

Supporting Information

Highly Conductive, and Solution-Processable N-Doped Transparent Organic Conductor

Zhifan Ke^{‡,1}, Ashkan Abtahi^{‡,1}, Jinhyo Hwang^{‡,1}, Ke Chen¹, Jagrity Chaudhary¹, Inho Song¹, Kuluni Perera¹, Liyan You¹, Kyle N. Baustert², Kenneth R. Graham², and Jianguo Mei^{1*}

¹Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

² Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States

[‡]Contribute equally

Correspondence to: jgmei@purdue.edu

This file includes:

1. Measurement of HOMO and LUMO of PBDF
2. Electrode configurations for conductivity and Hall effect measurements
3. Reductive doping of PBDF through water oxidation
4. Model Reactions and radical trapping
5. General procedure for the polymerization
6. Structural isomers of CCD and BDF and the impact of defect formation
7. n-PBDF morphology, optical and electronic characterization
8. n-PBDF as Transparent Conductor and Electrode Material
9. References

Table of Contents

1. HOMO and LUMO level of PBDF	5
Figure S1	5
Figure S2 Electrochemical properties of PBDF.	6
Figure S3 Energetic diagram of PBDF.....	8
2. Electrode configurations for conductivity and Hall effect measurements	8
Figure S4 Four-probe electrode configuration	8
Figure S5 Clover leaf shape Van de Pauw configuration	9
3. Reductive doping of PBDF via water oxidation	9
Figure S6 H ₂ O ₂ formation on PBDF.	10
4. Model reactions and radical trapping.....	11
Figure S7 In-situ high temperature (120 °C) ¹ H NMR spectra of BF with Cu(OAc) ₂ in DMSO-d ₆	11
Scheme S1. Synthesis of the title compounds.	12
Figure S8 Temperature-dependent ¹ H NMR spectrum of BFD with deuterated water in DMSO-d ₆	13
Synthesis of 3-(propan-2-ylidene)benzofuran-2(3H)-one (BF-ENE):.....	14
Figure S9 Crystal structure of radical trapping product (BF-ENE).	14
Figure S10 High resolution mass spectrum of BF-ENE.	14
Figure S11 ¹ H NMR spectrum of BF-ENE.	15
Figure S12 ¹³ C NMR spectrum of BF-ENE.....	15
Table S1. Crystal data and structure refinement for BF-ENE	16
Synthesis of (E)-2H,2'H-[3,3'-bibenzofuranylidene]-2,2'-dione (BFD):.....	17
Figure S13 Crystal structure of BFD.....	17
Figure S14 High resolution mass spectrum of BFD.....	17
Figure S15 ¹ H NMR spectrum of BFD	18
Figure S16 ¹³ C NMR spectrum of BFD.	18
Table S2. Crystal data and structure refinement for BFD	19
Synthesis of [3,3'-bibenzofuran]-2,2'-diol (CCD):.....	20
Figure S17 Crystal structure of CCD.	20
Figure S18 High resolution mass spectrum of BFD.....	20
Figure S19 ¹ H NMR spectrum of CCD.....	21
Figure S20 ¹³ C NMR spectrum of CCD.....	21

Table S3. Crystal data and structure refinement for CCD.	22
5. General procedure for the polymerization	23
Polymerization with copper acetate.....	23
Polymerization without copper acetate	23
6. Structural isomers of BDF and CCD, and the impact of defect formation	24
Figure S21 Absorbance spectrum of BFD and CCD in DMSO.....	24
Figure S22 DFT calculation of PCCD.	24
Figure S23 Absorbance spectroelectrochemistry of n-PBDF with different catalysts,.....	25
Scheme S2 Reaction summary of chemical transformations among BF, BFD and CCD under various reaction conditions.....	26
Table S4 Summary of conversion and selectivity using different reaction condition.....	27
Figure S24 Temperature-dependent ^1H NMR spectrum of BF with $\text{Cu}(\text{OAc})_2$ in DMSO-d_6 . 27	
Figure S25 Temperature-dependent ^1H NMR spectrum of BF with TMQ in DMSO-d_6 for (a) 2 hours and (b) 12hours.....	28
Figure S26. Temperature-dependent ^1H NMR spectrum of BF with BFD in DMSO-d_6 for (a) 2 hours and (b) 12hours.....	29
Figure S27 Polymerization time investigation by using 0.1 eq $\text{Cu}(\text{OAc})_2$ in open air. All the thin film samples were prepared by drop casting.....	30
Table S5 Polymerization condition investigation. Ink performance and thin film electrical performance from different polymerization conditions	30
7. n-TOC morphology, optical and electronic characterization	31
Figure S28 n-PBDF surface morphology.....	32
Table S6. Shows the spin coating condition for fabricating n-OTC with different thickness..	32
Figure S29 Hall effect results for n-PBDF.....	33
Figure S30 Log-log plot of temperature dependent conductivity of n-PBDF.....	34
Figure S31 n and k value of n-PBDF measured from Filmetrics.....	34
Figure S32 Absorption coefficient of n-PBDF.....	35
.....	35
Figure S33 Work function of n-PBDF.	35
Figure S34 n-PBDF patterning.....	36
Figure S35 Solvent resistance of the conductive for 10 minutes and 1 hour	36
8. n-PBDF as Transparent Conductor and Electrode Material	37
Figure S36 Electrochromic properties of ECP-Blue	37
Figure S37 In-situ conductivity of n-PBDF	37

Figure S38 Electrochromic properties of n-PBDF.	38
Figure S39 n-PBDF contrast at 850 nm.	40
Figure S40 Kinetics and CE of n-PBDF.	40
Figure S41 CV of PEDOT:PSS and n-PBDF device	41
Figure S42 Absorbance spectroelectrochemistry of PEDOT:PSS on ITO.	41
Figure S43 n-PBDF capacitance.	41
Figure S44 CV of PEDOT:PSS and n-PBDF.....	42
Figure S45 Transmittance decrease at 700 nm and 880 nm of OECD vs applied potential. ...	43
Figure S46 Coloration efficiency of PEDOT:PSS and n-PBDF device.....	43
9. References:	44

1. HOMO and LUMO level of PBDF

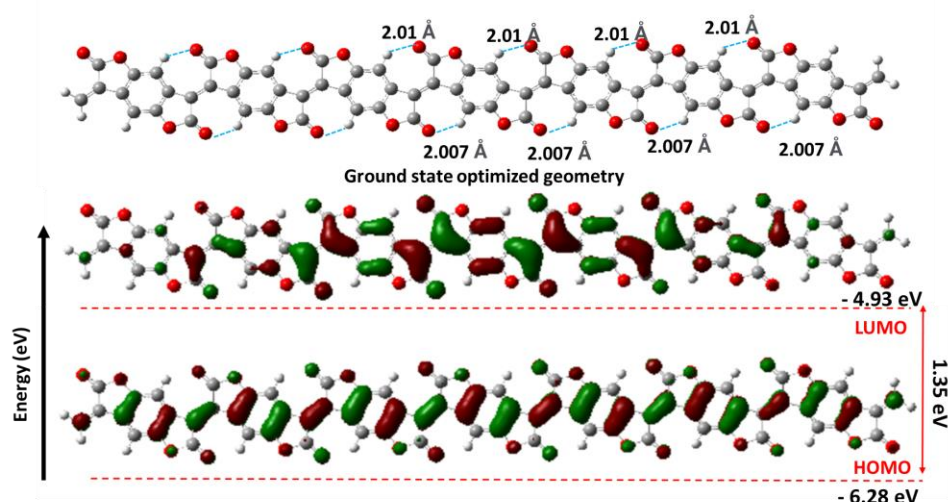


Figure S1 HOMO and LUMO frontier molecular orbitals of the PBDF with 7 repeating unit, obtained from DFT with B3LYP functional and 6-311G (d,p) basis set (calculated by using Gaussian 16).¹

To estimate the LUMO of the PBDF, we electrochemically measure the reduction potential of the PBDF with 0.2 M TBA-TFSI in propylene carbonate (PC) as supporting electrolyte in the glove box with water and oxygen level lower than 1 ppm.² PC was dried using activated molecular sieves prior to the measurements. n-PBDF was diluted to 1 mg/mL and drop cast on platinum disk electrode with 4 mm diameter as working electrode and a platinum wire was used as counter electrode. Our leakless reference electrode was calibrated with respect to ferrocene/ferrocenium (Fc/Fc^+) redox couple in 0.2M tetra-n-butylammonium hexafluorophosphate (TBA-PF_6) in PC. The half-wave potential of the Fc/Fc^+ redox couple ($E^{1/2}_{\text{Fc}/\text{Fc}^+}$) was estimated by averaging the cathodic and anodic peak potential in the cyclic voltammetry (CV) of the electrolyte to be 0.399 V (~ 0.4 V) vs. Ag/AgCl (Figure S2a). To convert the potential from our Ag/AgCl reference electrode to vacuum level equation below is used:

$$E_{\text{vacuum}} = eV_{\text{Ag/AgCl}} - eE_{\text{Fc/Fc}^+}^{1/2} + IP_{\text{Fc}} = eV_{\text{Ag/AgCl}} + 4.4 \quad \text{Eq. S1}$$

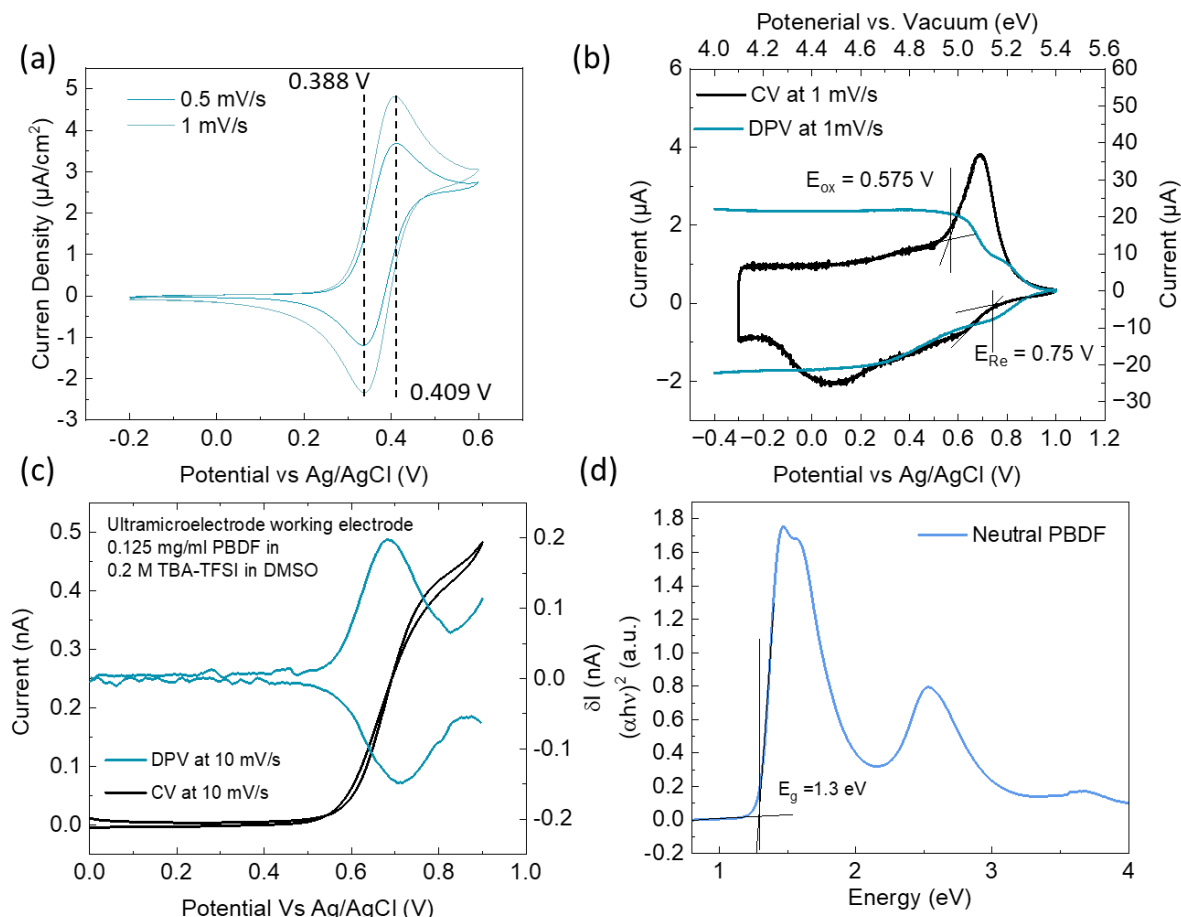


Figure S2 Electrochemical properties of PBDF. (a) CV of ferrocene at 0.5 mV/s and 1 mV/s in 0.2M TBA-PF₆ in PC. The dashed lines show the reduction and oxidation peaks vs. Ag/AgCl. (b) CV and DPV of PBDF thin film in 0.2 M TBA-TFSI in PC at 1 mV/s. Platinum micro electrode with diameter of 4mm was used as the working electrode. (c) CV and DPV of PBDF in DMSO solution at 0.125 mg/ml in 0.2 M TBA-TFSI in DMSO at 10 mV/s. Platinum ultramicroelectrode with diameter of 125μm was used as the working electrode. (d) Tauc plot of PBDF. The optical band gap can be estimated by using equation $(h\nu - E_g) = (a h\nu)^{1/\gamma}$ where γ is 0.5 for direct bandgap materials.

IP_{FC} is the energy level of Fc with respect to vacuum level which is equal to 4.8 eV.^{3,4} To measure the electrochemical properties of PBDF, the ink was diluted to 1 mg/mL and dropped cast on platinum disk electrode to measure the CV and differential pulse voltammetry (DPV) of PBDF in 0.2 M TBA-TFSI in PC (Figure S2b). Based on the reduction onset at 0.75 V, the electron affinity of PBDF can be estimated at 5.15 eV with respect to vacuum. DPV of polymer shows a maximum peak at same potential with a large capacitive behavior between -0.4V and 0.5 V Vs. Ag/AgCl. To confirm the faradic reaction of polymer at the desired potential, we perform CV and DPV of the PBDF in solution state in DMSO at 0.125 mg/mL using ultramicroelectrode as the working electrode with 25 μ m diameter (Figure S2c). Based on both CV and DPV, PBDF just shows a faradic peak at about 0.7V vs. Ag/AgCl which is consistent with thin film measurement. The polymer was electrochemically dedoped on an ITO coated glass in 0.2 M TBA-TFSI in PC, to measure its absorbance spectrum. The Tauc plot was used to estimate the optical band gap of PBDF (Figure S2d). The optical band gap is at 1.3 eV which puts the HOMO level at 6.45 eV. This is in good agreement with the measured LUMO level from DFT calculation (Figure S1 and S3).^{5,6}

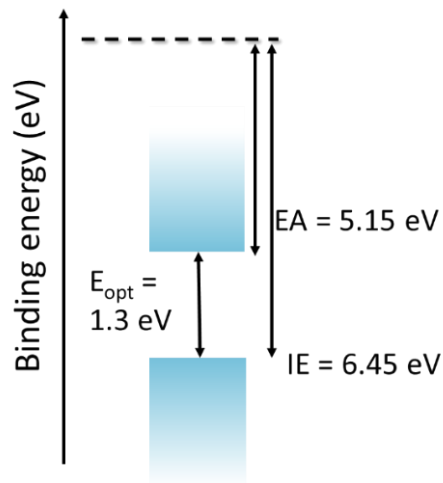


Figure S3 Energetic diagram of PBDF. LUMO was calculated from the CV and HOMO was estimated from optical bandgap of the PBDF after electrochemical dedoping.

2. Electrode configurations for conductivity and Hall effect measurements

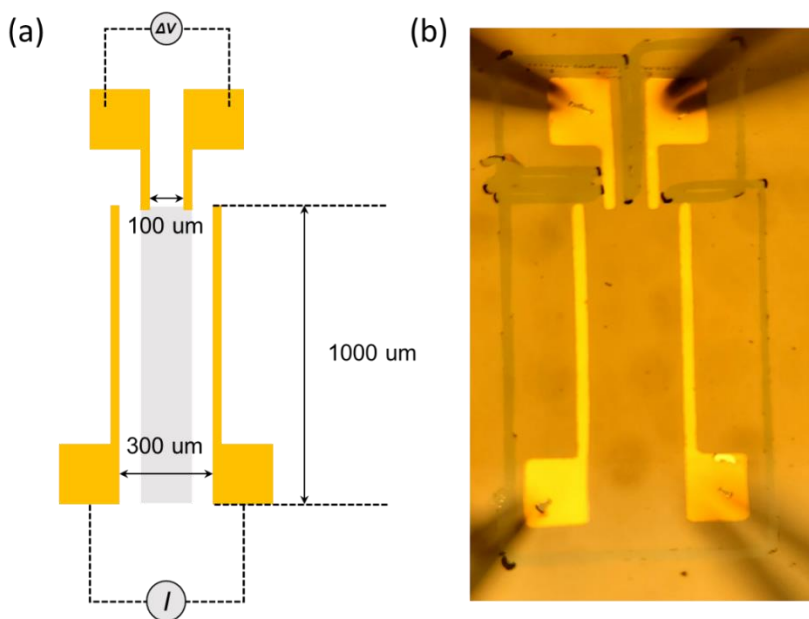


Figure S4 Four-probe electrode configuration. (a) Electrode configuration with grey rectangular as the active area and (b) scratching patterning of n-PBDF on the four-probe electrode.

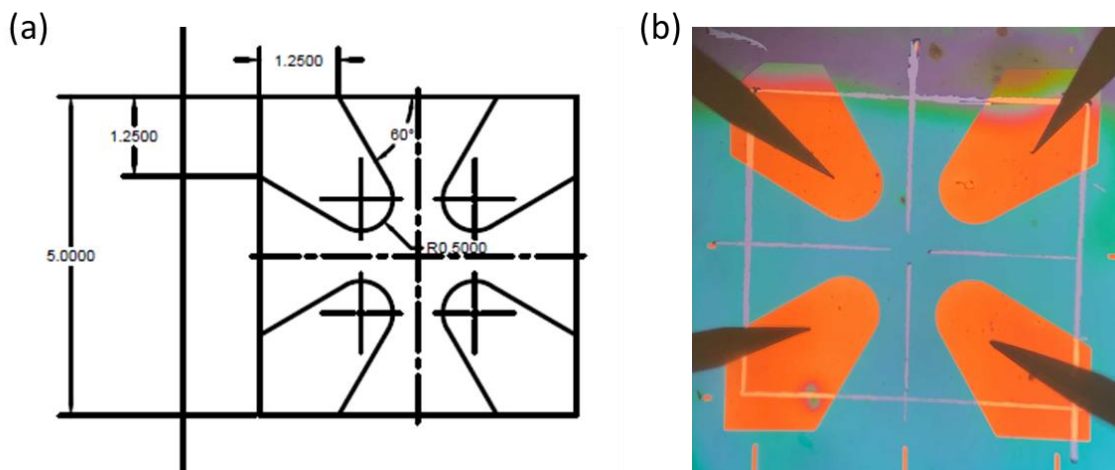


Figure S5 Clover leaf shape Van de Pauw configuration. (a) Electrode configuration and (b) scratching patterning of n-PBDF on the Van de Pauw electrode.⁷

We use bottom contact and four-probe configuration to measure thin film samples Figure S45a. In this configuration the electrodes with channel width of 100 μm and channel length of 1000 μm were prepatterned. 5nm titanium followed by 40 nm gold was used as the electrode (detail can be found in the method section). For each measurement, current (I) with range from (0.1 to 0.001 A) was sources through two electrodes with channel length (l) 300 μm and channel width (w) of 1000 μm and potential difference (ΔV) was measured in between the electrode with two other electrodes with 100 μm distance. In the four-probe configuration, the sheet resistance then was measured using following equation:

$$R_s = \frac{w}{l} \times \frac{\Delta V}{I} = 10 \frac{\Delta V}{I} \quad (\text{Eq. S2})$$

Conductivity of films were then calculated by equation below:

$$\sigma = \frac{1}{R_s t} \quad (\text{Eq. S3})$$

where t (film thickness) was measured by profilometer. This method of measurement is convenient for measuring multiple devices on a single substrate but scratching the polymer film will have a huge impact on the conductivity measurements, which make less reliable and reproducible for measuring highly conductive materials (Figure S5b).

3. Reductive doping of PBDF via water oxidation

Water can be oxidized into H_2O_2 at 1.76 V vs SHE via two electron transfer reaction and water can go through four electron oxidization at 1.23 V vs SHE with oxygen as the by product.⁸

Even though four electron reaction is kinetically more favorable, at presence of a catalyst or a material with strong electron accepting properties with energetics close to oxidation potential of water, the formation of H_2O_2 can lower to 1.4 V Vs SHE (Figure S6a).⁹ To confirm in situ doping of PBDF from water, a thick layer of n-PBDF (dropped cast from 5mg/mL ink) was electrochemically dedoped at 1.1 V (vs. Ag/AgCl) for 15 minutes on top of ITO coated glass after the film conditioning (0.2 M TBA-TFSI in PC). The film was then removed from the ITO substrate and was placed on a H_2O_2 strip test and 40 μL of DI water was then dropped on top of the polymer. The test strip under the polymer was turned to blue indicating at least 10 ppm H_2O_2 (Figure S6b). Pure DI water and electrolyte (after electrochemistry) show no significant concentration of H_2O_2 .

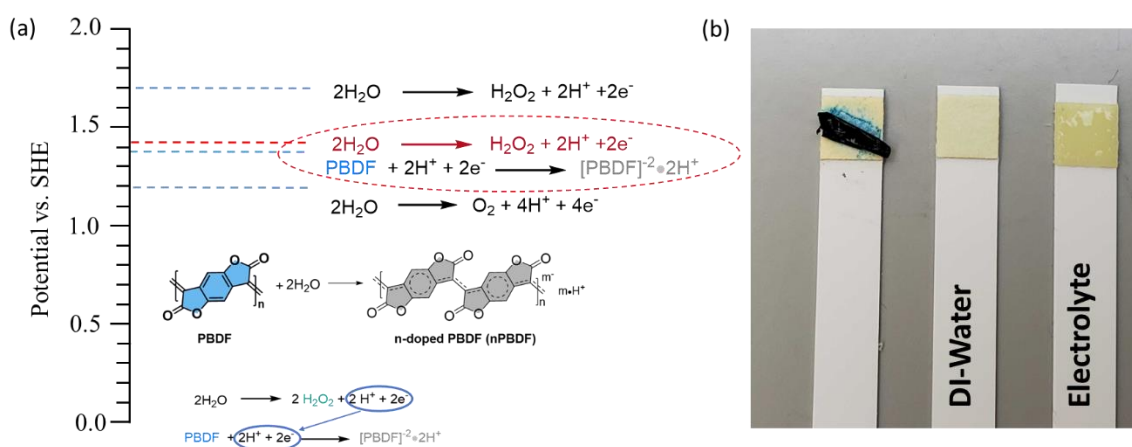


Figure S6 H_2O_2 formation on PBDF. (a) energy diagram of oxidation reaction of H_2O_2 generation via water and oxygen oxidation.⁹ The reduction potential of PBDF was converted to potential vs. SHE with assumption of pH 7. (b) Image of three H_2O_2 test strips. From left to right, dedoped PBDF with 40 μL of DI water, 40 μL of DI water, 40 μL of same electrolyte used for dedoping PBDF.

4. Model reactions and radical trapping

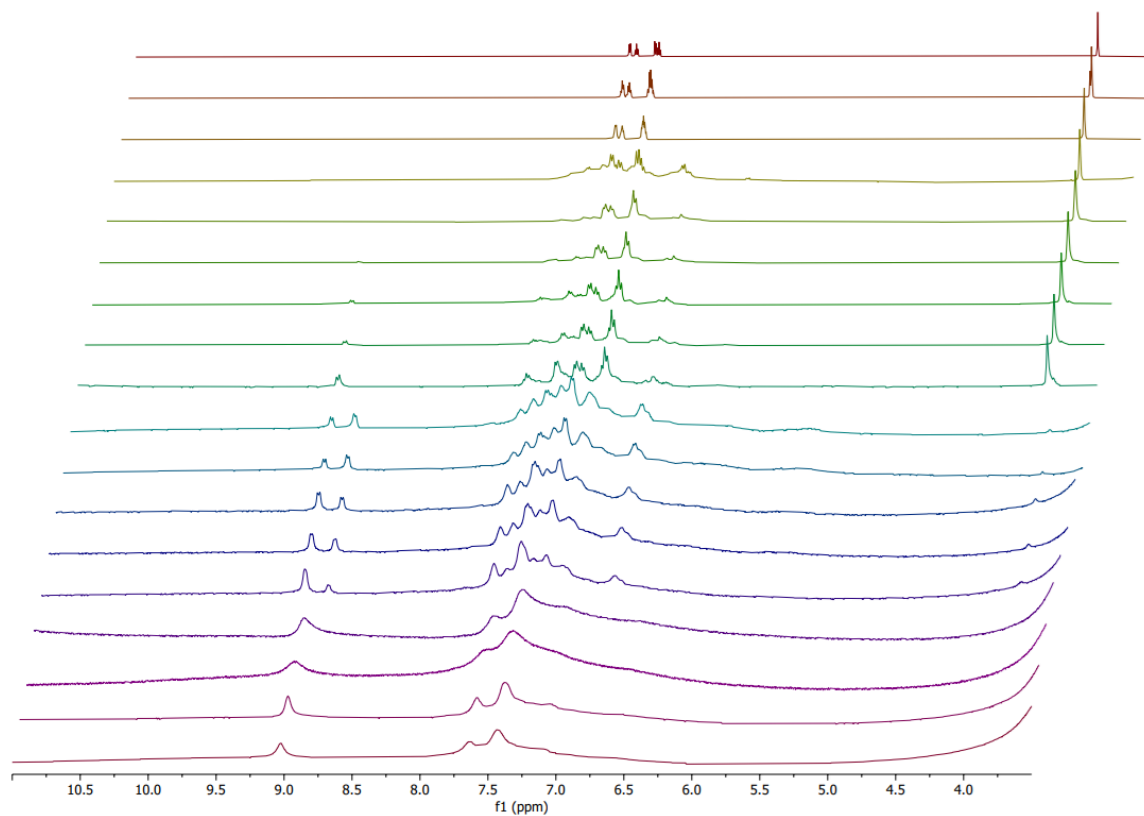
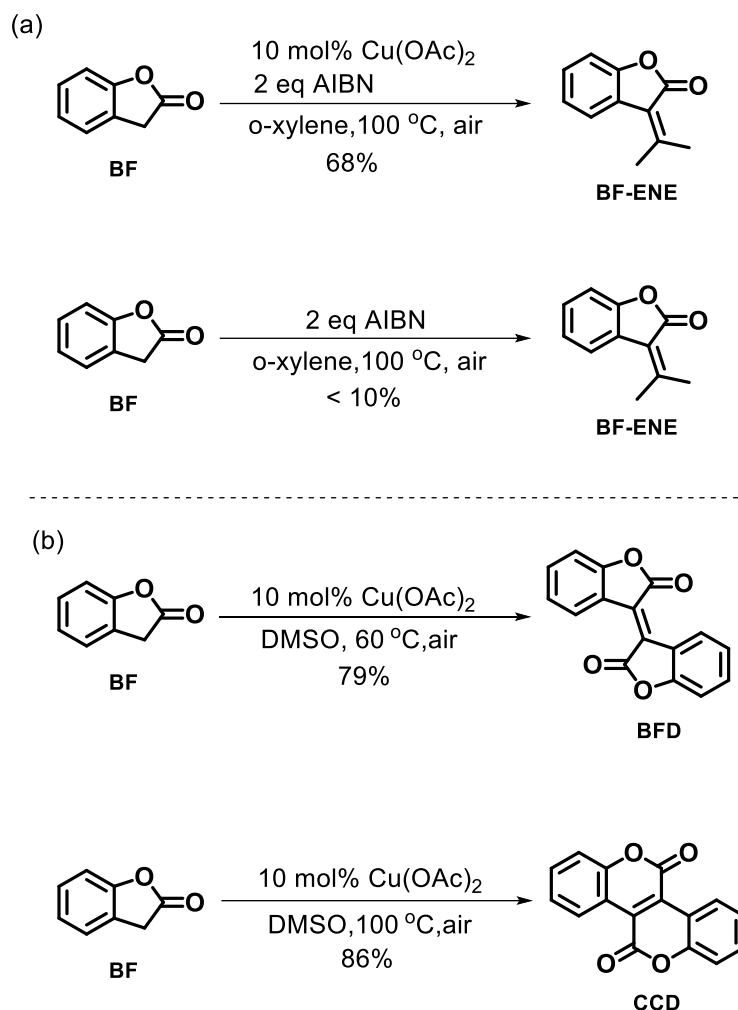


Figure S7 In-situ high temperature (120 °C) ¹H NMR spectra of BF with Cu(OAc)₂ in DMSO-d₆.



Scheme S1. Synthesis of the title compounds. (a) Radical trapping experiment in the presence and absence of copper catalyst. (b) Synthesis of BFD and CCD.

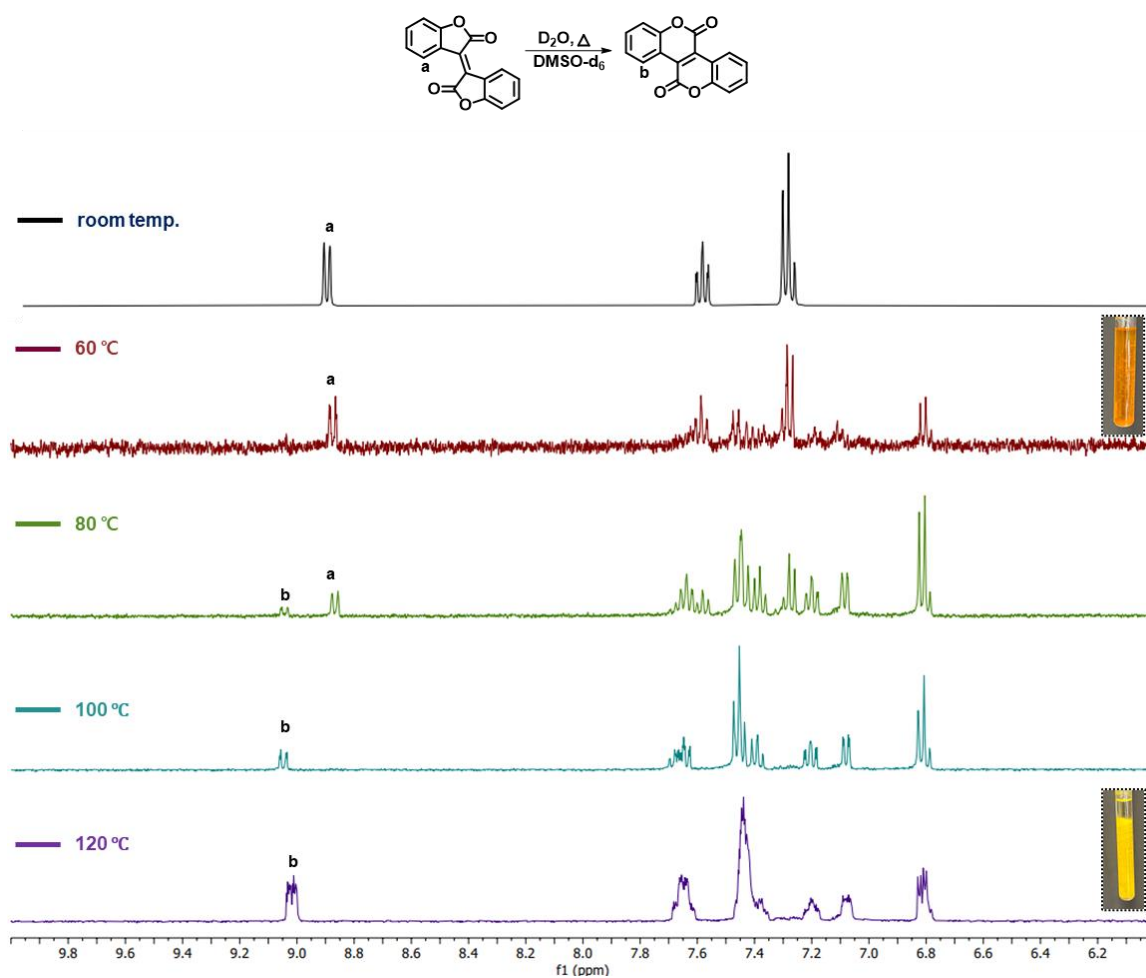


Figure S8 Temperature-dependent ^1H NMR spectrum of BFD with deuterated water in DMSO- d_6 .

Synthesis of 3-(propan-2-ylidene)benzofuran-2(3H)-one (BF-ENE):

Under an air atmosphere, benzofuran-2(3H)-one (0.50 g, 3.73 mmol) and Cu(OAc)₂ (0.24 g, 0.45mmol), AIBN (1.22 g, 7.46 mmol) were added to o-xylene (15 mL), and the mixture was stirred at 100 °C for 12 h. After the reaction was complete, DCM was added, and then the organic layer was extracted with H₂O three times. The crude product was purified via silica-gel column chromatography (hexane:DCM= 1:1 v/v) to obtain BF-ENE. The yield was 0.44 g (68%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.53 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.20 – 6.99 (m, 2H), 2.57 (s, 3H), 2.40 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 167.01, 159.09, 152.28, 128.45, 124.34, 123.39, 123.18, 118.26, 110.45, 24.92, 23.33. HRMS (ESI): calcd. for C₁₁H₁₀O₂ 175.075 [M⁺]; found 175.075

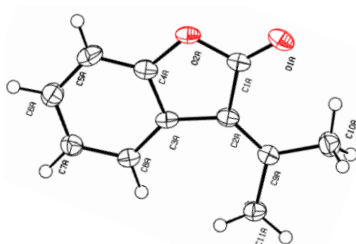


Figure S9 Crystal structure of radical trapping product (BF-ENE).

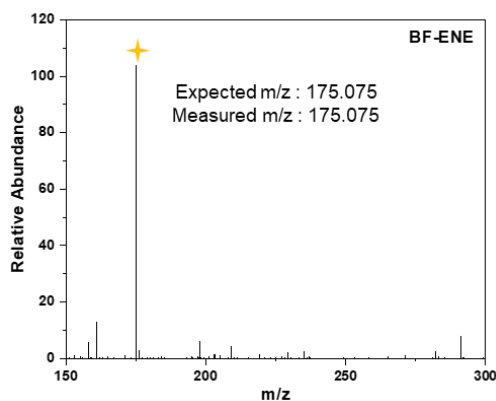


Figure S10 High resolution mass spectrum of BF-ENE.

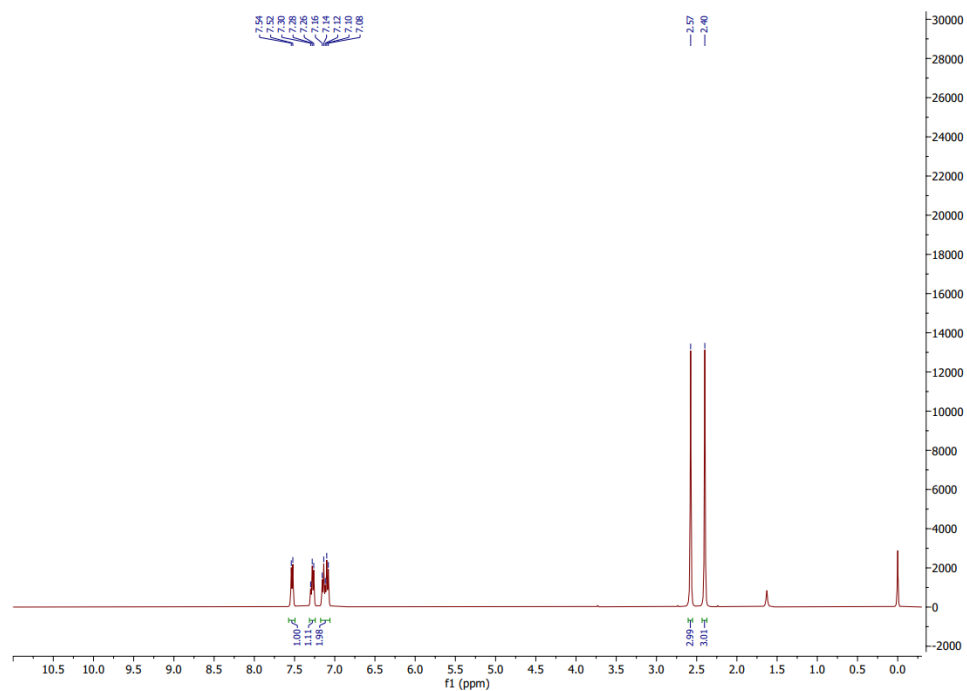


Figure S11 ¹H NMR spectrum of BF-ENE.

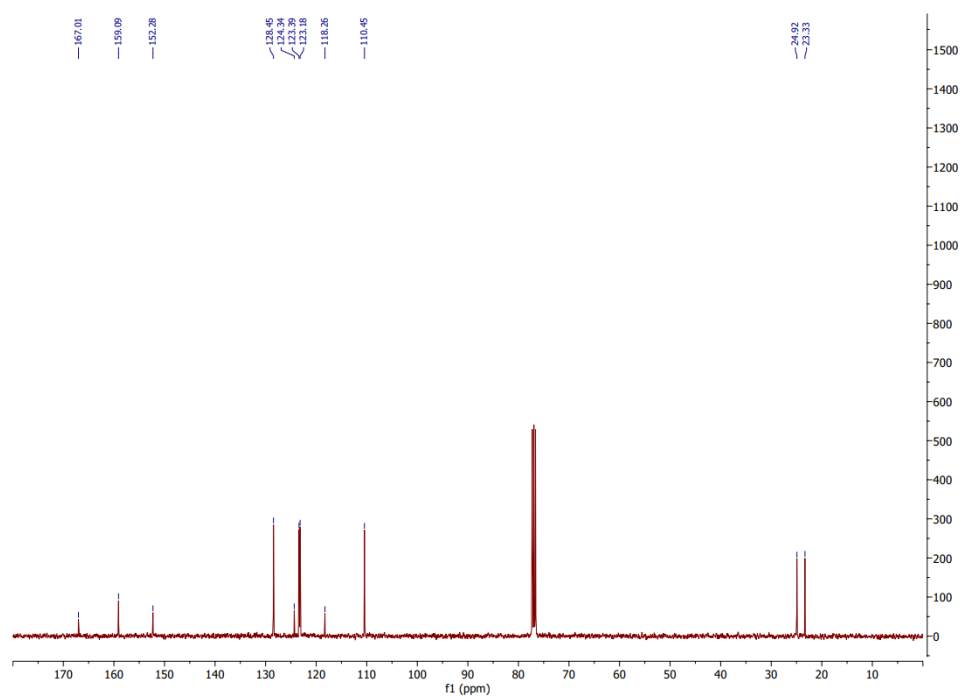


Figure S12 ¹³C NMR spectrum of BF-ENE.

Table S1. Crystal data and structure refinement for **BF-ENE**.

Empirical formula	C ₁₁ H ₁₀ O ₂	
Formula weight	174.19	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 7.1960(8) Å	a = 90°.
	b = 18.069(2) Å	b = 96.897(7)°.
	c = 13.1978(14) Å	γ = 90°.
Volume	1703.7(3) Å ³	
Z	8	
Density (calculated)	1.358 Mg/m ³	
Absorption coefficient	0.753 mm ⁻¹	
F(000)	736	
Crystal size	0.350 x 0.030 x 0.030 mm ³	
Theta range for data collection	4.168 to 79.831°.	
Index ranges	-9<=h<=9, -22<=k<=23, -16<=l<=16	
Reflections collected	32904	
Independent reflections	3670 [R(int) = 0.0950]	
Completeness to theta = 67.679°	99.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3670 / 0 / 239	
Goodness-of-fit on F ²	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1519	
R indices (all data)	R1 = 0.0872, wR2 = 0.1628	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.285 and -0.275 e.Å ⁻³	

Synthesis of (E)-2H,2'H-[3,3'-bibenzofuranylidene]-2,2'-dione (BFD):

Under an air atmosphere, benzofuran-2(3H)-one (0.50 g, 3.73 mmol) and Cu(OAc)₂ (0.24 g, 0.45mmol) were added to o-xylene (15 mL), and the mixture was stirred at 100 °C for 6 h. After the reaction was complete, the reaction mixture was filtered through Celite and washed with DCM. The crude product was purified via silica-gel column chromatography (hexane:DCM= 1:1 v/v) to obtain BFD, which was an orange solid. The yield was 0.39 g (79%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.10 (ddd, *J* = 8.7, 1.3, 0.5 Hz, 1H), 7.54 (ddd, *J* = 8.1, 7.5, 1.3 Hz, 1H), 7.28 (ddd, *J* = 8.3, 7.6, 1.2 Hz, 1H), 7.17 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 166.77, 155.87, 134.49, 129.65, 129.02, 124.57, 122.43, 110.74. HRMS (ESI): calcd. for C₁₆H₈O₄ 265.049 [M⁺]; found 265.049

The same reaction can be carried out in DMSO at 60 °C and only BFD is observed.

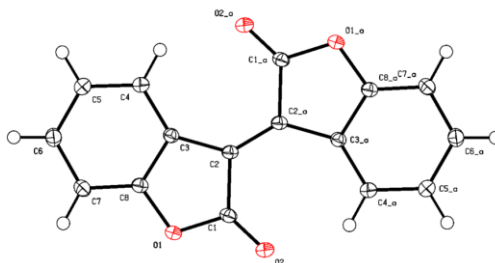


Figure S13 Crystal structure of BFD.

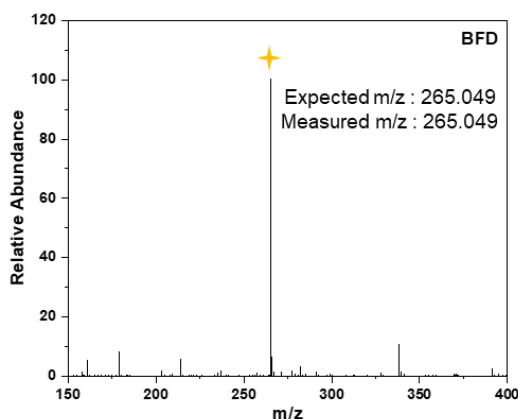


Figure S14 High resolution mass spectrum of BFD.

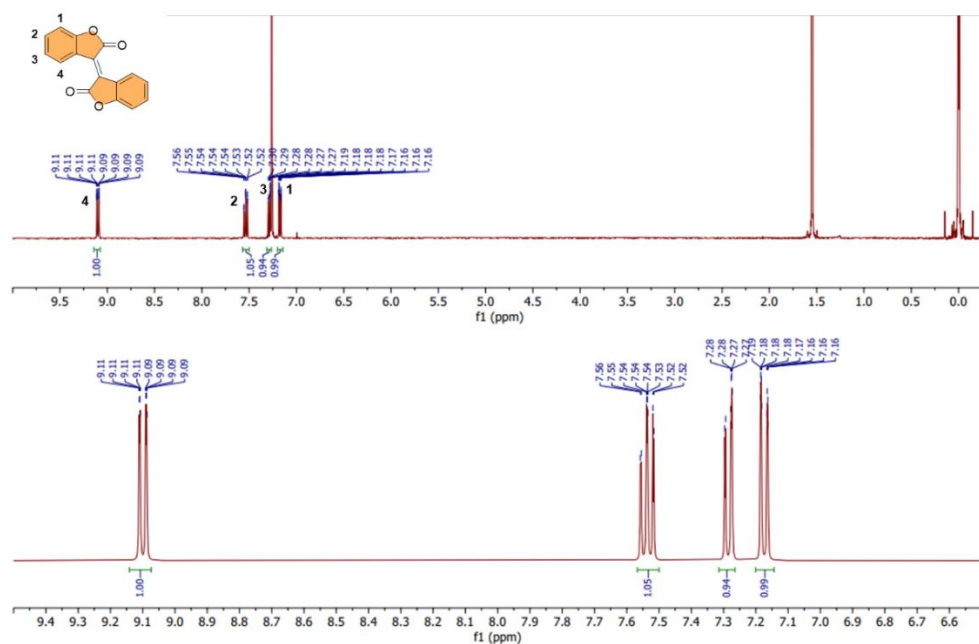


Figure S15 ^1H NMR spectrum of BFD (top) and detailed zoom between 7.5 and 6.5 ppm (bottom).

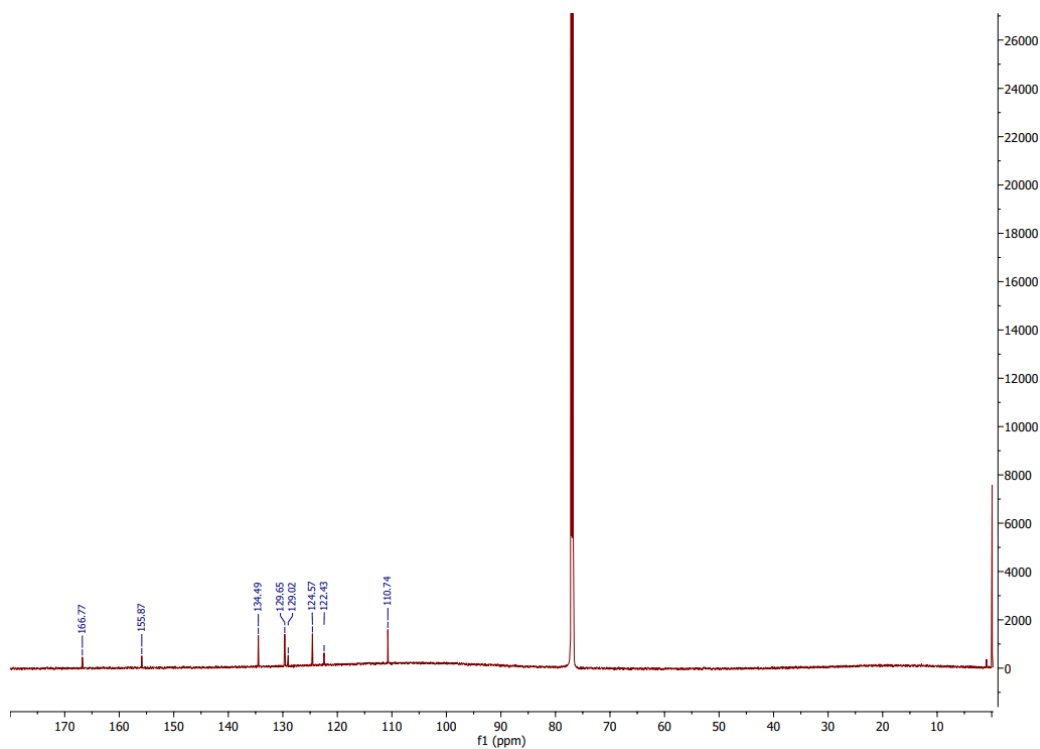


Figure S16 ^{13}C NMR spectrum of BFD.

Table S2. Crystal data and structure refinement for **BFD**.

Empirical formula	C ₁₆ H ₈ O ₄	
Formula weight	264.22	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 5.5852(3) Å	α = 90°.
	b = 5.5998(3) Å	β = 96.490(2)°.
	c = 17.5399(9) Å	γ = 90°.
Volume	545.06(5) Å ³	
Z	2	
Density (calculated)	1.610 Mg/m ³	
Absorption coefficient	0.117 mm ⁻¹	
F(000)	272	
Crystal size	0.420 x 0.410 x 0.180 mm ³	
Theta range for data collection	3.672 to 33.168°.	
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -26 ≤ l ≤ 26	
Reflections collected	14458	
Independent reflections	2080 [R(int) = 0.0350]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7465 and 0.6888	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2080 / 0 / 91	
Goodness-of-fit on F ²	1.061	
Final R indices [I > 2σ(I)]	R1 = 0.0376, wR2 = 0.1024	
R indices (all data)	R1 = 0.0447, wR2 = 0.1065	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.517 and -0.219 e.Å ⁻³	

Synthesis of [3,3'-bibenzofuran]-2,2'-diol (CCD):

Under an air atmosphere, benzofuran-2(3H)-one (0.50 g, 3.73 mmol) and Cu(OAc)₂ (0.24 g, 0.45mmol) were added to DMSO (15 mL), and the mixture was stirred at 100 °C for 6 h. After the reaction was complete, the reaction mixture was filtered through Celite and washed with DCM. The crude product was purified via silica-gel column chromatography (hexane:DCM= 1:1 v/v) to obtain CCD, which was an yellow solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.26 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.64 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 1H), 7.48 – 7.35 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) 132.36, 128.25, 125.41, 116.50. HRMS (ESI): calcd. for C₁₆H₈O₄ 265.049 [M⁺]; found 265.049

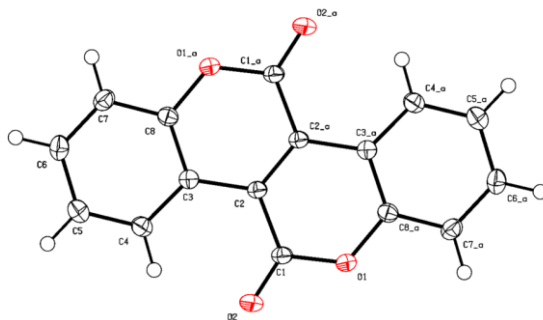


Figure S17 Crystal structure of CCD.

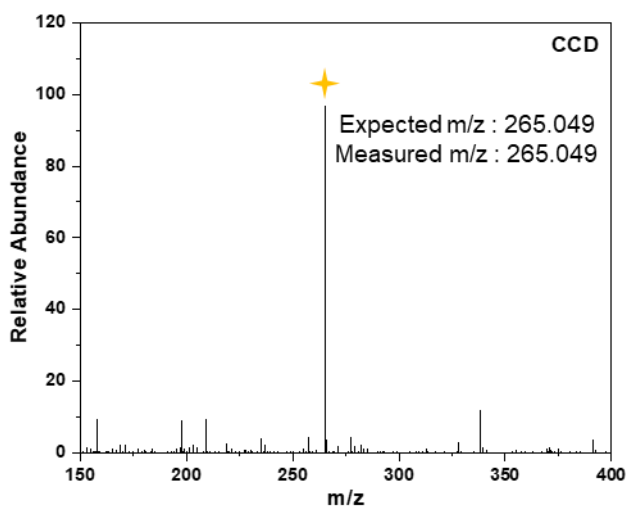


Figure S18 High resolution mass spectrum of BFD.

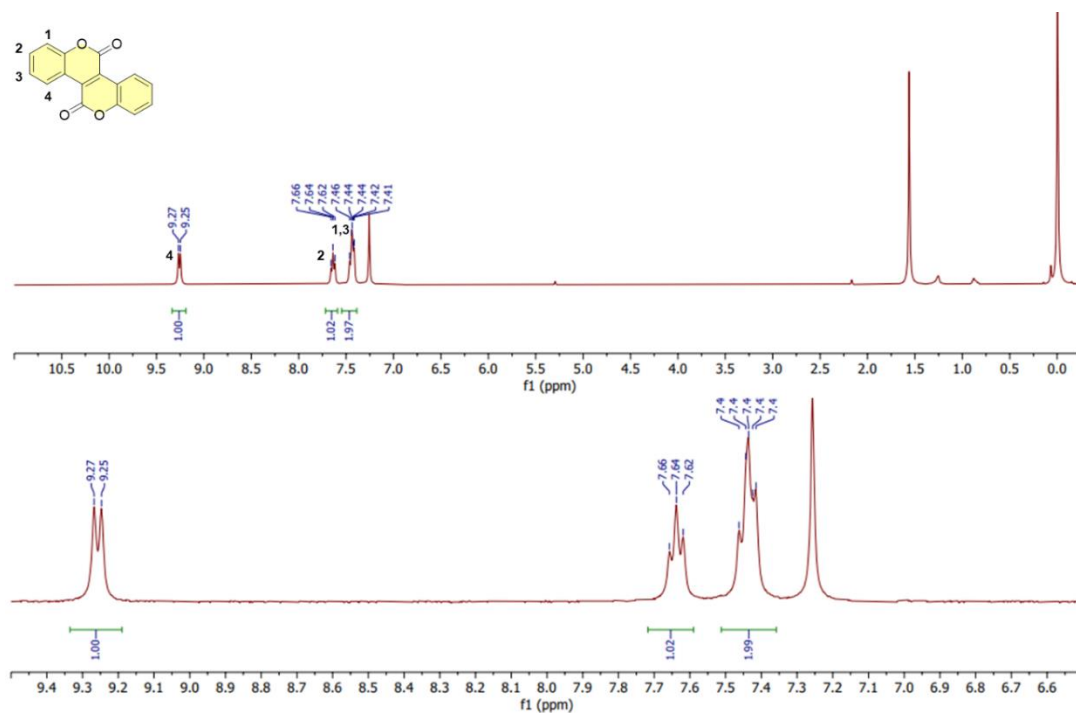


Figure S19 ^1H NMR spectrum of CCD (top) and detailed zoom between 7.5 and 9.5 ppm (bottom).

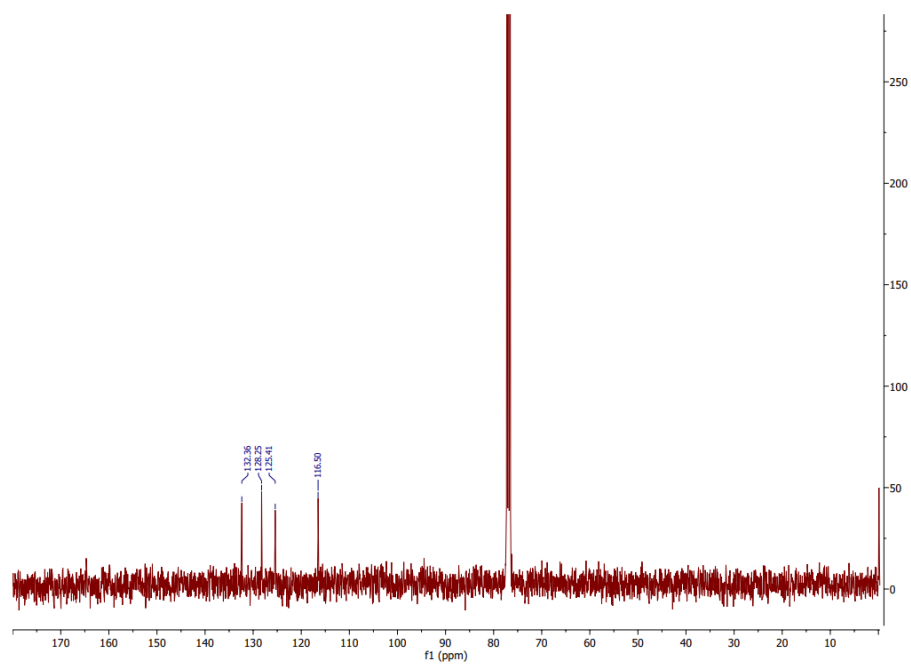


Figure S20 ^{13}C NMR spectrum of CCD.

Table S3. Crystal data and structure refinement for **CCD**.

Empirical formula	C ₁₆ H ₈ O ₄	
Formula weight	264.22	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 4.5964(5) Å	α = 90°.
	b = 9.4515(13) Å	β = 95.096(5)°.
	c = 12.6982(16) Å	γ = 90°.
Volume	549.47(12) Å ³	
Z	2	
Density (calculated)	1.597 Mg/m ³	
Absorption coefficient	0.116 mm ⁻¹	
F(000)	272	
Crystal size	0.450 x 0.050 x 0.030 mm ³	
Theta range for data collection	2.690 to 33.184°.	
Index ranges	-6 ≤ h ≤ 7, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19	
Reflections collected	24090	
Independent reflections	2089 [R(int) = 0.0543]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7465 and 0.7107	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2089 / 0 / 91	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0498, wR2 = 0.1358	
R indices (all data)	R1 = 0.0677, wR2 = 0.1494	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.558 and -0.216 e.Å ⁻³	

5. General procedure for the polymerization

Polymerization with copper acetate

The monomer 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (BDF), Cu(OAc)₂ and additives were dissolved in DMSO (~15 mg/mL for BDF). The mixture was heated with stirring at various temperatures for 6 hours in air. After the solution was cooled to RT, the mixture was diluted to 10 mg/mL for BDF and dialyzed against DMSO using a dialysis bag with a cut-off molecular weight of 10 kDa (Viskase, USA) to remove low molecular weight fractions, copper catalyst and additives.

Polymerization without copper acetate

The monomer BDF (1 eq) and additive (benzoquinone (BQ) or tetramethylbenzoquinone (TMQ), 2 eq) were dissolved in anhydrous DMSO (~15 mg/mL for BDF). The mixture was gradually heated up to 100 °C and kept at 100 °C for 1.5 hours in N₂ or open air. After the solution was cooled to RT, the mixture was diluted to 10 mg/mL for BDF and dialyzed against DMSO using a dialysis bag with a cut-off molecular weight of 10 kDa (Viskase, USA) to remove low molecular weight fractions and catalyst. After purification, the yield of n-PBDF is around 50 % and the concentration of n-PBDF in the ink is ~ 5 mg/mL.

6. Structural isomers of BFD and CCD, and the impact of defect formation

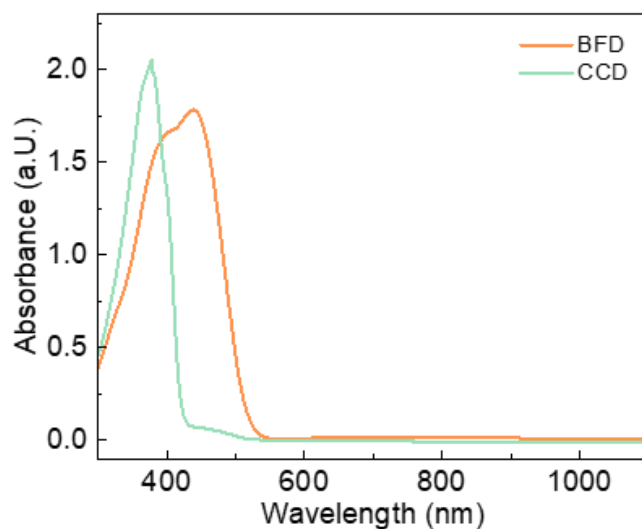


Figure S21 Absorbance spectrum of BFD and CCD in DMSO.

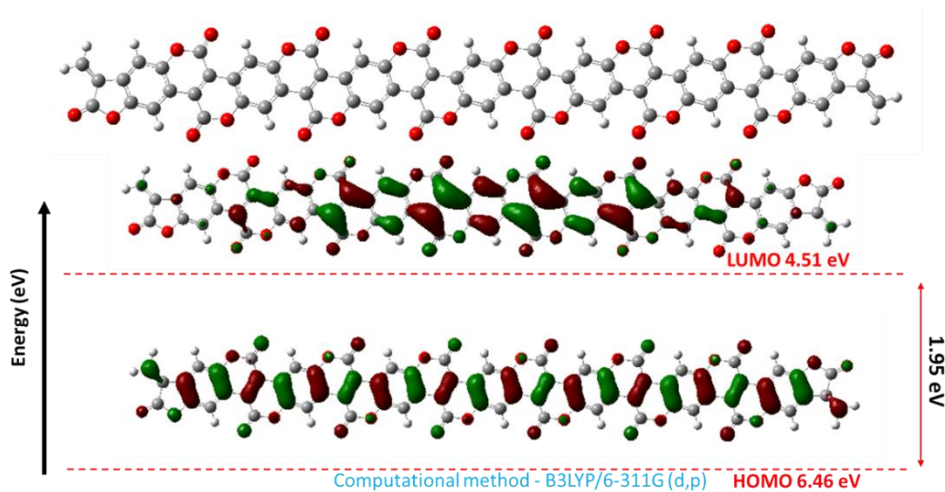


Figure S22 DFT calculation of PCCD. HOMO and LUMO frontier molecular orbitals of the PCCD with 7 repeating unit, obtained from DFT with B3LYP functional and 6-311G (d,p) basis set (calculated by using Gaussian 16).¹

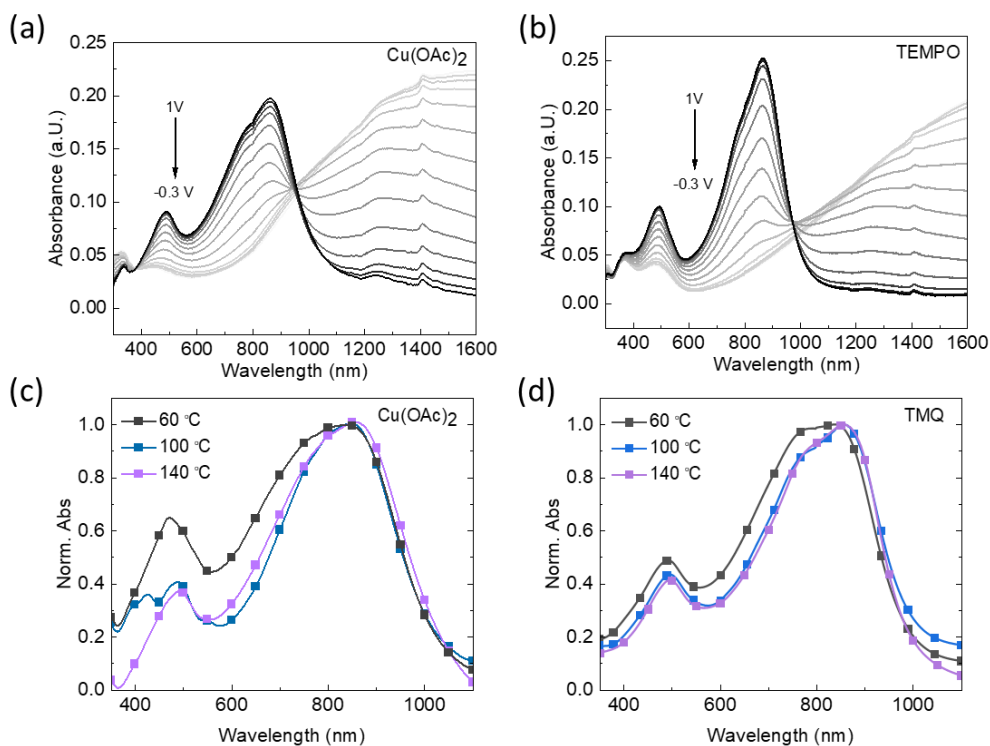


Figure S23 Absorbance spectroelectrochemistry of n-PBDF with different catalysts, (a) Cu(OAc)₂, (b) TEMPO. Absorbance of n-PBDF at its neutral state synthesized with (c) Cu(OAc)₂ and (d) TMQ catalysts at different temperatures.

Table S4 Summary of conversion and selectivity using different reaction condition.

	<i>o</i> -xylene			DMSO					
Temp (°C)	Cu(OAc) ₂ (conv. (%))	TMQ (conv. (%))	BFD (conv. (%))	Cu(OAc) ₂ (conv. (%))	CCD (conv. (%))	TMQ (2h) (conv. (%))	TMQ (12h) (conv. (%))	BFD (2h) (conv. (%))	BFD (12h) (conv. (%))
60				BFD (>99 %)		N.R	N.R	BFD:CCD 1:0.16 (33 %)	BFD:CCD 1:0.2 (35 %)
80				BFD:CCD 1:2 (>99 %)		N.R	N.R	BFD:CCD 1:0.16 (47 %)	BFD:CCD 1:0.2 (60 %)
100	BFD (>99 %)	N.R	BFD (4%)	CCD (>99 %)	CCD (18%)	BFD (0.7 %)	BFD:CCD 1:5 (68 %)	BFD:CCD 1:0.11 (75 %)	BFD:CCD 1:0.3 (80 %)
120	BFD (>99 %)	N.R	BFD (77 %)	CCD (>99 %)	CCD (66%)	BFD:CCD 1:1.5 (11 %)	CCD (84 %)	BFD:CCD 1:0.66 (77 %)	BFD:CCD 1:2.6 (91 %)

N.R.= no reaction.

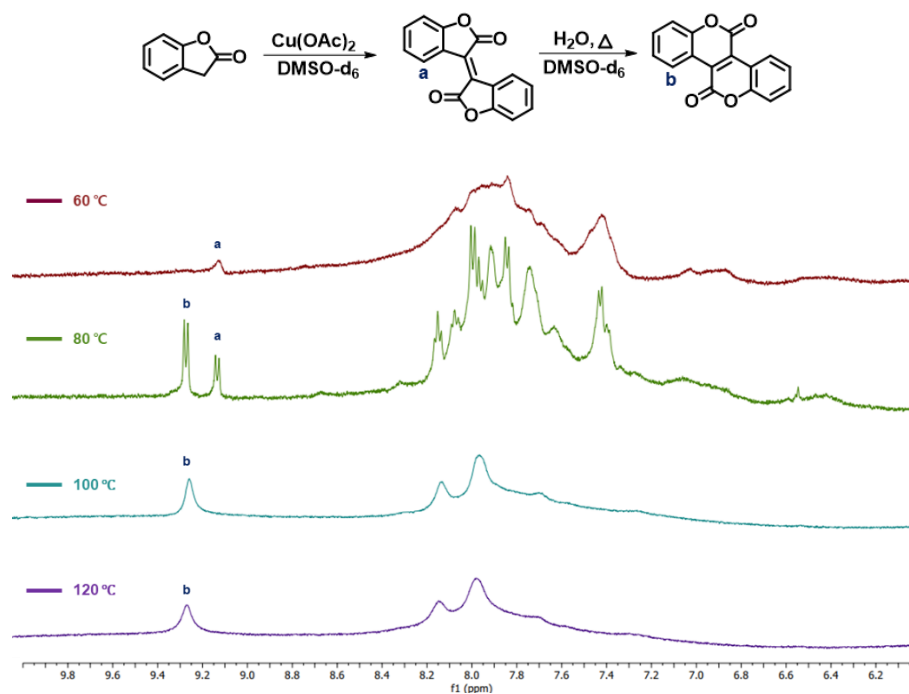


Figure S24 Temperature-dependent ¹H NMR spectrum of BF with Cu(OAc)₂ in DMSO-d₆.

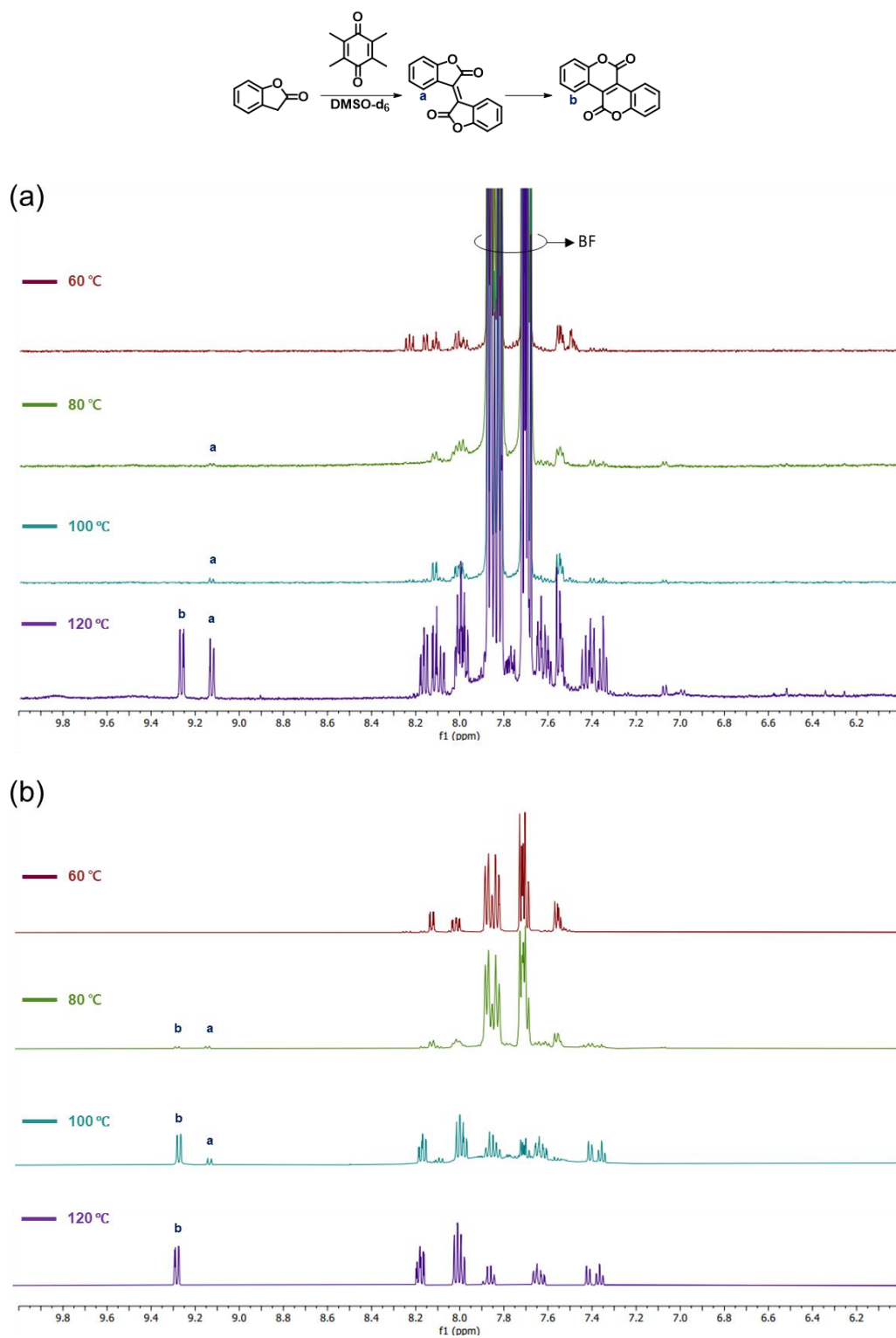


Figure S25 Temperature-dependent ^1H NMR spectrum of BF with TMQ in DMSO-d_6 for (a) 2 hours and (b) 12hours.

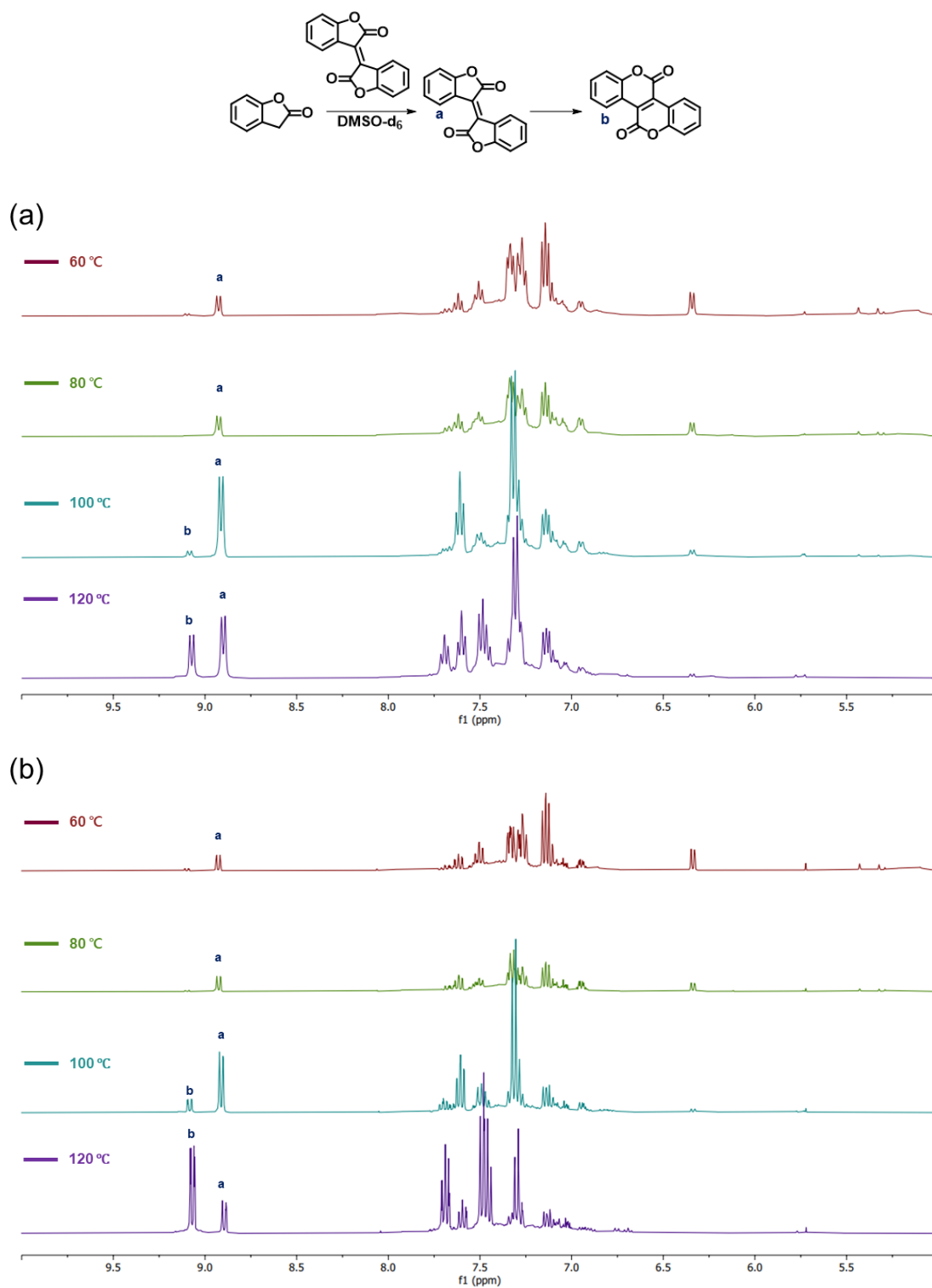


Figure S26. Temperature-dependent ^1H NMR spectrum of BF with BFD in DMSO-d_6 for (a) 2 hours and (b) 12 hours.

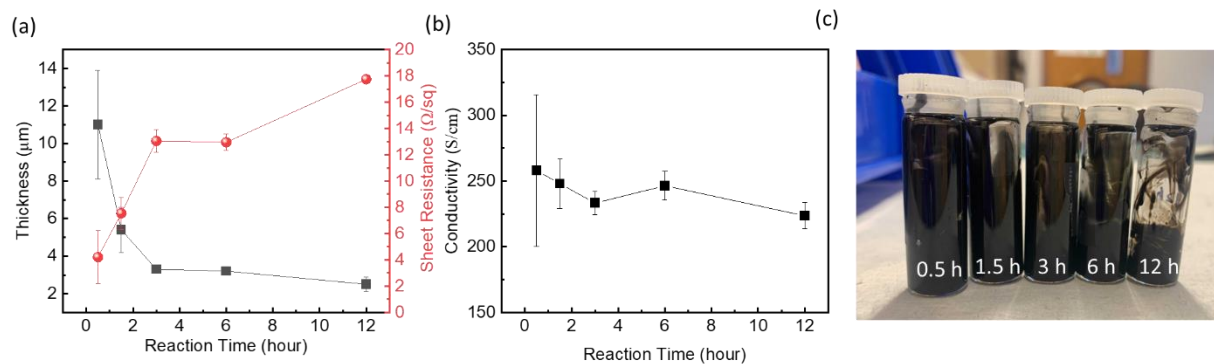


Figure S27 Polymerization time investigation by using 0.1 eq $\text{Cu}(\text{OAc})_2$ in open air. All the thin film samples were prepared by drop casting. Variation of (a) film thickness and sheet resistance, (b) conductivity with reaction time, and (c) photo of polymers with different reaction time.

Table S5 Polymerization condition investigation. Ink performance and thin film electrical performance from different polymerization conditions. ^[a]: air condition. ^[b]: N_2 condition. ^[c]: spin coating.

Entry	$\text{Cu}(\text{OAc})_2$ (equiv.)	Additive (equiv.)	Temperature (°C)	Solubility	Sheet Resistance (Ω/sq)	Thickness (μm)	Conductivity (S/cm)
1 ^[a]	0.02	-	100	Solution	450 ± 10	1.9	11.7 ± 0.4
2 ^[a]	0.1	-	100	Solution-gel	34.2 ± 0.8	1.2	250 ± 10
3 ^[a]	1.0	-	100	Gel-solid	1.2 ± 0.2	4.0	2100 ± 300
4 ^[a]	0.1	-	60	Solution-gel	12.1 ± 0.7	2.7	310 ± 20
5 ^[a]	0.1	-	140	Gel	130 ± 20	1.9	40 ± 5
6 ^[a]	0.1	-	180	Gel	210 ± 10	2.6	33 ± 3
7 ^[a]	0.1	TEMPO (2.0)	100	Viscous solution	113 ± 2	2.9	31.0 ± 0.5
8 ^[a]	0.1	HQ (0.1)	100	Solution-gel	4.4 ± 0.2	2.7	840 ± 40

9 ^[a]	0.1	HQ (2.0)	100	Solution-gel	61 ± 9	2.4	68 ± 8
10 ^[a]	0.1	HQ (5.0)	100	Solution-gel	136 ± 1	1.2	61.3 ± 0.5
11 ^[a]	0.1	TMHQ (0.1)	100	Solution-gel	6 ± 1	2.9	600 ± 100
12 ^[a]	0.1	TMHQ (2.0)	100	Solution-gel	3 ± 1	3.1	1200 ± 300
13 ^[a]	0.1	TMHQ (5.0)	100	Gel	2.2 ± 0.8	4.4	1000 ± 300
14 ^[b]	-	BQ (2.0)	100	Viscous solution	~4 × 10 ⁻⁷	3.2	~8.1 × 10 ⁻⁵
15 ^[b]	-	TMQ (2.0)	100	Viscous solution	1.40 ± 0.04	2.2	3200 ± 300
16 ^{[a][c]}	-	TMQ (2.0)	100	Clear solution	1350 ± 50	0.045	165 ± 6
17 ^[b]	-	BFD (2.0)	100	Viscous solution	11605 ± 100	2.1	0.4 ± 0.1
18 ^[b]	-	CCD (2.0)	100	Viscous solution	9069 ± 300	2.3	0.5 ± 0.1

7. n-TOC morphology, optical and electronic characterization

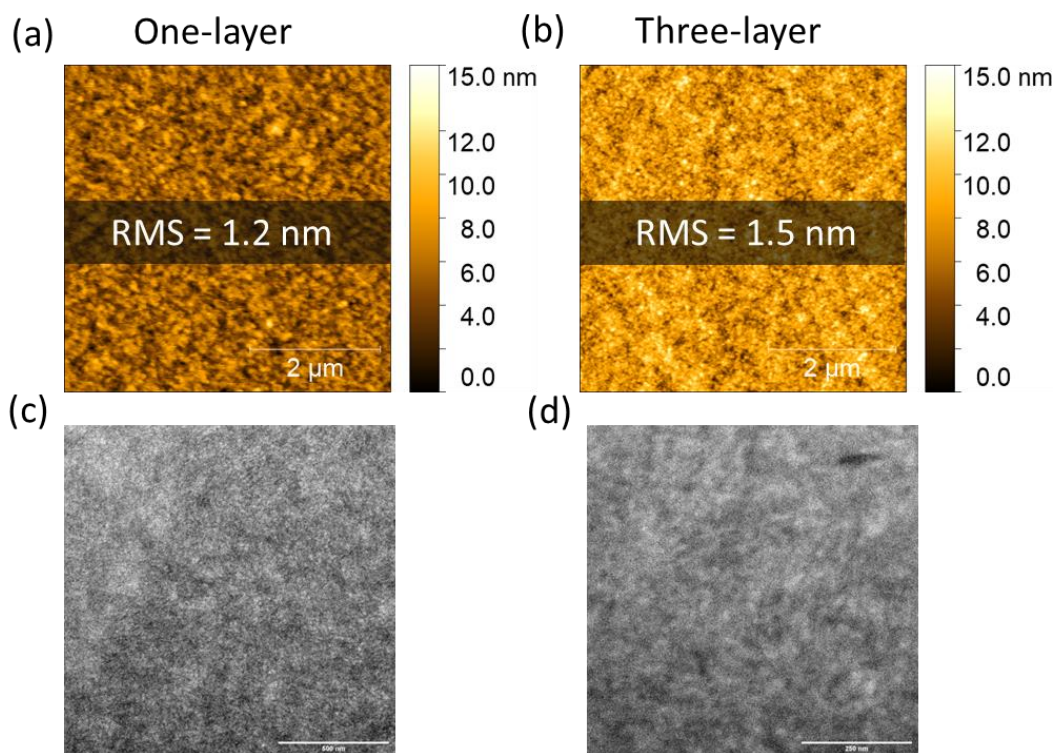


Figure S28 n-PBDF surface morphology. (a) the AFM images of one layer and (b) three layers of n-PBDF conducting ink on silicon substrate. The mean square (RMS) roughness of 1 layer is about 1.2 nm and 3 layers 1.5 nm. (c) and (d) TEM images of one-layer n-PBDF. Small surface roughness reduces the contact resistance between n-OTC and other organic layers.¹⁰

Table S6. Shows the spin coating condition for fabricating n-OTC with different thickness.

Spin rate (rpm)	# Of layers	Thickness (nm)	Conductivity (s/cm)	Conductivity error (S/cm)	Relative conductivity error (%)
2000	1	17	3100	400	13
1500	1	19	3800	400	11
1000	2	36	4600	200	4
1000	3	59	5200	200	4
1000	4	74	5800	200	3
1000	5	94	6100	400	7

R_H (Hall coefficient) can be calculated using equation below:

$$V_{Hall} = \frac{IB R_H}{t} \quad \text{Eq. S3}$$

where I is the current, B is the applied magnetic field and t is sample thickness. From V_{Hall} vs. B graph (Figure S 29a), the slope can be fitted and then R_H can be calculated. I was 0.01A for all the measurements. Then charge carrier density (n), Figure S29b can be calculated using the equation below:

$$R_H = \frac{1}{n|e|} \quad \text{Eq. S4}$$

Where e is elementary charge of electron, 1.602×10^{-19} C. Here, we have assumed transport is ideal. In case of non-ideal transport, n will be lower than reported value. σ was directly measured (Figure S29c). μ shown in Figure S29d, was calculated using equation below:

$$\mu = \frac{\sigma}{en} \quad \text{Eq. S4}$$

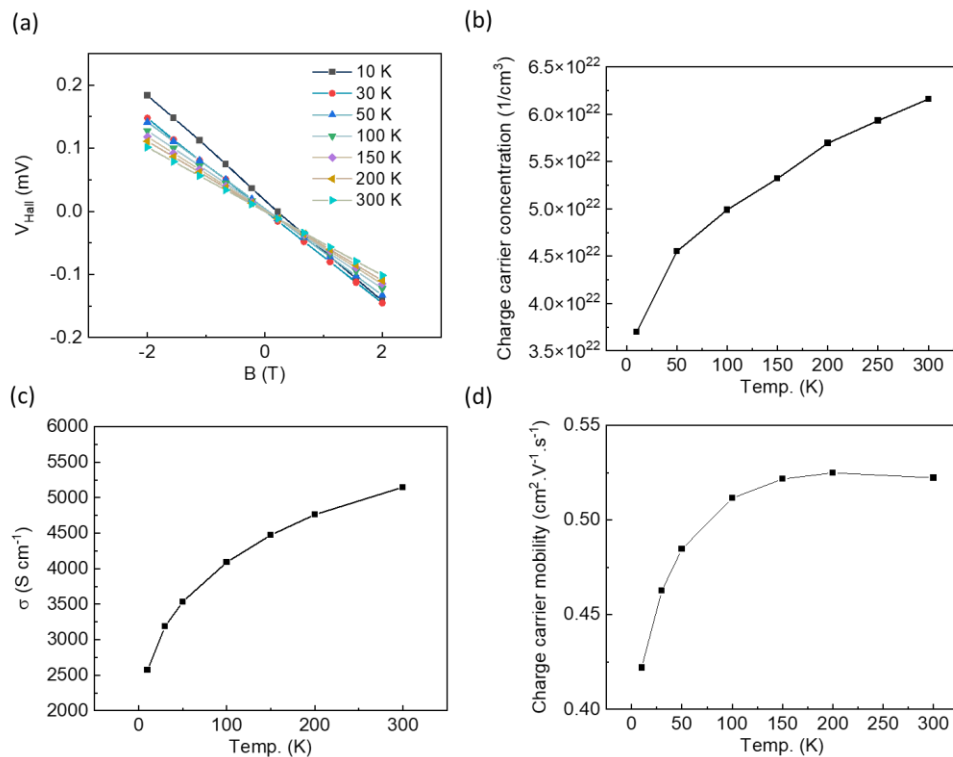


Figure S29 Hall effect results for n-PBDF. Temperature dependent (a) Hall potential (V_{Hall}), (b) charge carrier concentration (n), (c) electrical conductivity (σ) and (d) charge carrier mobility (μ), and (d).

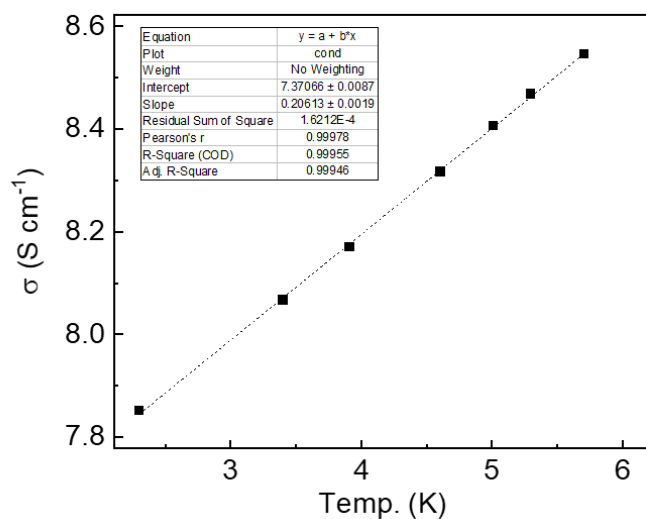


Figure S30 Log-log plot of temperature dependent conductivity of n-PBDF. Conductivity follows power law of temperature, $\sigma = T^{0.206}$, which suggest a critical regime for charge transport.^{11,12}

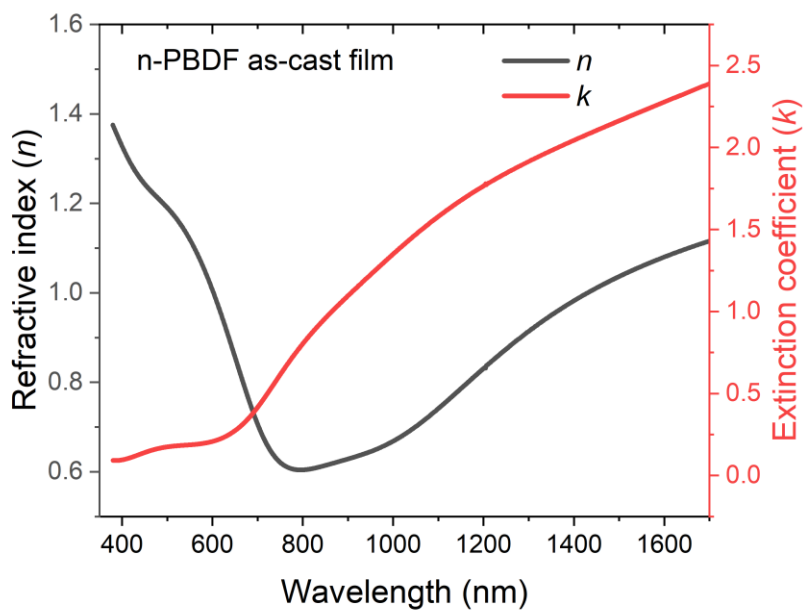


Figure S31 n and k value of n-PBDF measured from Filmetrics.

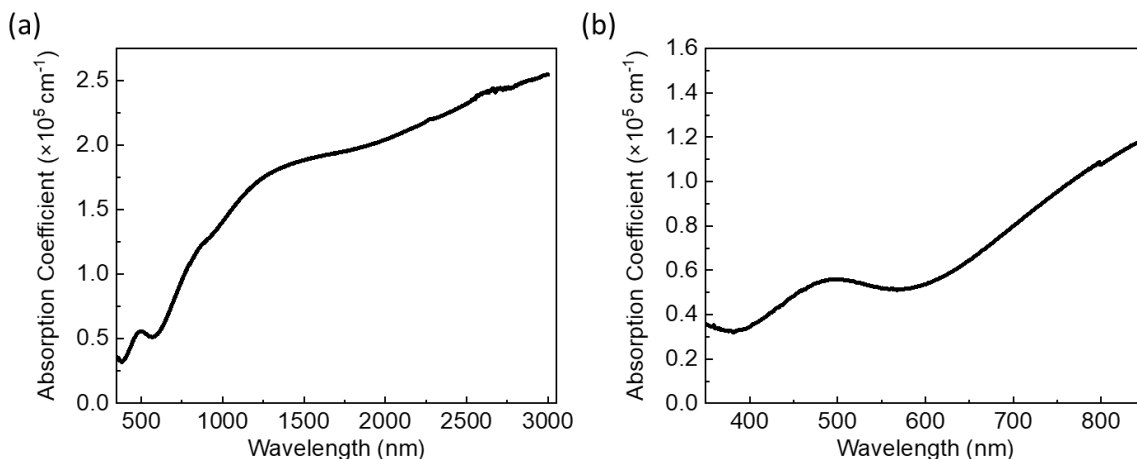


Figure S32 Absorption coefficient of n-PBDF (a) from 350 nm to 3000 nm, (b) Vis range, calculated from Figure 2b using following equation, $Abs = \alpha \times t$, where α is absorption coefficient and t is film thickness.

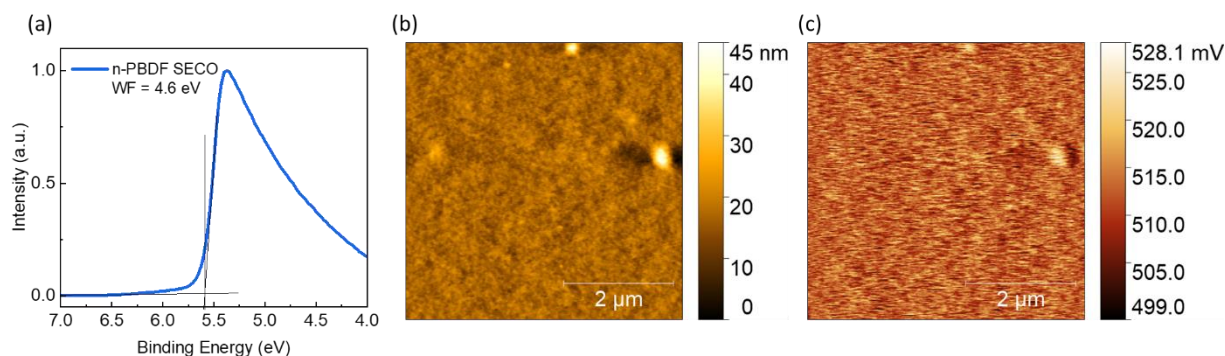


Figure S33 Work function of n-PBDF. (a) Secondary cut-off region from UPS spectrum of n-PBDF thin film. WF is estimated at 4.6 eV. (b) Surface topography and (c) surface potential of the n-PBDF thin film. The KPFM (Kelvin Probe Force Microscopy) tip potential is at 4.9 ± 0.005 eV with estimated WF at 4.4 eV.¹³

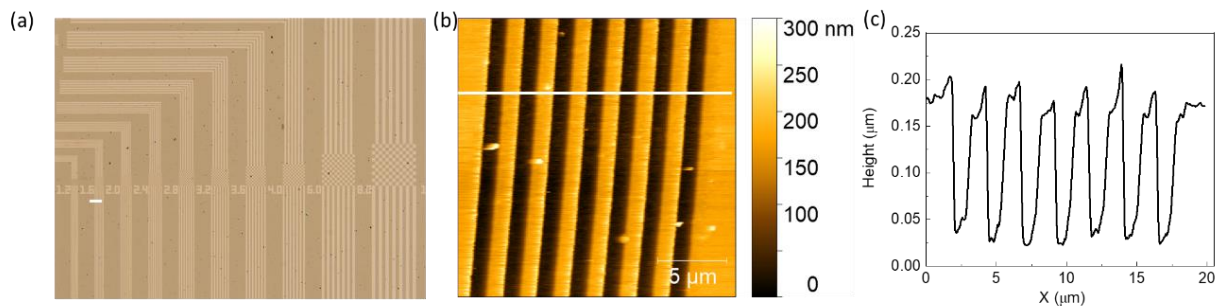


Figure S34 n-PBDF patterning. (a) microscope image and (b) AFM image of patterning shown with white line in (a). (c) shows the AFM profile of the pattern indicated by white line in (b)

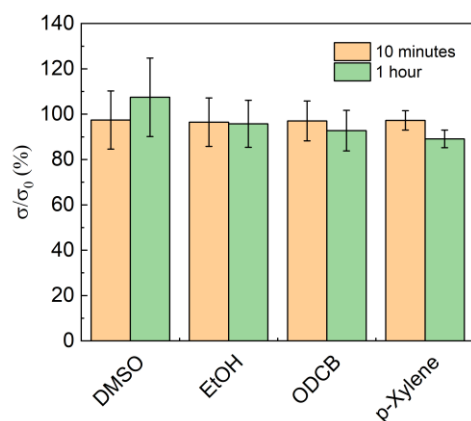


Figure S35 Solvent resistance of the conductive for 10 minutes and 1 hour to DMSO, ethanol, ODCB and p-xylene. The error bars on the data points represent the standard error.

8. n-PBDF as Transparent Conductor and Electrode Material

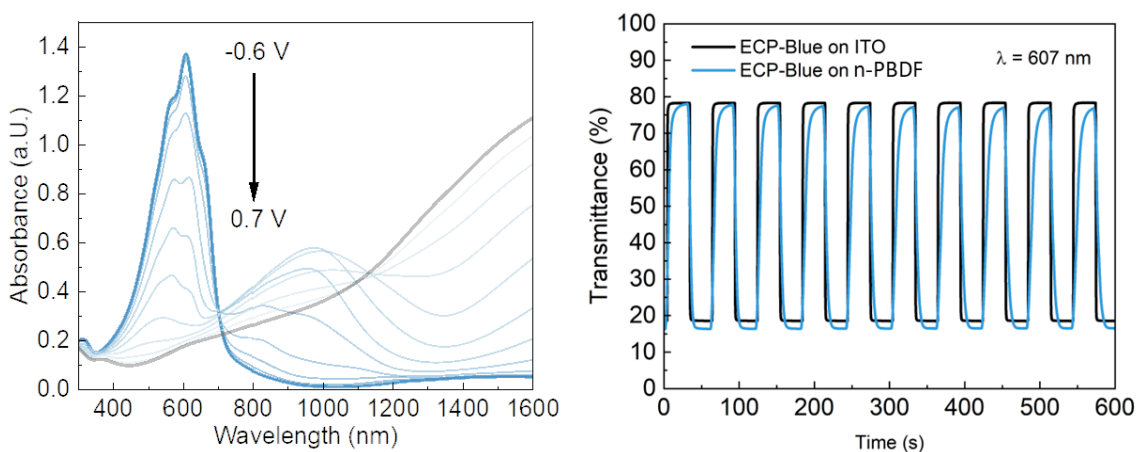


Figure S36 Electrochromic properties of ECP-Blue. (a) Absorbance spectroelectrochemistry of ECP-blue on ITO. (b) switching kinetics of ECP-Blue on ITO and n-PBDF at 607 nm.

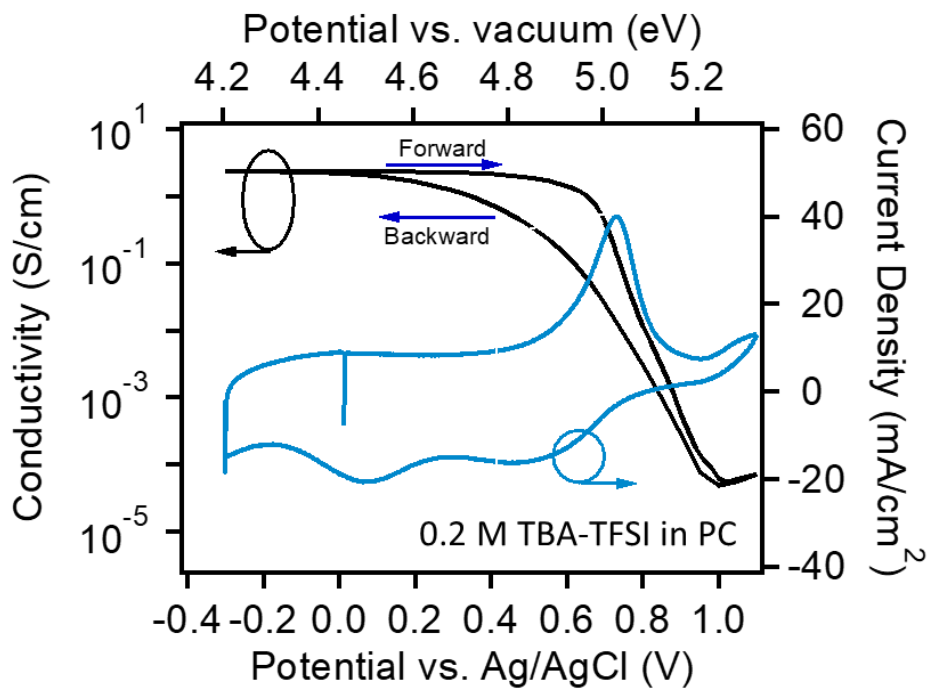


Figure S37 In-situ conductivity of n-PBDF during electrochemical oxidation and reduction with CV of n-PBDF in 0.2 M TBA-TFSI.

Absorbance spectroelectrochemistry of the thin film n-PBDF show absorbance spectrum of reduced/bleached and neutral/colored state of the polymer (Figure S38 a). As cast polymer (light blue color) shows strong absorbance in NIR region and a small peak at 490 nm. Upon oxidation of the film to its neutral form, two main absorbance peaks, one at 490 nm and the other at 850 nm grow with decrease in absorbance in NIR region indicating disappearance of polaron and bipolaron peaks. The corresponding CIE D65 1976 L*, a*, b* color space is shown in Figure S38 b and c. Based on the color coordination, the polymer has a* and b* value 0.85 and -2.7 in neutral state and 0.3 and 0.75 in the colored state, respectively. To show the color neutrality if the n-PBDF Chroma is defined as $\sqrt{(a^*)^2 + (b^*)^2}$. If chroma is less than 10, the human eye has difficulty telling apart the exact color of the film and the film would appear neutral grey.¹⁴ Chroma for colored state is 2.9 and in bleached state is at 0.8 indicating the film is colorless (neutral grey) in both neutral and reduced state.

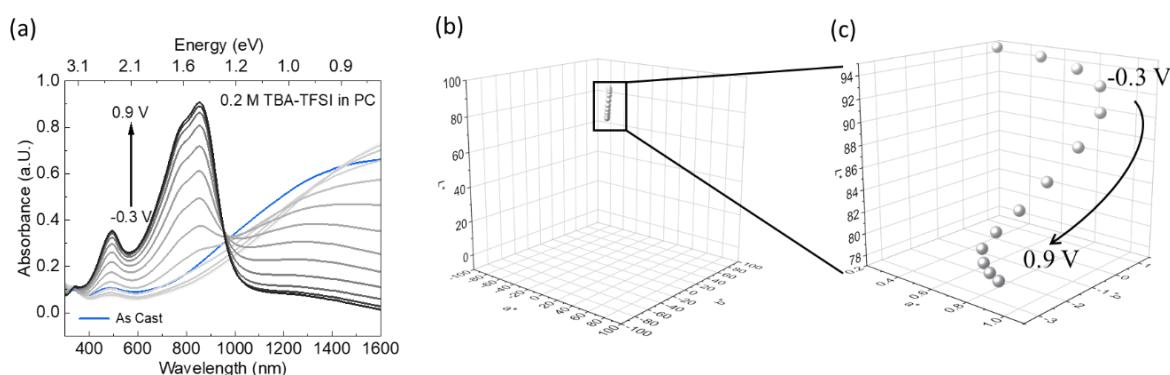


Figure S38 Electrochromic properties of n-PBDF. (a) Absorbances spectroelectrochemistry of n-PBDF in 0.2M TBA-TFSI in PC. The blue line shows the as-cast film of n-PBDF. Color coordination CEI D65 of n-PBDF thin film (b) full scale and (c) small range.

The absorption coefficient of the n-PBDF at 850 nm in bleached (α_B) and colored state (α_C) is calculated by fitting the following equation to thickness dependent transmittance of colored and bleached state (Figure S39a).

$$T = 100 \times e^{-\alpha t} \quad \text{Eq. S7}$$

where t is the thickness of the film. α_B and α_C to be $0.7 \times 10^5 \text{ cm}^{-1}$ and $4.42 \times 10^5 \text{ cm}^{-1}$ respectively. Contrast of the film can be calculated using equation below:

$$\text{Contrast} = T_B - T_C = 100 \times (e^{-\alpha_B t} - e^{-\alpha_C t}) \quad \text{Eq. S8}$$

The maximum contrast can be calculated by finding the local maximum of the above equation to find the thickness at which contrast is maximum.

$$d_{\max} = \frac{\beta \ln(\beta)}{\alpha_C(\beta - 1)} \quad \text{Eq. S9}$$

where $\beta = \alpha_C / \alpha_B$. $d_{\max}$ and maximum contrast is calculated 49.5 nm. The calculated contrast and fitted line are shown in Figure S39b. The contrast at 49.5 nm is 59.5% at 850 nm.

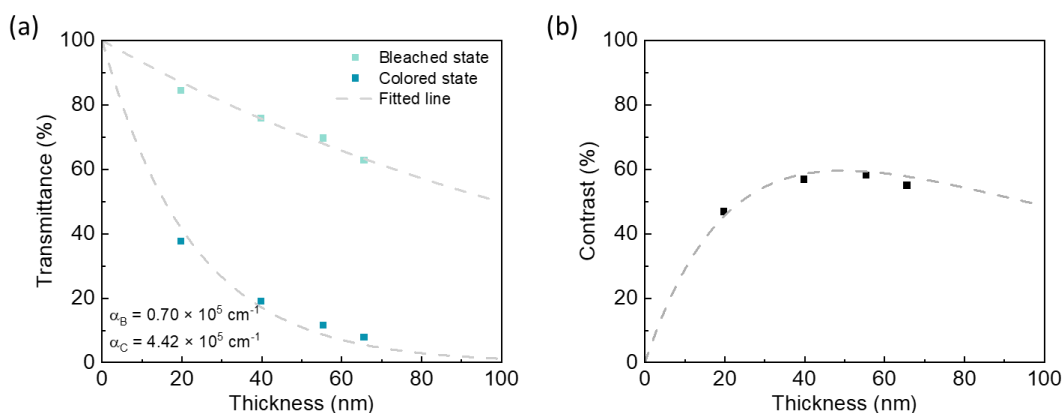


Figure S39 n-PBDF contrast at 850 nm. (a) Transmittance of colored and bleached state of n-PBDF at four different thicknesses at 850 nm. The dashed line shows the exponential fit to extract absorption coefficient. (b) Contrast of n-PBDF at 850 nm.

Polymer shows fast switching speed 0.5 to 1 second for range of thickness from 20 to 65 nm film (Figure S40a) Polymer shows high coloration efficiency, as high as $762 \text{ cm}^2/\text{C}$, which agrees with fast switching speed and electrical conductivity of n-PBDF (Figure S40b).

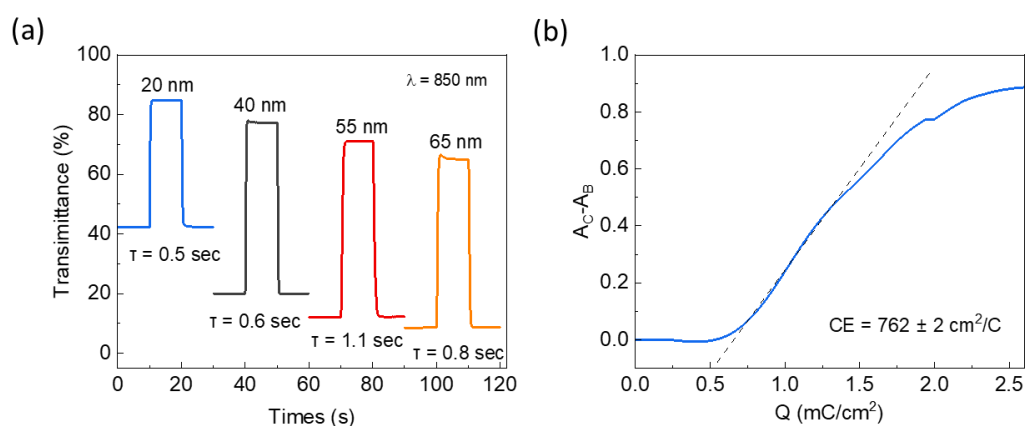


Figure S40 Kinetics and CE of n-PBDF. (a) Kinetics of n-PBDF thin film at 850 nm for different polymer thickness. (b) Coloration efficiency of n-PBDF.

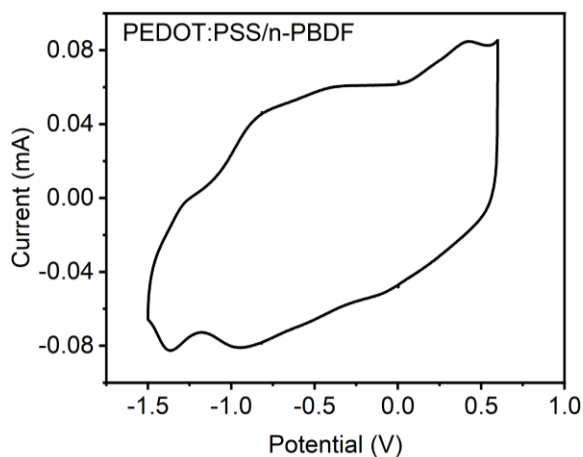


Figure S41 CV of PEDOT:PSS and n-PBDF device in solid electrolyte 0.2M TBA-TFSI in solid electrolyte of PC and PEGMA.

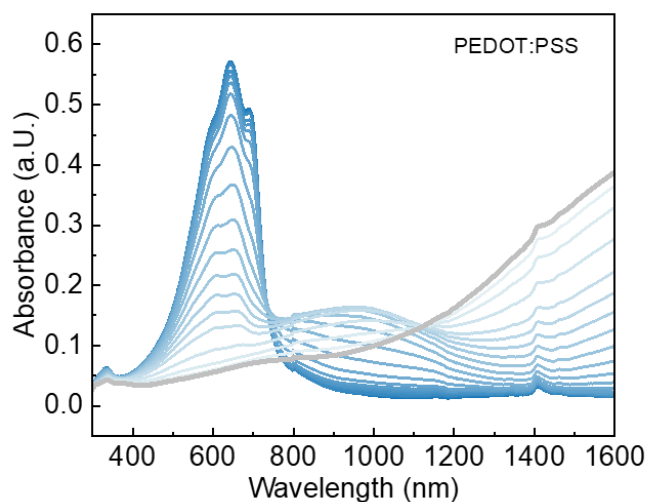


Figure S42 Absorbance spectroelectrochemistry of PEDOT:PSS on ITO.

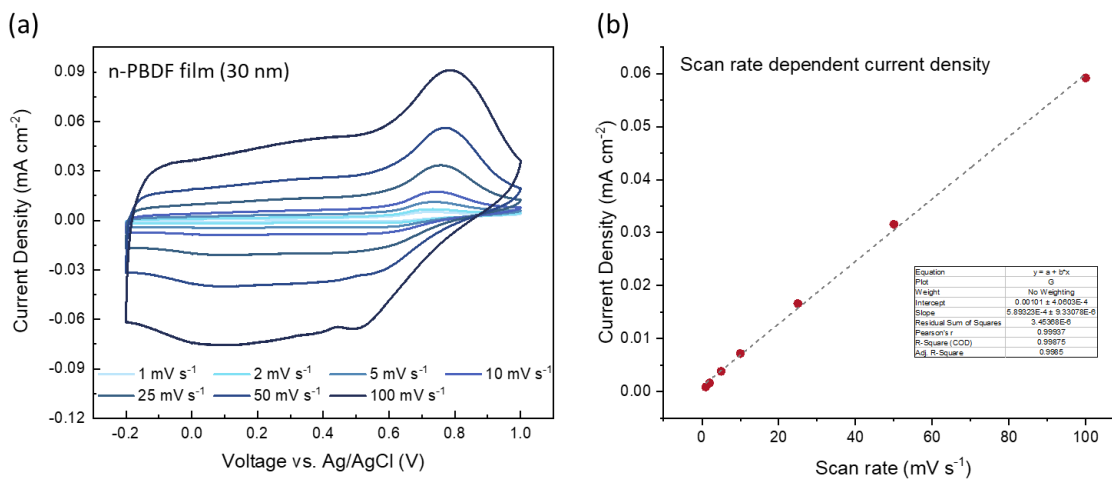


Figure S43 n-PBDF capacitance. (a) CV of 30 nm thick n-PBDF at different rates on ITO in 0.2M TBA-TFSI (PC). (b) Averaged anodic and cathodic current at 0.3 V (vs. Ag/AgCl) plotted vs scan rate from (a).

The specific volumetric capacitance (C^*) of a n-PBDF thin film was measured by recording cyclic voltammograms at different scan rates in 0.2 M TBA-TFSI (PC) electrolyte. According to the cyclic voltammograms, the non-zero current plateau in the -0.2 V to +0.4 V range represents double-layer capacitance. Capacitive behavior is confirmed by the linear increase of the current density with the scan rate, plotted using the following equation:

$$(I_a - I_c)/2 = C v \quad \text{Eq. S10}$$

I_a and I_c represent the anodic and cathodic current densities measured at 0.3 V (which falls within the voltage range showing capacitive behavior), v is the scan rate and C is the volumetric capacitance. Specific volumetric capacitance (C^*) is calculated by dividing C by the film thickness (30 nm). According to the slope, $C \approx 6 \times 10^{-4} \text{ F cm}^{-2}$, which translates to a specific capacitance (C^*) approximating 200 F cm^{-3} . This value is comparable to C^* reported for PEDOT:PSS.^{15,16}

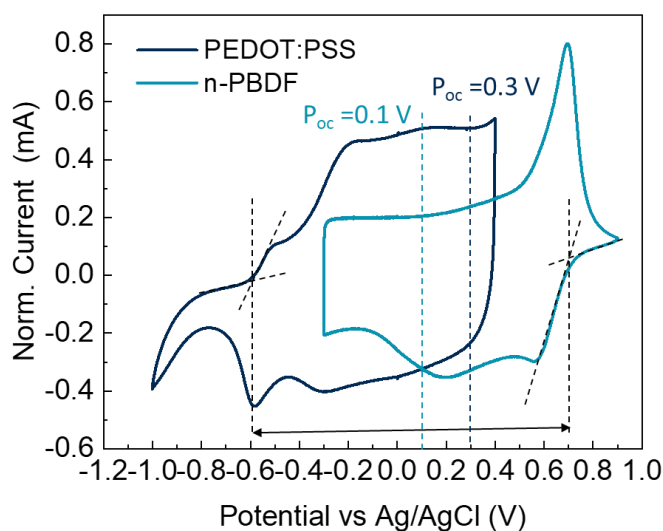


Figure S44 CV of PEDOT:PSS and n-PBDF in 0.2 M TBA-TFSI in PC. Oxidation onset of PEDOT:PSS, reduction potential of n-PBDF and their open circuit potentials (P_{oc}) are indicated in the figure.

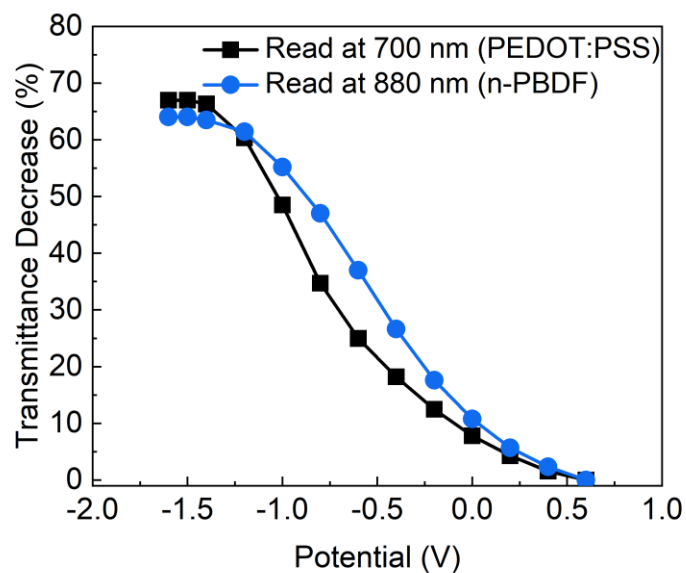


Figure S45 Transmittance decrease at 700 nm and 880 nm of OECD vs applied potential.

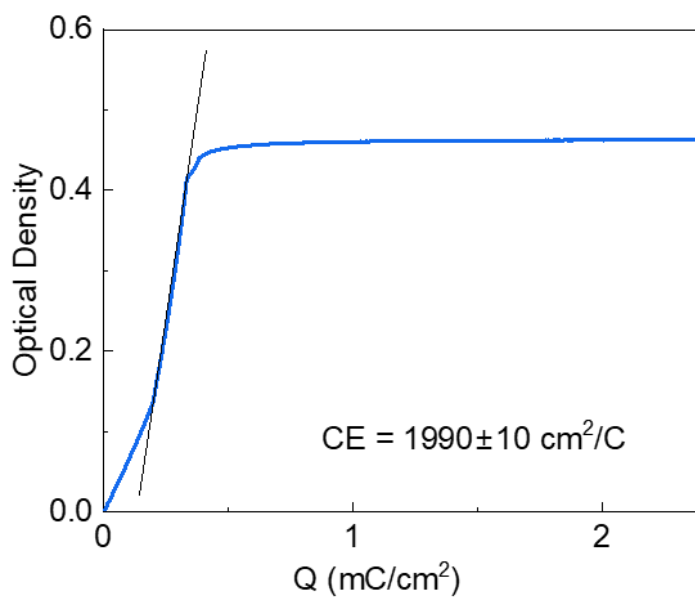


Figure S46 Coloration efficiency of PEDOT:PSS and n-PBDF device

9. References:

- (1) Frisch, M. ea; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Petersson, G.; Nakatsuji, H. Gaussian 16. **2016**.
- (2) Deng, P.; Liu, L.; Ren, S.; Li, H.; Zhang, Q. N-Acylation: An Effective Method for Reducing the LUMO Energy Levels of Conjugated Polymers Containing Five-Membered Lactam Units. *Chem. Commun.* **2012**, 48 (55), 6960.
- (3) Jinnai, K.; Kabe, R.; Lin, Z.; Adachi, C. Organic Long-Persistent Luminescence Stimulated by Visible Light in p-Type Systems Based on Organic Photoredox Catalyst Dopants. *Nat. Mater.* **2022**, 21 (3), 338–344.
- (4) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, 23 (20), 2367–2371.
- (5) Amin, P. O.; Ketuly, K. A.; Saeed, S. R.; Muhammadsharif, F. F.; Symes, M. D.; Paul, A.; Sulaiman, K. Synthesis, Spectroscopic, Electrochemical and Photophysical Properties of High Band Gap Polymers for Potential Applications in Semi-Transparent Solar Cells. *BMC Chem.* **2021**, 15 (1), 25.
- (6) Willems, R. E. M.; Weijtens, C. H. L.; de Vries, X.; Coehoorn, R.; Janssen, R. A. J. Relating Frontier Orbital Energies from Voltammetry and Photoelectron Spectroscopy to the Open-Circuit Voltage of Organic Solar Cells. *Adv. Energy Mater.* **2019**, 9 (10), 1803677.
- (7) Rolin, C.; Kang, E.; Lee, J.-H.; Borghs, G.; Heremans, P.; Genoe, J. Charge Carrier Mobility in Thin Films of Organic Semiconductors by the Gated van Der Pauw Method. *Nat. Commun.* **2017**, 8 (1), 14975.
- (8) Siahrostami, S.; Li, G.-L.; Viswanathan, V.; Nørskov, J. K. One- or Two-Electron Water Oxidation, Hydroxyl Radical, or H₂O₂ Evolution. *J. Phys. Chem. Lett.* **2017**, 8 (6), 1157–1160.
- (9) Yu, T.; Breslin, C. B. Review—2D Graphene and Graphene-Like Materials and Their Promising Applications in the Generation of Hydrogen Peroxide. *J. Electrochem. Soc.* **2020**, 167 (12), 126502.
- (10) Azani, M.; Hassanpour, A.; Torres, T. Benefits, Problems, and Solutions of Silver Nanowire Transparent Conductive Electrodes in Indium Tin Oxide (ITO)-Free Flexible Solar Cells. *Adv. Energy Mater.* **2020**, 10 (48), 2002536.
- (11) Bhatia, R.; Kumari, K.; Rani, R.; Suri, A.; Pahuja, U.; Singh, D. A Critical Review of Experimental Results on Low Temperature Charge Transport in Carbon Nanotubes Based Composites. *Rev. Phys.* **2018**, 3 (December 2017), 15–25.
- (12) Stadler, P. Isotropic Metallic Transport in Conducting Polymers. *Synth. Met.* **2019**, 254 (June), 106–113.
- (13) Lorenzoni, M.; Giugni, A.; Torre, B. Oxidative and Carbonaceous Patterning of Si Surface in an Organic Media by Scanning Probe Lithography. *Nanoscale Res. Lett.* **2013**, 8 (1), 75.
- (14) Strand, M. T.; Hernandez, T. S.; Danner, M. G.; Yeang, A. L.; Jarvey, N.; Barile, C. J.; McGehee, M. D. Polymer Inhibitors Enable >900 Cm² Dynamic Windows Based on Reversible Metal Electrodeposition with High Solar Modulation. *Nat. Energy* **2021**, 6 (5), 546–554.
- (15) Bianchi, M.; Carli, S.; Di Lauro, M.; Prato, M.; Murgia, M.; Fadiga, L.; Biscarini, F. Scaling of Capacitance of PEDOT:PSS: Volume vs. Area. *J. Mater. Chem. C* **2020**, 8 (32), 11252–11262.

- (16) Volkov, A. V.; Wijeratne, K.; Mitraka, E.; Ail, U.; Zhao, D.; Tybrandt, K.; Andreasen, J. W.; Berggren, M.; Crispin, X.; Zozoulenko, I. V. Understanding the Capacitance of PEDOT:PSS. *Adv. Funct. Mater.* **2017**, 27 (28), 1700329.