrier (i.e., the highest  $\Delta G^\ddagger$  among the multistep reaction pathway) of 28.2 kcal/mol and absolute barrier (i.e., relative  $\Delta G$  of the highest

energy TS among the multistep reaction pathway with respect to the reactant) of 37.2 kcal/mol. The comprehensive exploration of the reaction network and subsequent barrier analysis presented here provides a sound basis for explaining the observed CCD formation in the model system at 100 °C.

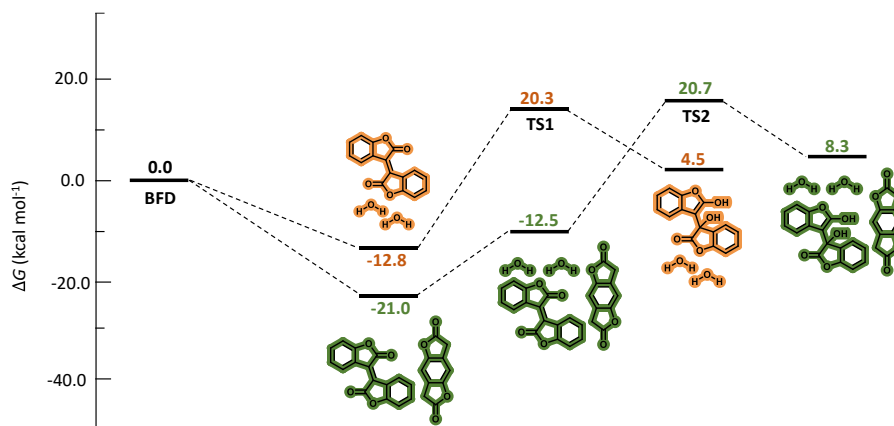


**Figure S34.** The effect of an additional monomer forming a charge-transfer complex with BFD is shown, which stabilizes BFD by 21 kcal/mol and increases the barrier of the first step isomerization by 10 kcal/mol compared to BFD alone. The intermediates that involve an external water molecule indicate that the reaction is catalyzed by water.

To investigate the effect of charge-transfer complex formation between BFD and a monomer BDF on CCD formation, we recalculated the first step of BFD isomerization in the presence of a monomer BDF (Figure S34). The results showed that the charge-transfer complex was considerably more stable than the individual BFD, as evidenced by a large negative binding energy of -21 kcal/mol, reflecting the strong and stabilizing interaction between BFD and BDF. Interestingly, the relative energies (with respect to BFD) of the transition states were found to be similar in both scenarios, with and without the presence of BDF. As a result, the formation of the charge-transfer complex inhibits CCD formation by increasing the overall barrier of the first step of CCD formation.

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