
Supplementary information

A solution-processed n-type conducting polymer with ultrahigh conductivity

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A solution-processed n-type conducting polymer with ultrahigh conductivity

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Fig. S1 ~ Fig. S58

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A. Materials.

Idebenone (>98%, D054367), *N,N*-Dimethylformamide (DMF, 99.9%, Extra Dry, with molecular sieves, Water $\leq$ 30 ppm, W610944) and dimethyl sulfoxide (DMSO, 99.7%, Extra Dry, with molecular sieves, Water $\leq$ 50 ppm, E080132) were purchased from Energy Chemical (www.energy-chemical.com) and were used as received. Tetramethyl-1,4-benzoquinone (TMQ, >98.0% GC, T161852) and tetramethylhydroquinone (TMQH, >95.0% GC, T162658) was purchased from Shanghai aladdin biochemical technology Co., Ltd. *N*-Benzylidene-2-methylpropan-2-amine oxide (PBN, 96% HPLC, BD00777106) was purchased from Shanghai Bide Pharmatech Co., Ltd. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS, CLEVIOSTM PH 1000) was purchased from Xi'an Polymer Light Technology Corp. 11-(Bromomethyl)tricosane was purchased from Jiujiang Design Optoelectronic Materials Co., Ltd. All other mentioned reagents were purchased from Energy Chemical and were used as received.

3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (H-BFDO) was synthesised following previously reported procedures^{1,2}. The white crystals were recrystallized from toluene and its single crystal information was shown as follows (CCDC Number: 2181371). **Crystal Data** for H-BFDO ($M = 190.15$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 4.21144(13)$ Å, $b = 5.5183(2)$ Å, $c = 16.6675(6)$ Å, $\beta = 94.298(3)^\circ$, $V = 386.26(2)$ Å³, $Z = 2$, $T = 149.99(10)$ K, $\mu(\text{Cu K}\alpha) = 1.097$ mm⁻¹, $D_{\text{calc}} = 1.635$ g/cm³, 1642 reflections measured ($10.646^\circ \leq 2\theta \leq 133.948^\circ$), 676 unique ($R_{\text{int}} = 0.0172$, $R_{\text{sigma}} = 0.0205$) which were used in all calculations. The final R_1 was 0.0296 ($I > 2\sigma(I)$) and wR_2 was 0.0779 (all data).

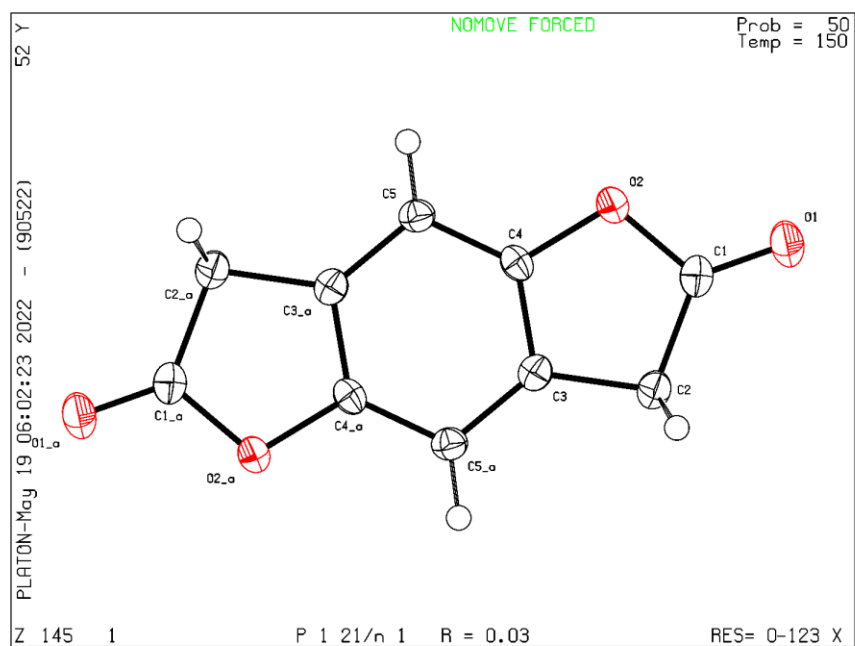


Fig. S1. Single crystal of H-BFDO monomer.

B. Reaction mechanism investigations.

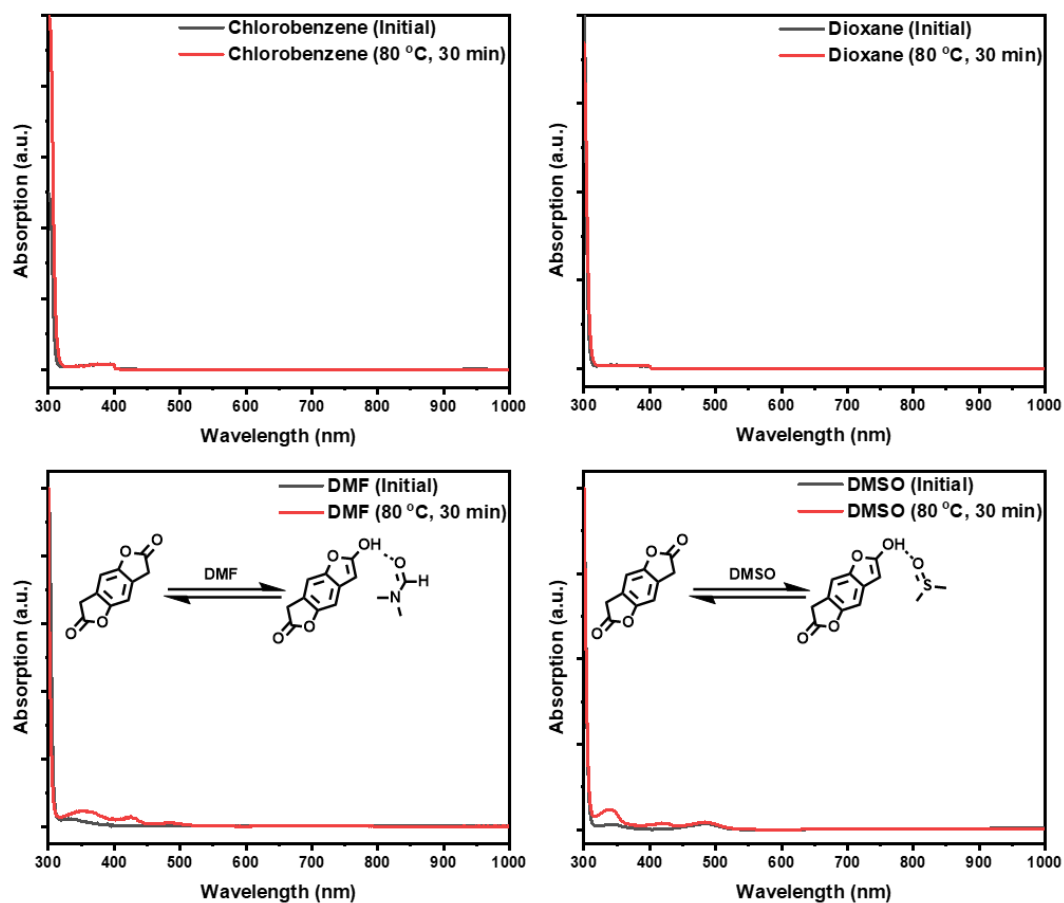


Fig. S2. UV-vis absorption of H-BFDO in different solvents. No change was observed for H-BFDO in chlorobenzene and dioxane, while the absorption at 422 and 480 nm slightly increased for that in DMSO and DMF after heating.



Fig. S3. Pictures of H-BFDO in different solvents (15 mg ml^{-1}) after being heated at 100°C for 30 min (H-BFDO exhibited better solubility in DMF/DMSO than that in chlorobenzene/dioxane/chloroform.).

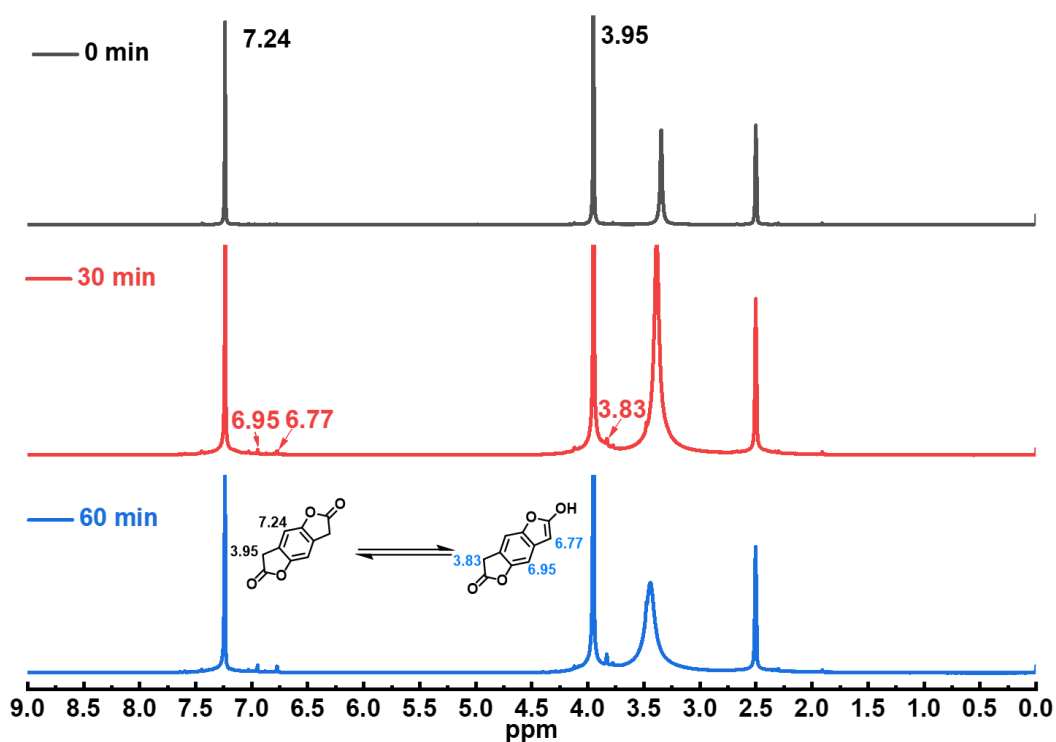


Fig. S4. ^1H -NMR spectra of H-BFDO in DMSO-d_6 heated at 100°C for different times. The peak at 7.24 and 3.95 ppm were attributed to the hydrogen on the aromatic ring and on the active methylene group of H-BFDO monomer, respectively. After being heated under nitrogen, new signal peaks appear around 6.95, 6.77, and 3.83 ppm, which can be attributed to the enol transition products of the monomer.

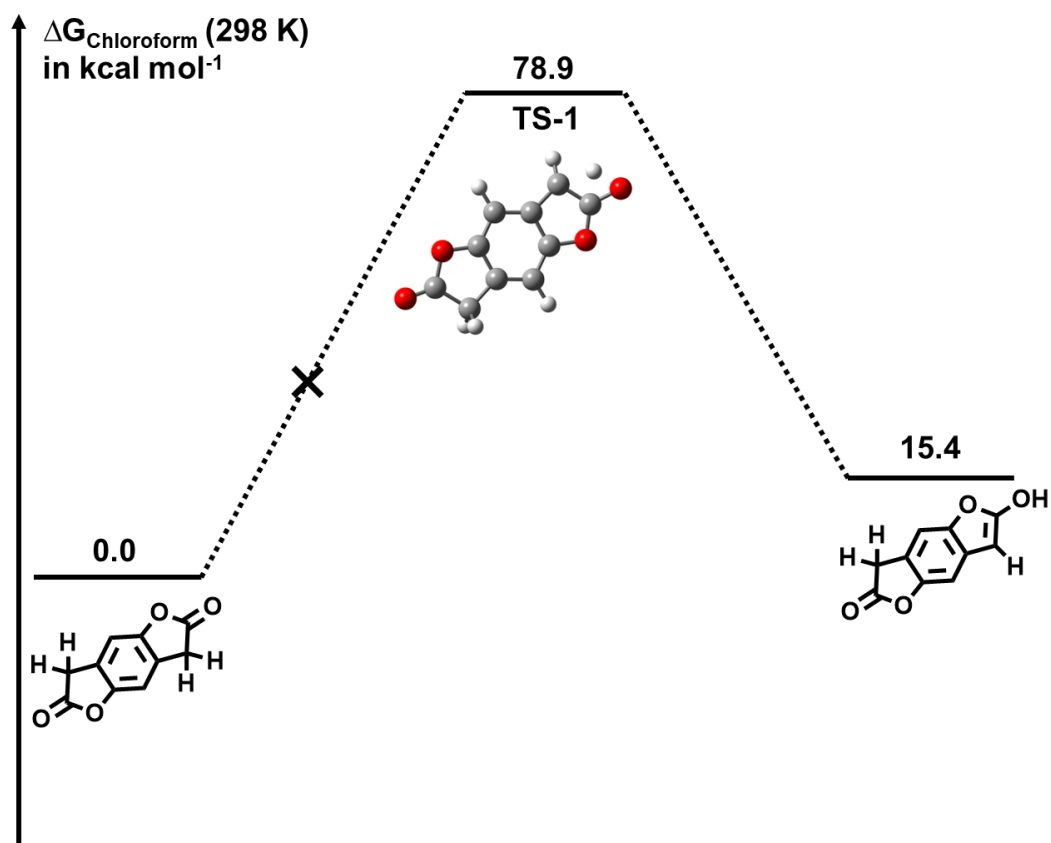


Fig. S5. Gibbs free-energy profile of enol transformation of H-BFDO monomer in chloroform. The calculations were performed at the wb97xd/6-311+g(d,p) level with SMD solvation model. The Gibbs energy barrier of proton-transfer transition state for Keto-Enol tautomerism of H-BFDO was calculated to be $78.9 \text{ kcal mol}^{-1}$, which are too large to overcome, in accordance with the experimental result that no change of H-BFDO was observed in chloroform.

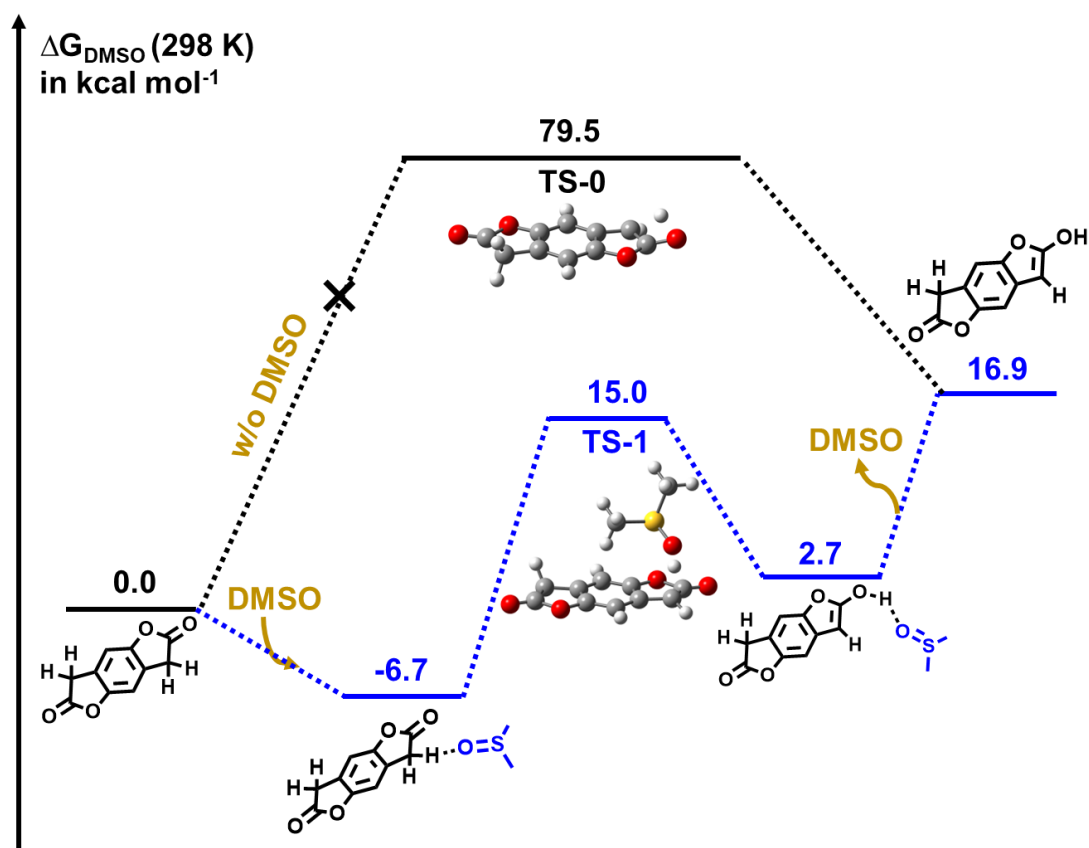


Fig. S6. Gibbs free-energy profile of enol transformation of H-BFDO monomer in DMSO. The interaction between H-BFDO and DMSO greatly decreased the energy barrier required for proton-transfer transition state of Keto-Enol tautomerism (from 79.5 to 21.7 kcal mol^{-1}), thus enabling the one-side enolisation of H-BFDO.

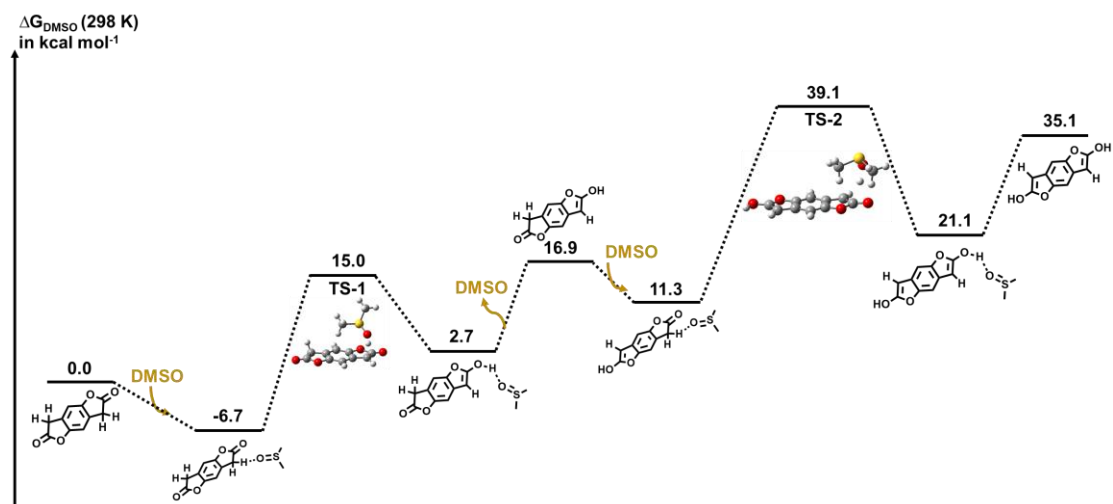


Fig. S7. Gibbs free-energy profile of bilateral enol transformation of H-BFDO in DMSO. The second Keto-Enol tautomerism requires to overcome the transition state with an energy barrier of 27.8 kcal mol^{-1} , which is relatively large to overcome. Therefore, we proposed that the reaction was initialized by the one-side enol transformation of H-BFDO.

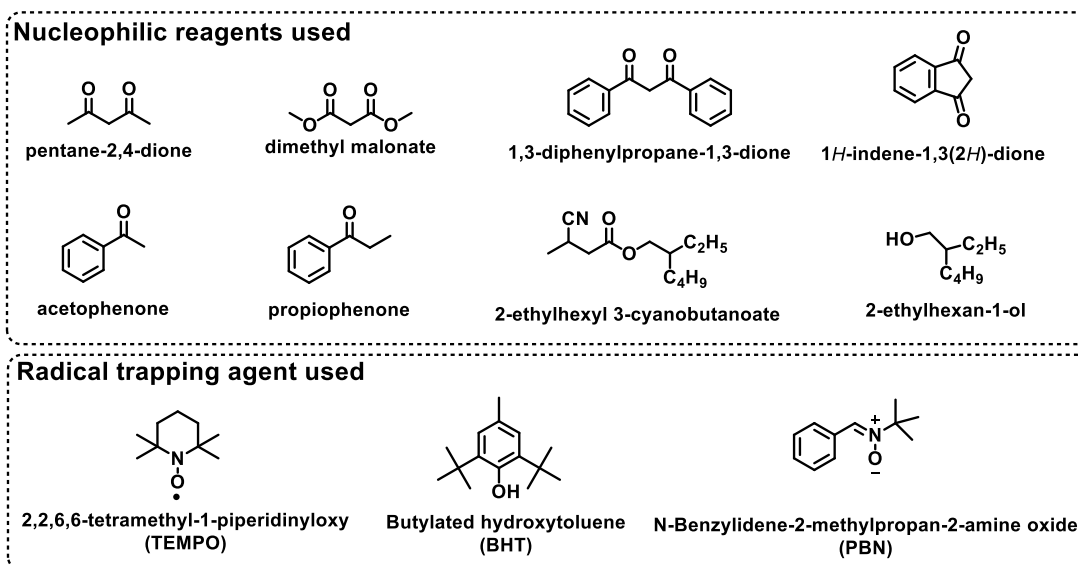


Fig. S8. The chemical structure of different reagents used for reaction mechanism investigations.

Table S1 Phenomena summary of the reaction with different reagents participated.^a

Reagent	Phenomenon
H ₂ O (1 eq)	No significant hindering effect on the reaction and almost no effect on the final polymer properties.
AcOH (0.1 eq)	No significant hindering effect.
EtOH (1 eq)	No significant hindering effect.
pentane-2,4-dione (1 eq)	No significant hindering effect.
dimethyl malonate (1 eq)	No significant hindering effect.
1,3-diphenylpropane-1,3-dione (1 eq)	No significant hindering effect.
1 <i>H</i> -indene-1,3(2 <i>H</i>)-dione (1 eq)	No significant hindering effect.
Acetophenone (1 eq)	No significant hindering effect.
Propiophenone (1 eq)	No significant hindering effect.
2-ethylhexyl 3-cyanobutanoate (1 eq)	No significant hindering effect.
2-ethylhexan-1-ol (1 eq)	No significant hindering effect.
Triethylamine (0.1 eq) ^b	The reaction mixture turned green upon the addition of triethylamine. A large amount of insoluble solid precipitates after heating for about half an hour.
Pyridine (0.1 eq) ^b	Similar to the reaction system with the addition of triethylamine
BHT (1 eq)	The reaction rate was significantly slower and a small amount of H-BFDO monomer was left after 2 hours reaction.
PNB (1 eq)	The polymerisation was greatly inhibited, and the spin adducts can be detected.
TEMPO (1 eq)	No significant hindering effect, but the reduction product of TEMPO, 2,2,6,6-tetramethylpiperidin-1-ol, could be isolated. The oxidative nature of TEMPO may account for this phenomenon ³ , allowing TEMPO to be present in the reaction system primarily as an oxidant rather than a radical trapping agent.

^a All the reactions were performed with H-BFDO (57 mg), TMQ (74 mg, 1.5 eq), and DMSO (Extra Dry, 4 ml) at 100 °C under nitrogen. The reagents for reaction inhibiting were added with the raw material before heating.

^b The addition of small amounts of triethylamine or pyridine to the prepared polymer solution (DMSO) also caused the polymer to precipitate out of the solution, but the addition of acetic acid did not, probably because the addition of the alkaline substances disrupted the interaction of the polymer with the solution.

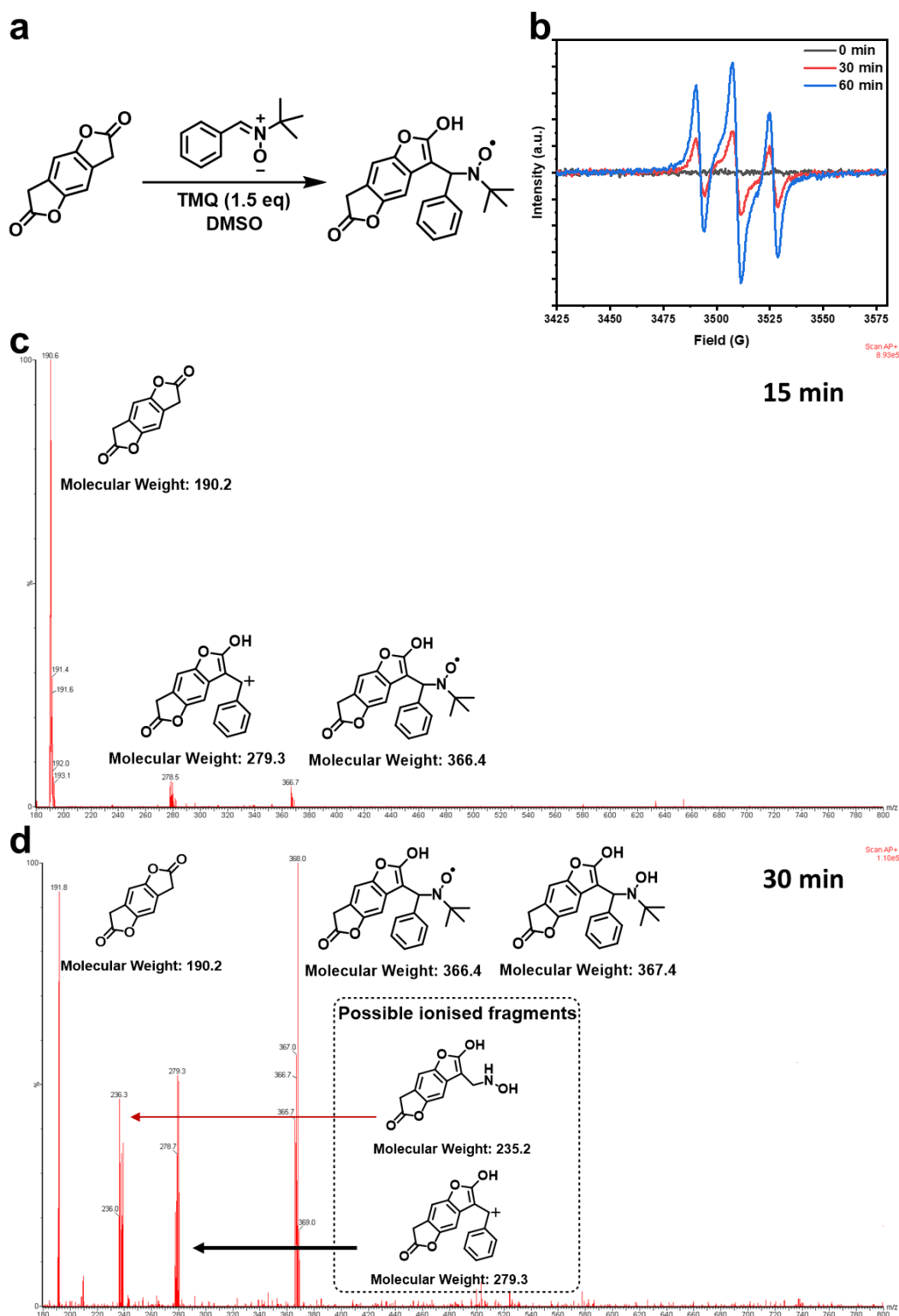
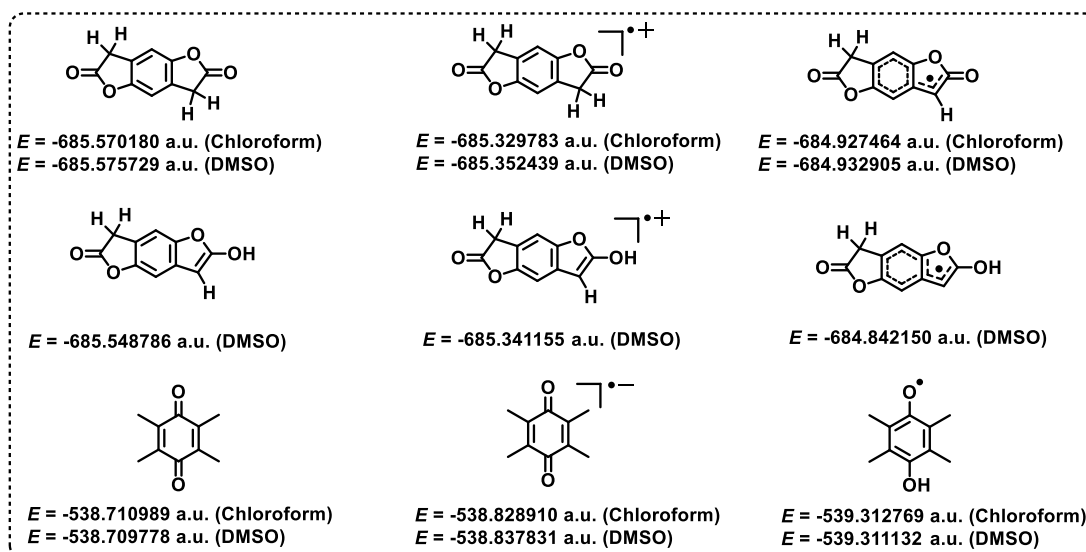
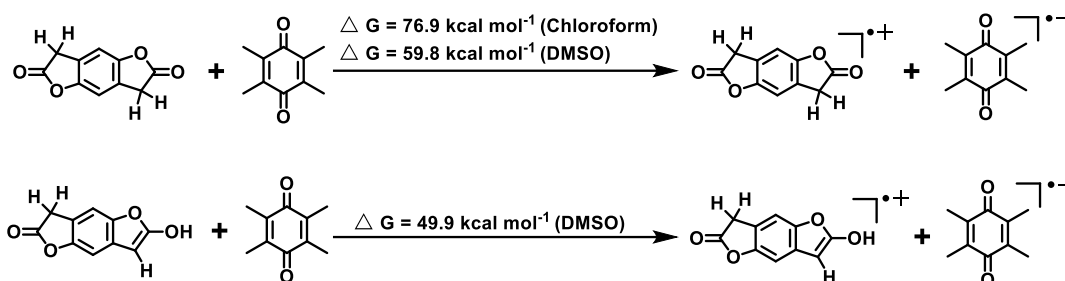


Fig. S9. Radical capture experiments with PBN participated. **a**, Reaction formula with PBN as radical trapping agent. **b**, *In-situ* ESR spectra of spin adducts generated during reaction. The raw materials did not exhibit distinct ESR signal while triplet signals attributable to the nitrogen-oxygen radical⁴ appeared after heating. **c-d**, LC-MS spectra of the reaction at different heating times measured using APCI+ mode.

Low resolution mass spectrometry was adopted mainly because DMSO/DMF was not allowed to be used in high resolution LC-MS due to the potential damage it could cause to the column and the accuracy of the instrument. Here, spin adducts of H-BFDO and PBN could be detected in LC-MS, which increased with increasing reaction time, further evidencing that the reaction went through a radical pathway.



The electron transfer (ET) pathway for the formation of radical:



The hydrogen atom transfer (HAT) pathway for the formation of radical:

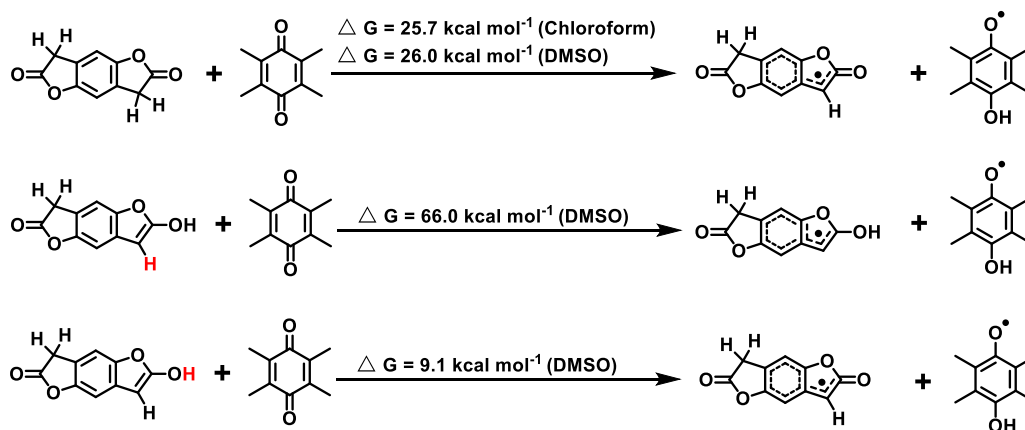


Fig. S10. The energy of possible radical intermediates and calculated Gibbs free energy of possible reaction routes. The Gibbs free energy of electron transfer (ET) pathway between H-BFDO or its enolized product and quinone is too large to overcome, indicating the radical was produced from hydrogen atom transfer (HAT) pathway. The enol transition of the monomer significantly downgrades the energy barrier to be overcome for the formation of radical intermediates via the HAT process.

Furthermore, theoretical calculations indicate that the HAT process occurs mainly at the hydrogen atom on the phenolic hydroxyl group in the enolised product.

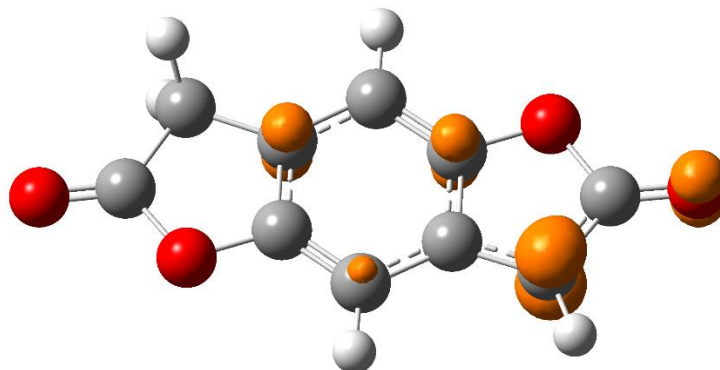
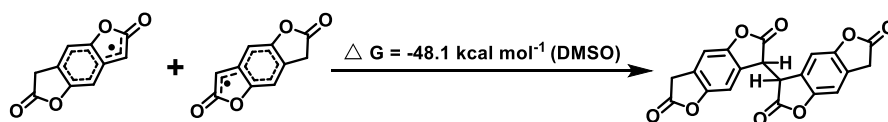


Fig. S11. The spin density diagram of H-BFDO radical intermediate. The spin density was analysed through Multiwfn⁵. The radicals on the intermediates have certain delocalised property, which can be located mainly on the carbon atom of the active methylene attached to the benzene and on the carbonyl oxygen atom. The spin of the carbon radical center is predominantly close to the *p* orbital and is delocalised towards the neighbouring pair of benzene rings, mainly due to the hyper-conjugation of the benzene to the radical center. In addition, the carbon atom of the methylene has a higher spin density, indicating that it is more likely to act as a reaction center for radical coupling reactions.

The radical-radical self-coupling pathway for extended backbone formation:



The dehydrogenation step after radical-radical coupling for conjugation formation:

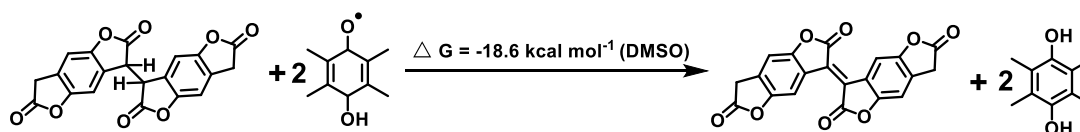
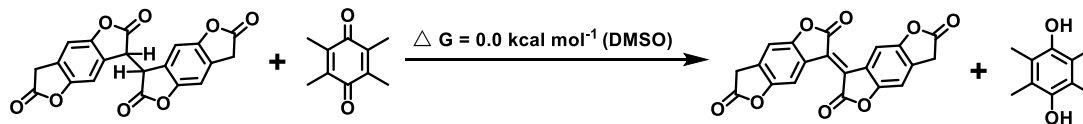
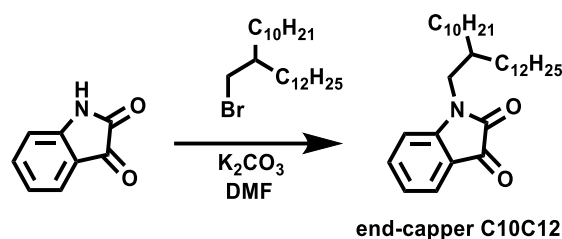


Fig. S12. The calculated Gibbs free energy of radical-radical self-coupling and following dehydrogenation step. The dehydrogenation step involving semi-quinone radicals has a lower Gibbs free energy and is more likely to occur than that involving quinones.

C. Oligomer model reactions.



Synthesis of the end-capper C10C12. Indoline-2,3-dione (10 g, 68 mmol) was dissolved in 150 ml DMF and then K_2CO_3 (10.33 g, 74.7 mmol) was added. The mixture was stirred at 80 °C under nitrogen for nearly 1 h. Then 11-(Bromomethyl)tricosane (26.11 g, 62.5 mmol) was added and the mixture was stirred at 80 °C for another 16 h. After cooling to room temperature, the solvent was removed under reduced pressure and the product was purified by silica gel column chromatography with petroleum ether/dichloromethane (2:1, v/v) as the eluent to give orange viscous oil (27.53 g, 83.7%). 1H NMR (500MHz, $CDCl_3$) δ (ppm): 7.61-7.56 (2H, m), 7.12-7.09 (1H, t), 6.88-6.84 (1H, d), 3.64-3.58 (2H, d), 1.89-1.82 (1H, dt), 1.41-1.14 (40H, m), 0.90-0.76 (6H, t). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 183.64, 158.49, 151.53, 138.23, 125.39, 123.54, 117.63, 110.38, 44.78, 36.06, 31.94, 31.92, 31.53, 29.95, 29.69, 29.66, 29.63, 29.58, 29.37, 29.34, 26.42, 22.70, 14.13.

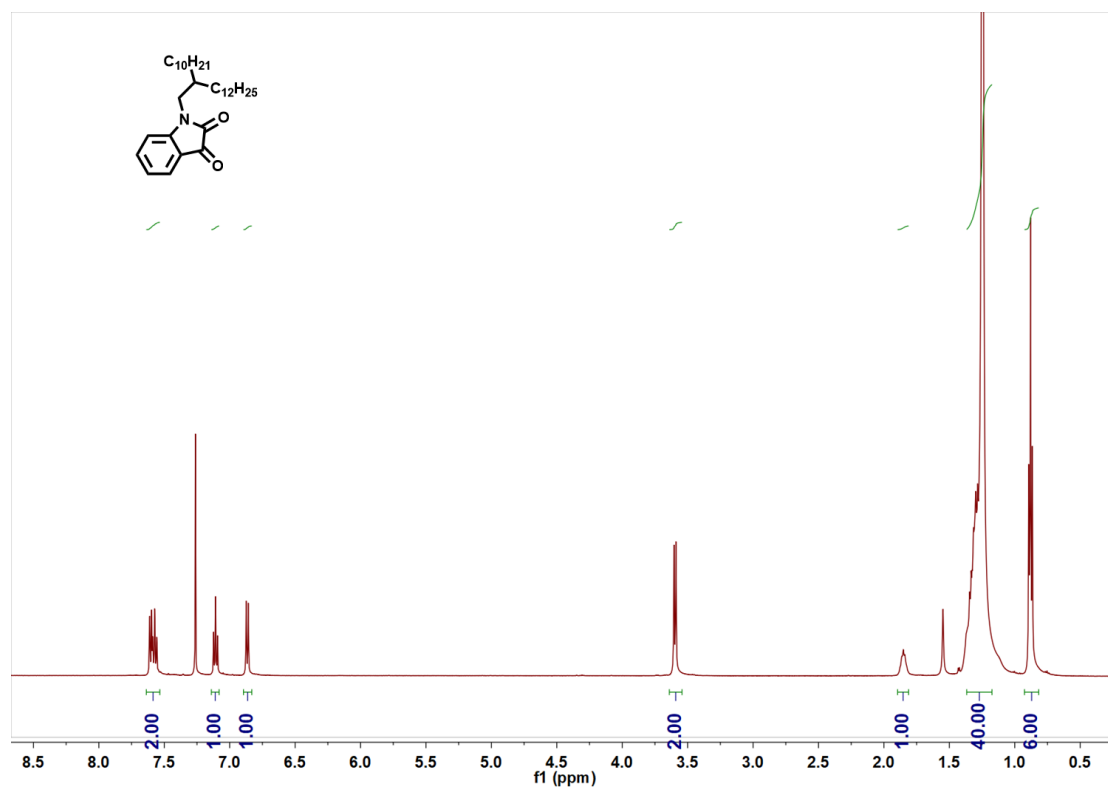


Fig. S13. 1H -NMR spectrum of end-capper C10C12.

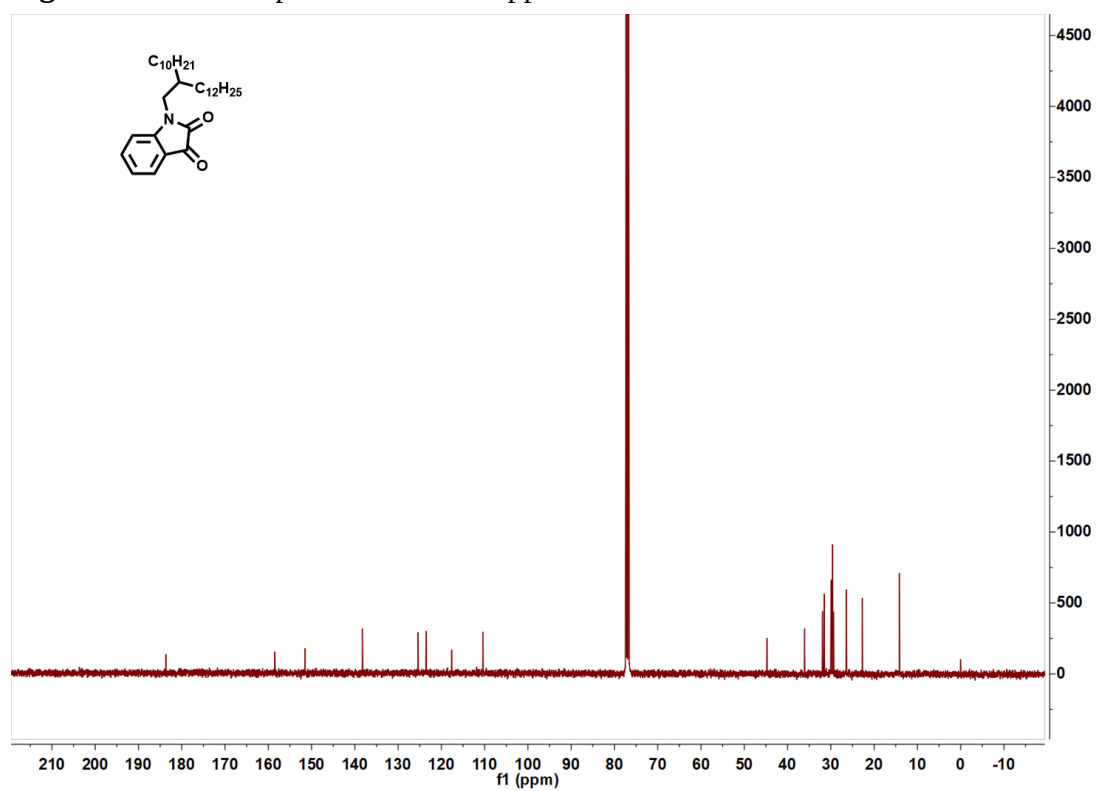
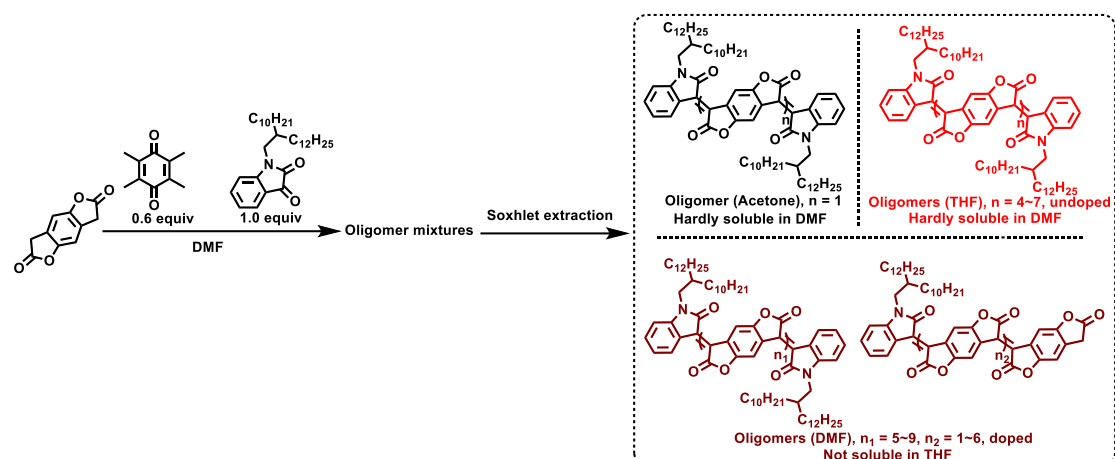


Fig. S14. ^{13}C -NMR spectrum of end-capper C10C12.



Synthesis of the model oligomers with end-capper C10C12. 3,7-Dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (1.52 g, 8 mmol), TMQ (920 mg, 5.6 mmol) and end-capper C10C12 (3.87 g, 8 mmol) were dissolved in 200 ml DMF under nitrogen. The mixture was heated to 100 °C with vigorous stirring for 1 h. After being cooled to room temperature, the solvent was removed under reduced pressure and 100 ml of methanol was added. The resulting precipitate was recovered by filtration through a funnel and then charged into the Soxhlet extractor, which was extracted by methanol, acetone, tetrahydrofuran (THF), and DMF in sequence. The obtained solution was collected separately and concentrated. It was found that the acetone part consisted of the oligomer $n = 1$, which is pure enough as verified by the NMR spectra and matrix assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF MS). The success formation of oligomer $n = 1$ indicated that aldol condensation could occur in DMF without requirement of extra acid catalysts, which facilitates its application as a model reaction. Also, the components in THF and DMF were investigated by the MALDI-TOF, verifying the self-polymerisation of H-BFDO monomer.

Table S2 Weight of oligomers obtained in different solvents.

Solvents	Acetone	THF	DMF	Residues ^a
Weight	3.42 g	12 mg	635 mg	910 mg

^a The residues left after extraction with DMF for 3 days. This part could be soluble in DMF or DMSO very slowly.

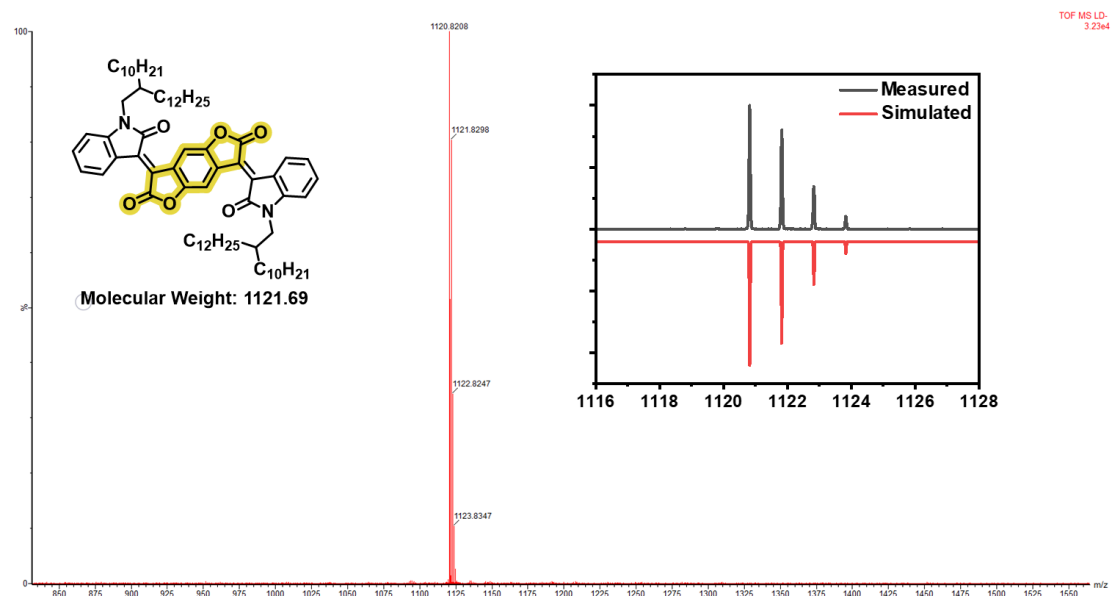


Fig. S15. MALDI-TOF MS spectrum of oligomer (Acetone), $n = 1$. The inset shows a comparison of the isotopic distribution between the measured value and instrumental simulation.

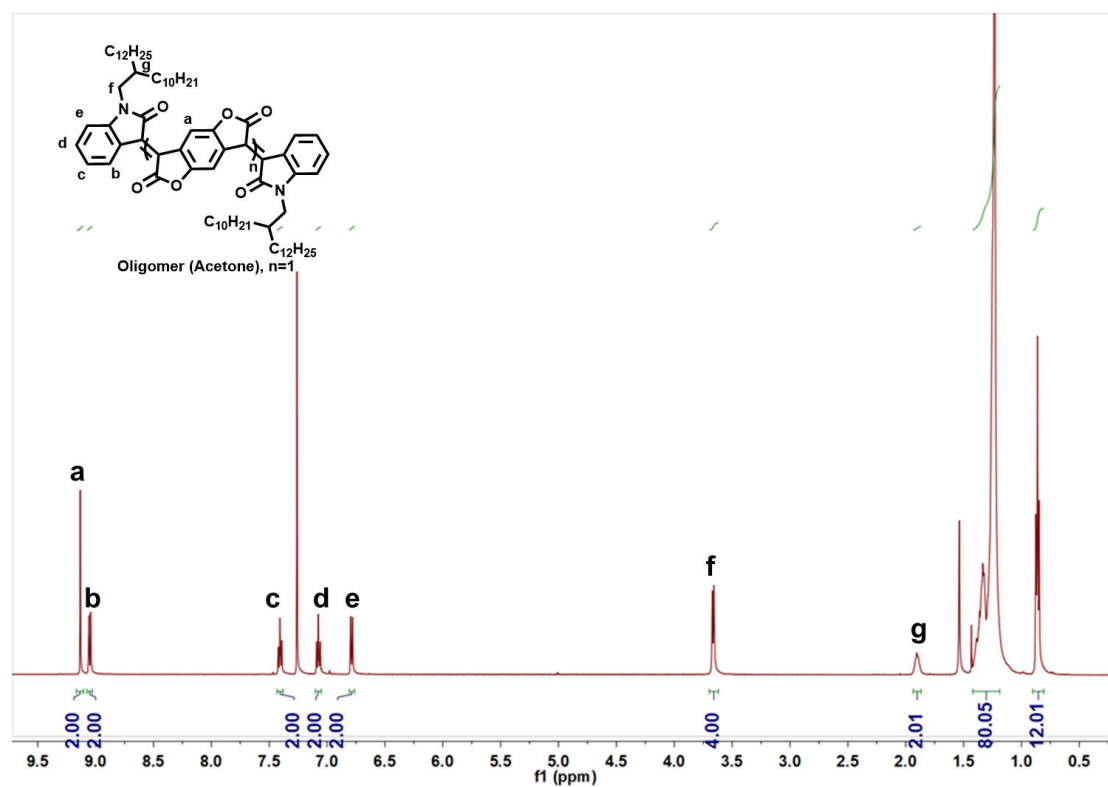


Fig. S16. ^1H -NMR spectrum of oligomer (Acetone). ^1H NMR (500MHz, CDCl_3) δ (ppm): 9.20-9.10 (2H, s), 9.07-9.02 (2H, d), 7.46-7.36 (2H, t), 7.12-7.04 (2H, t), 6.81-5.76 (2H, d), 3.70-3.62 (4H, d), 1.92-1.88 (2H, m), 1.48-1.17 (80H, m), 0.96-0.78 (12H, t).

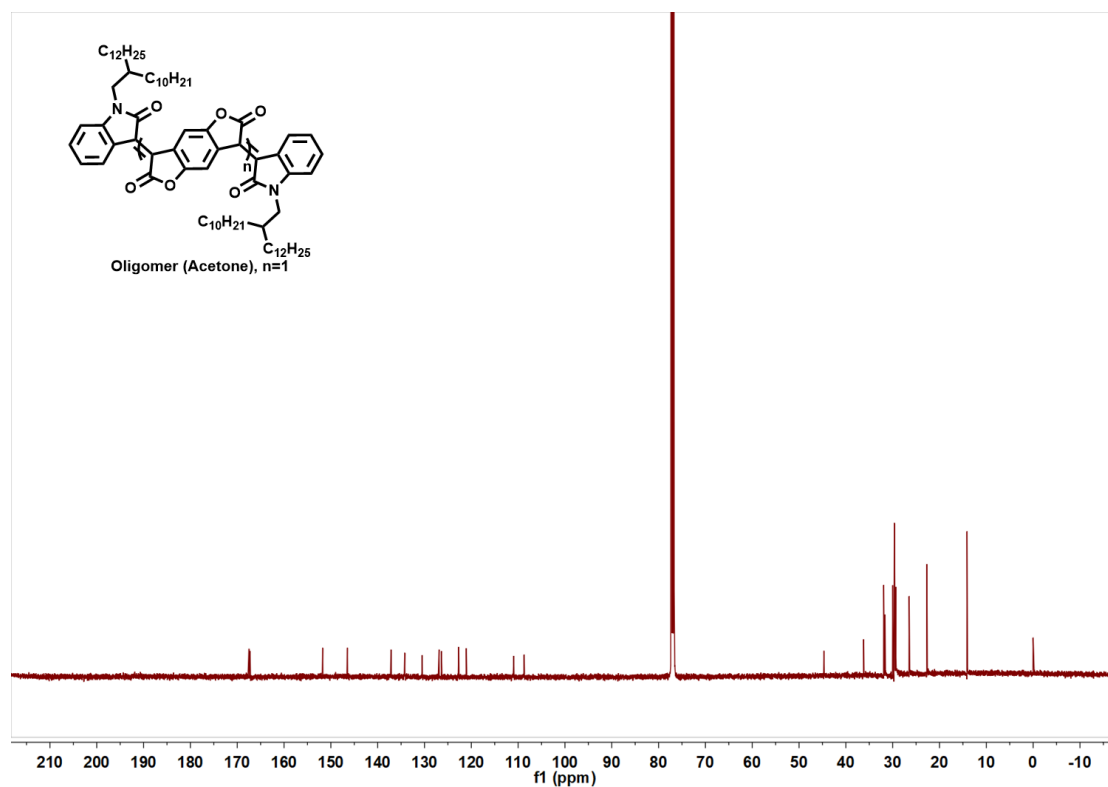


Fig. S17. ¹³C-NMR spectrum of oligomer (Acetone). ¹³C NMR (126MHz, CDCl₃) δ (ppm): 167.49, 167.26, 151.75, 146.47, 134.22, 130.49, 126.88, 126.38, 122.69, 121.07, 110.94, 108.70, 44.68, 36.20, 31.93, 31.64, 29.99, 29.69, 29.67, 29.64, 29.62, 29.59, 29.37, 29.35, 26.48, 22.69, 14.12.

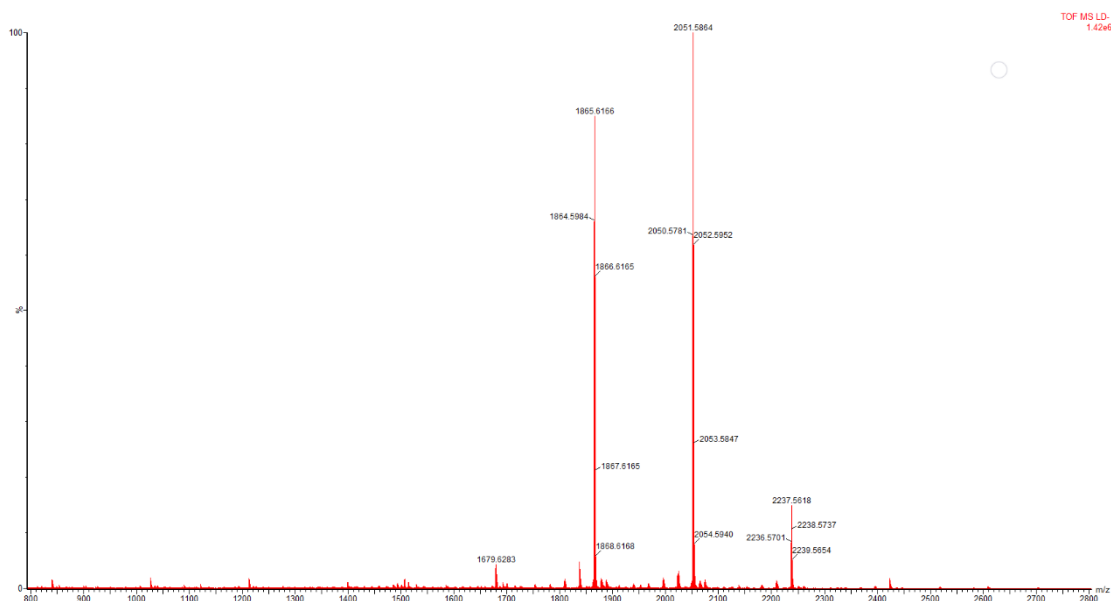


Fig. S18. MALDI-TOF MS spectrum of oligomers (THF).

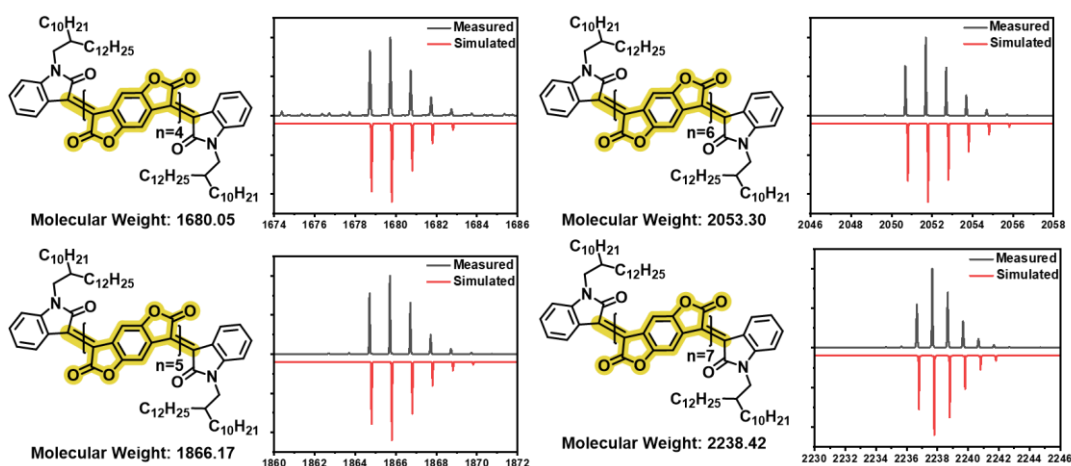


Fig. S19. The interpretation of MALDI-TOF MS spectrum of oligomers (THF). The measured isotopic distribution is in good agreement with the simulated values, further demonstrating the self-polymerisation of the H-BFDO monomer.

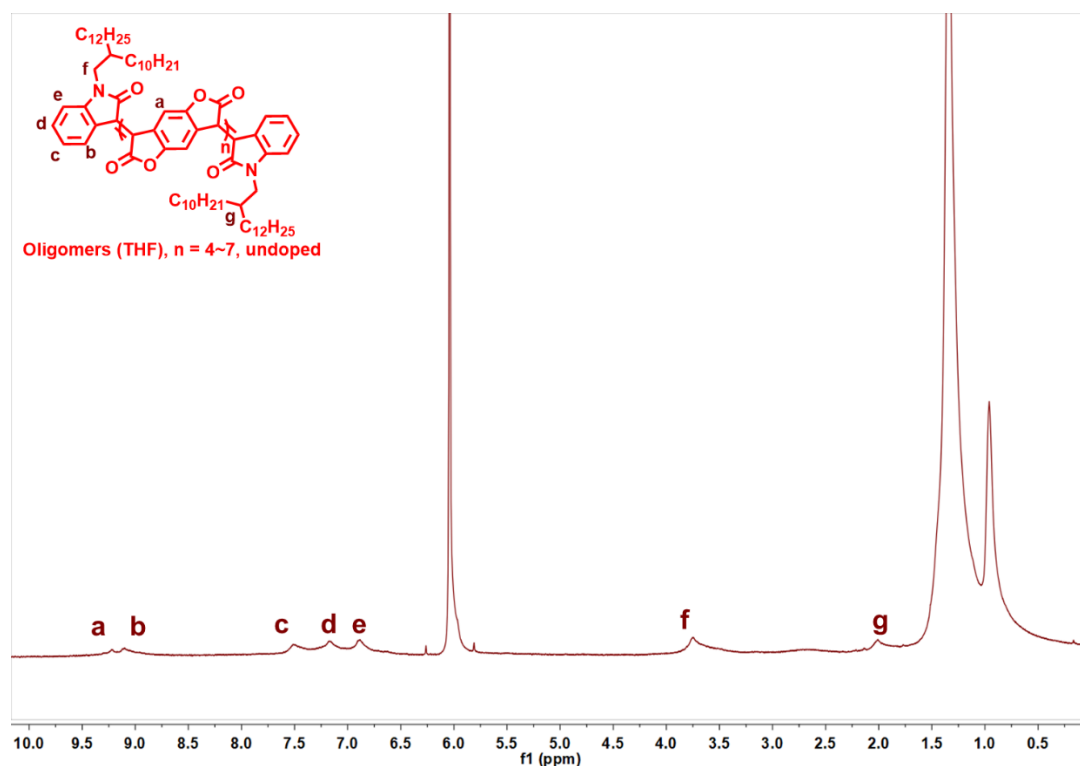


Fig. S20. ^1H -NMR spectrum of oligomers (THF) measured in 1,1,2,2-tetrachloroethane- d_2 at 80 $^\circ\text{C}$. Due to the long conjugated backbone and the possible radical nature of the substance, it is difficult to present a clear signal peak in the NMR spectrum, especially in the aromatic ring region. Nevertheless, a rough estimate of the hydrogen attribution can be made by comparison with the NMR spectrum of oligomer $n = 1$, as shown in the figure.

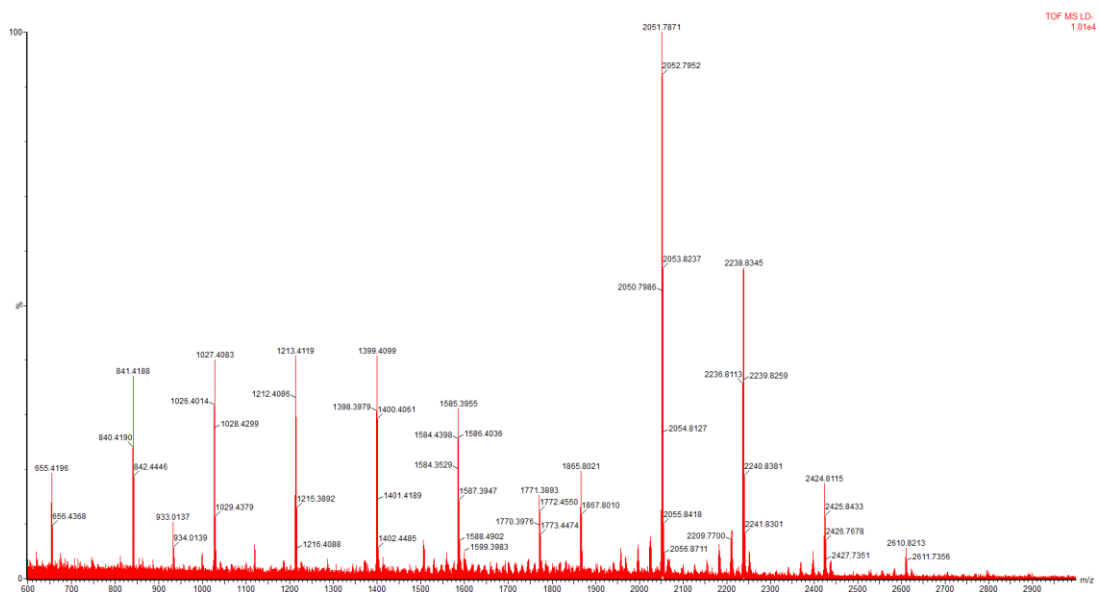


Fig. S21. MALDI-TOF MS spectrum of oligomers (DMF).

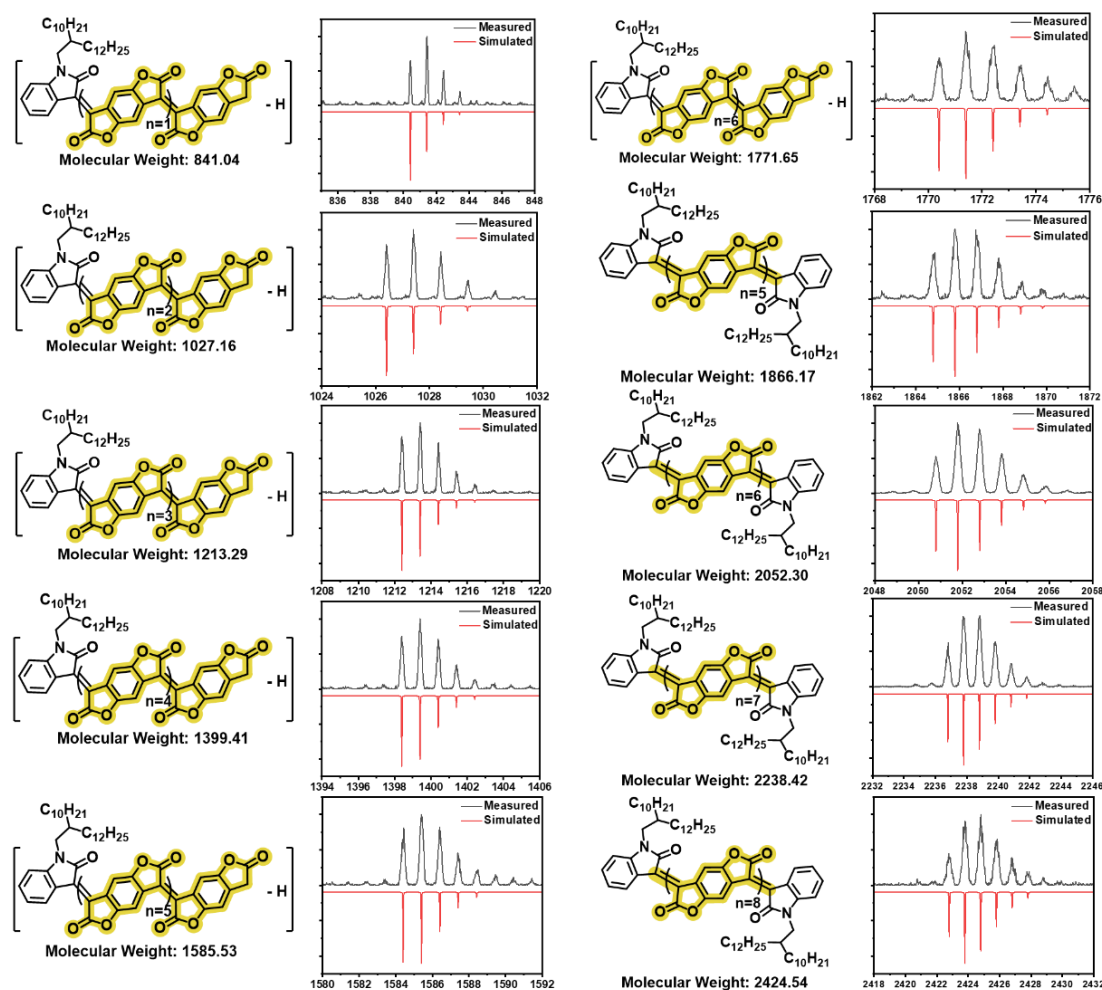


Fig. S22. The interpretation of MALDI-TOF MS spectrum of oligomers (DMF). For one-side end-capped oligomers, the measured isotopic distributions do not match well with the simulated values, probably due to the presence of substances with different numbers of hydrogen dissociated under negative ion mode and mixture of protonated doping products. For two-side end-capped oligomers, the measured isotopic distribution is in fine agreement with the simulated ones with minor errors that may come from isotopic broadening and the effect of mixing of protonated doping products.

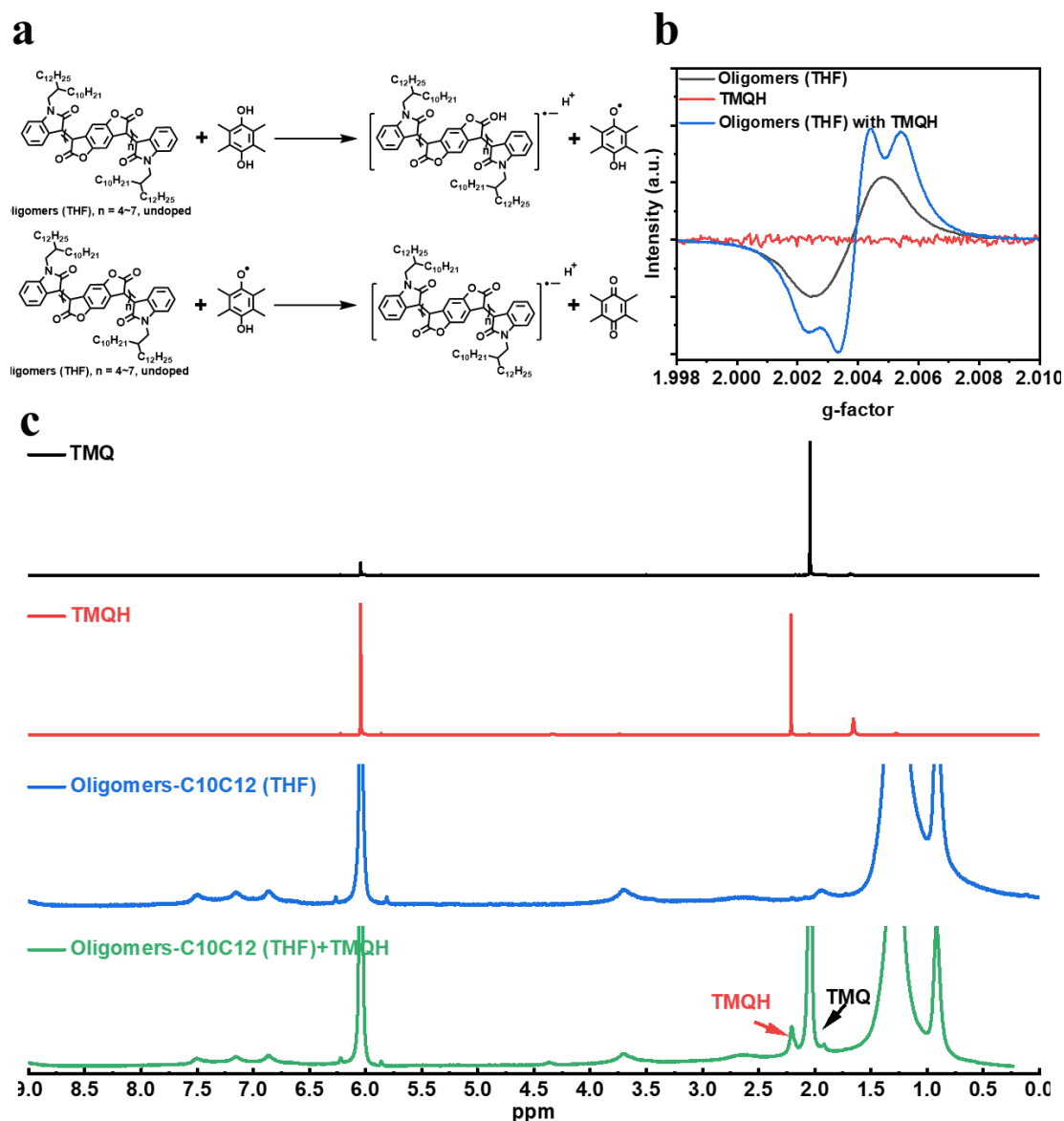


Fig. S23. The proposed *in-situ* doping procedure from TMQH. **a**, The proposed doping process between oligomers (THF) and TMQH. **b**, *In-situ* ESR monitoring of the doping process from TMQH. The experiment was conducted with chloroform as solvent. The oligomers (THF) exhibited ESR signal with a g-value of 2.0037, which could be attributed to the carbon-centered radicals with a nearby heteroatom, such as oxygen⁶. The presence of heteroatoms increases the spin-orbit coupling constants⁷. After mixing with TMQH, new multiple ESR signals with g-value over 2.0040 appeared (difficult to calculate accurately because of overlap with carbon radicals of oligomers), which could be attributed to the oxygen radical belonging to the semi-quinone intermediate⁸. **c**, *In-situ* ^1H NMR monitoring of the doping process from TMQH. The production of TMQ was observed (peak at 2.04 ppm) after mixing the oligomers (THF) and TMQH, further verifying n-doping from TMQH.

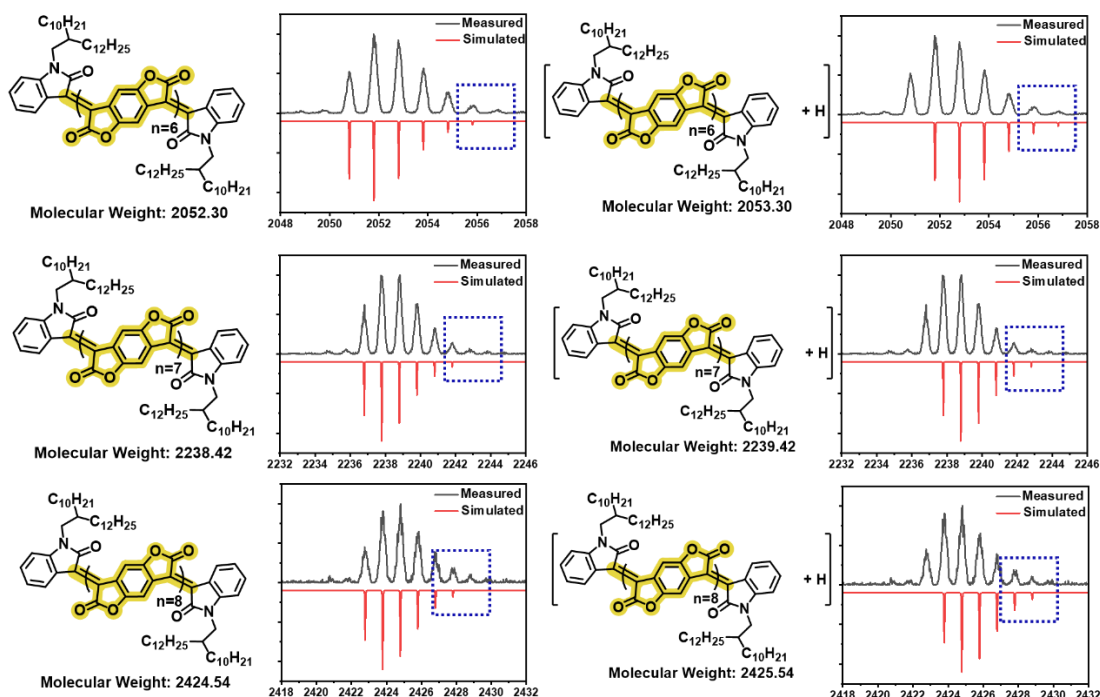
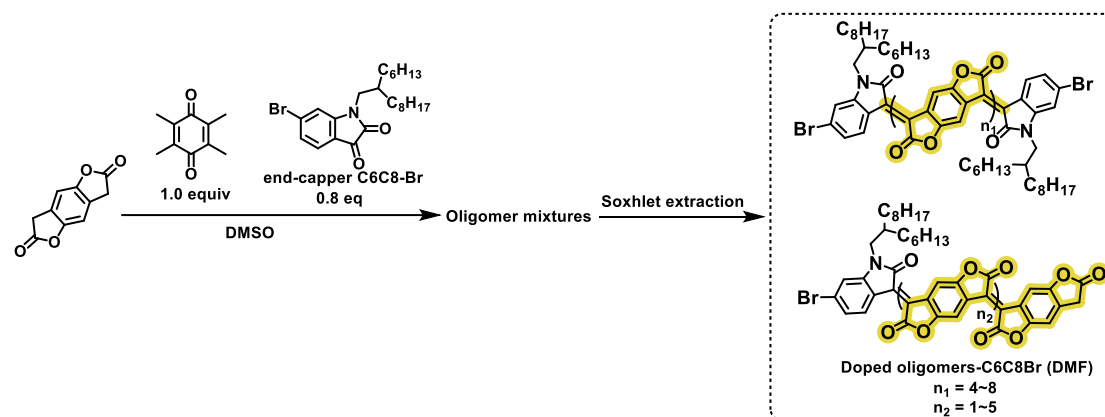


Fig. S24. The protonated doping products of oligomers (DMF) observed in high-resolution mass spectroscopy. The dissociation of hydrogen atoms usually occurs under the negative ion mode, allowing the substance to become negatively charged ions that can be flown out and detected by the instrument. In such case, single proton doping products are often difficult to detect by mass spectrometry. Although the mass spectra of oligomers (DMF) were obtained under the negative ion mode, hydrogen added products can still be observed, which may be due to the fact that the substances have been doped with multiple protons, further demonstrating that protonated doping products are generated due to the *in-situ* doping effect of TMQH.



Synthesis of the model oligomers with end-capper C6C8-Br. To further validate the accuracy of the high-resolution mass spectrometry and verify the existence of protonated doping products, another end-capper C6C8-Br⁹ was chosen which contained halogenated bromine atoms to provide different isotopic distributions. Detailed steps are as follows: 3,7-Dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (570 mg, 3.0 mmol), TMQ (493 mg, 3.0 mmol) were dissolved in 60 ml DMSO under nitrogen. The mixture was heated to 100 °C while end-capper C6C8 (1.081 g, 2.4 mmol) in DMSO (20 mL) was added dropwise during 1 h. After being heated for another 6 h, the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure. The resulting solid was charged into the Soxhlet extractor, which was extracted by tetrahydrofuran (THF) and DMF in sequence. The DMF solution extracted fraction was collected and used for MALDI-TOF MS characterization (**Fig. S25 ~ S27**).

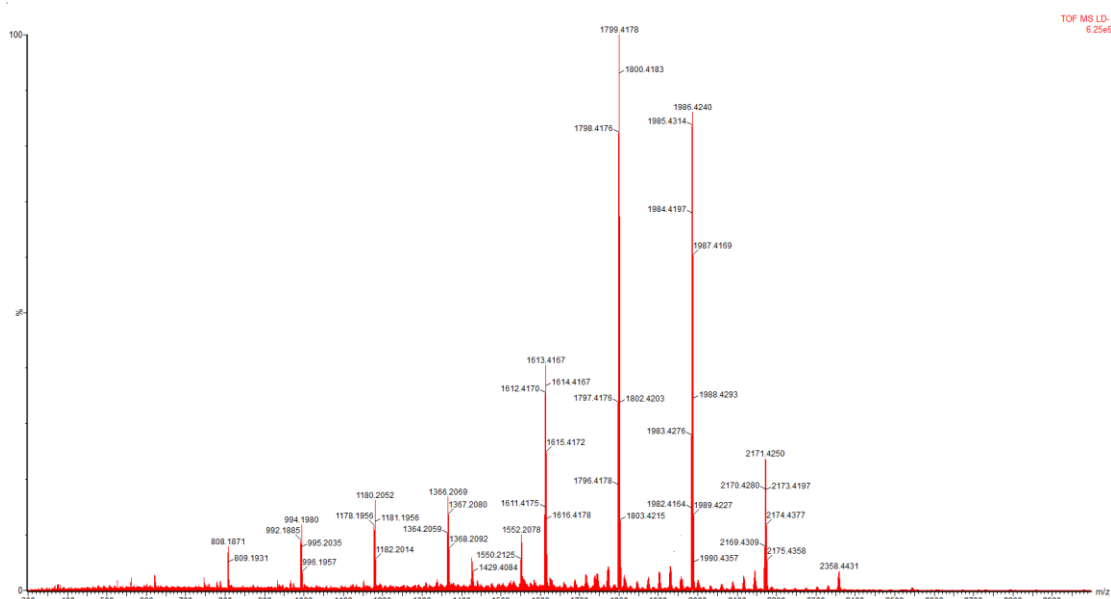


Fig. S25. MALDI-TOF MS spectrum of oligomers-C6C8Br (DMF).

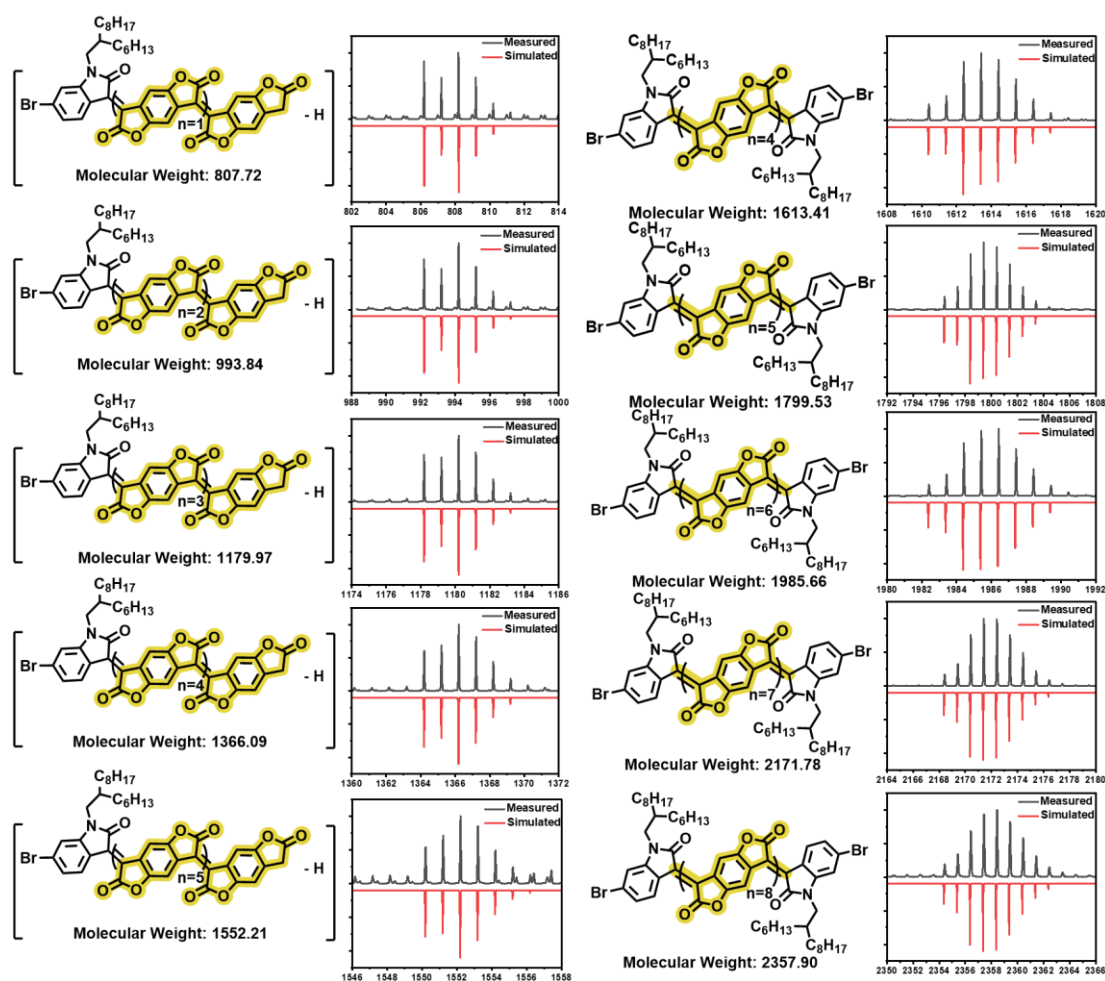


Fig. S26. The interpretation of MALDI-TOF MS spectrum of oligomers-C6C8Br (DMF). In this system, the bromine atoms provide a different isotopic distribution. The measured isotopic distribution of the material maintains good agreement with the simulated values, further verifying the accuracy of high-resolution mass spectroscopy and the self-polymerization of H-BFDO.

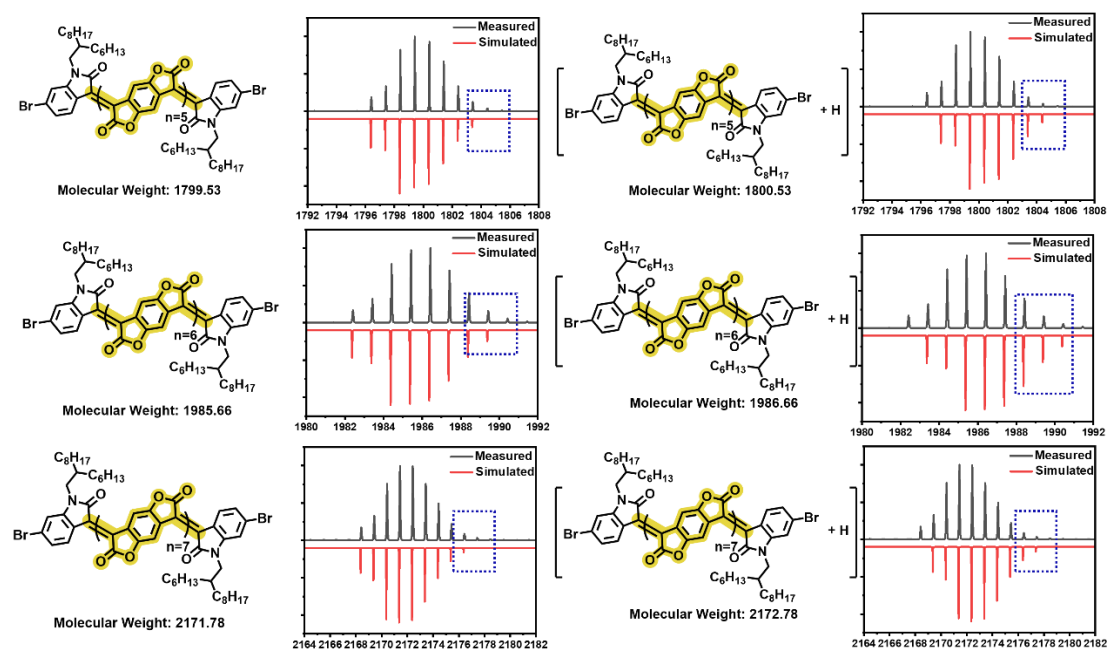


Fig. S27. The protonated doping products of oligomers-C6C8Br (DMF) observed in high-resolution mass spectroscopy.

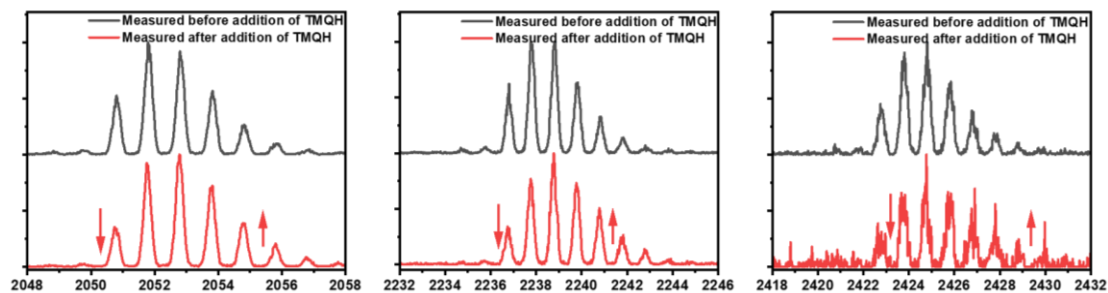


Fig. S28. High-resolution MS spectra of oligomers (DMF) before and after addition of TMQH. The addition of TMQH enables further n-doping of the oligomers, resulting in an increase in the content of the protonated doping product, as observed in MS spectra.

D. Pyridine infrared (Py-IR) measurements.

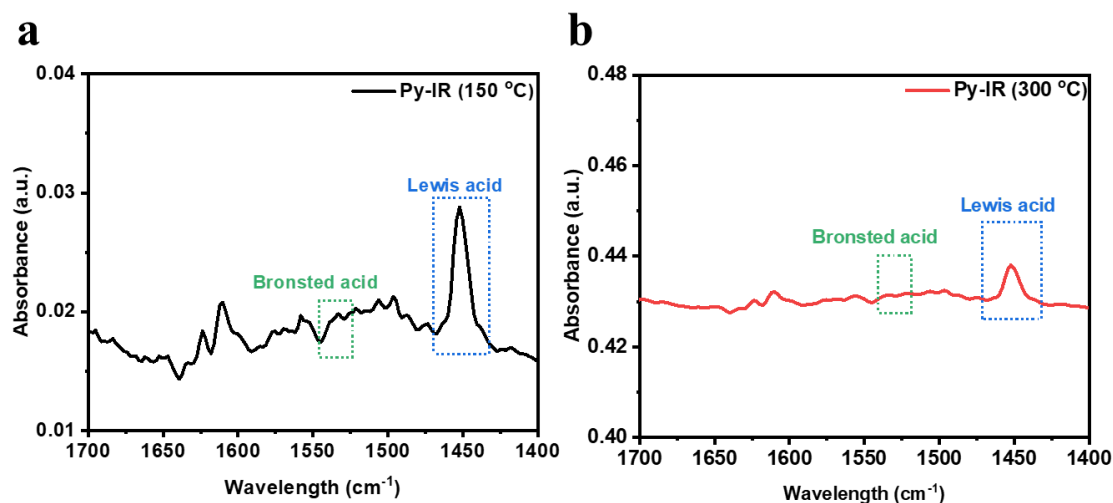


Fig. S29. Py-IR spectra of PBFDO at different temperatures. The acidic sites of the material can be observed by interacting with the basic probe molecules. Pyridine is a very strong adsorbent and can interact with both Lewis and Bronsted acids, with a characteristic absorption peak of 1540 cm⁻¹ for the Bronsted site and 1450 cm⁻¹ for the Lewis site. The sample showed a strong signal peak at 1450 cm⁻¹, indicating that PBFDO was dominated by Lewis acidity, which may come from its deep-lying reduction potential. The amount of acid in the material can be estimated by calculating the peak area. The semi-quantitative results of desorption at 150 °C showed that the amount of Bronsted acid was only 1.05 μmol g⁻¹ in PBFDO, which is much lower than that of Lewis acid (19.8 μmol g⁻¹), proving that the proton for charge balance was difficult to ionise because of the interaction with carbonyl group.

E. In-situ NMR characterization of polymerization for doping efficiency determination.

Introduction of quinones dramatically improved the oxidative polymerisation and *in situ* n-doping efficiency, producing the highly conducting products within a short reaction time. To quantitatively identify the interplay between the oxidative polymerisation and reductive n-doping, *in situ* ^1H -NMR spectra of different equivalents TMQ (1 equiv., 1.5 equiv., and 2 equiv.) as oxidant were recorded. To avoid the deviation caused by the weighing, the mixtures of 60 mg H-BFDO and corresponding equivalents of TMQ were fully dissolved in 6 ml DMSO- d_6 and 0.6 ml of the mixture was charged into an NMR tube. The whole process requires strictly oxygen-free atmosphere in case of the adverse effect on quantification caused by the oxidation of oxygen. The mixture was then heated to 100 $^\circ\text{C}$, and ^1H -NMR signals of different reaction times were recorded. The results were shown in **Fig. S30-S32**. The gradual consumption of H-BFDO monomer (s, 7.24 ppm) and the transition from tetramethyl-1,4-benzoquinone (s, 1.94 ppm) to 2,3,5,6-tetramethylbenzene-1,4-diol (s, 2.08 ppm) were observed, confirming the oxidative process in this reaction. Detailed quantitative characterisation indicated that about 1.56 equivalents of TMQ were required to fully consume the H-BFDO monomer, from which we speculated that nearly 88% of the repeating units in PBFDO were charge-doped, and this result was consistent with the XPS measurement in the main text. It is worth noting that the product obtained under different equivalents TMQ (1 equiv., 1.5 equiv., and 2 equiv.) exhibited similar conductivity after dialysis, indicating that this reaction is not sensitive to the accurate feeding ratio and the balance between oxidative polymerisation and reductive n-doping could be maintained by the reaction itself.

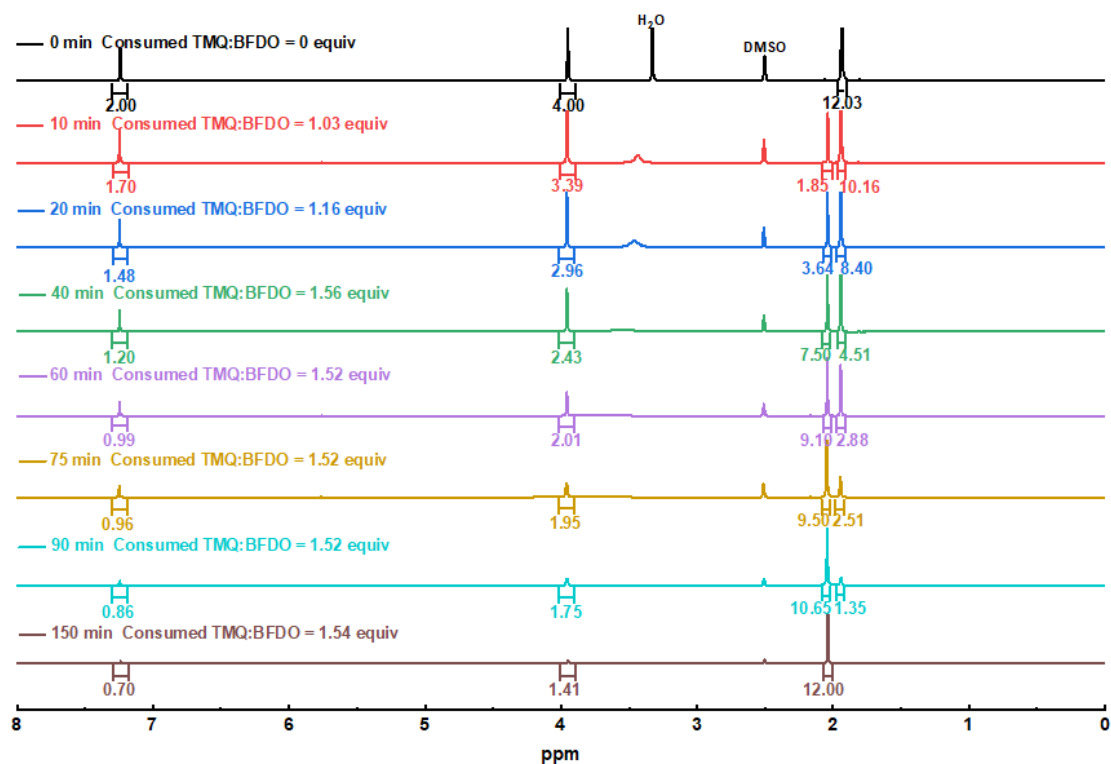


Fig. S30. *In situ* ^1H -NMR results of reactions with 1 equiv. TMQ. The signal of product PBFDO cannot be clearly distinguished due to the heavily *in situ* n-doping. The proton signals belonging to phenol were not detected because of proton-exchange in deuterated solvent. Considering the deviation in NMR measurement, the consumed ratio of TMQ:H-BFDO took the average of ^1H -NMR signals after 40 min for calculation, which is ca. 1.54.

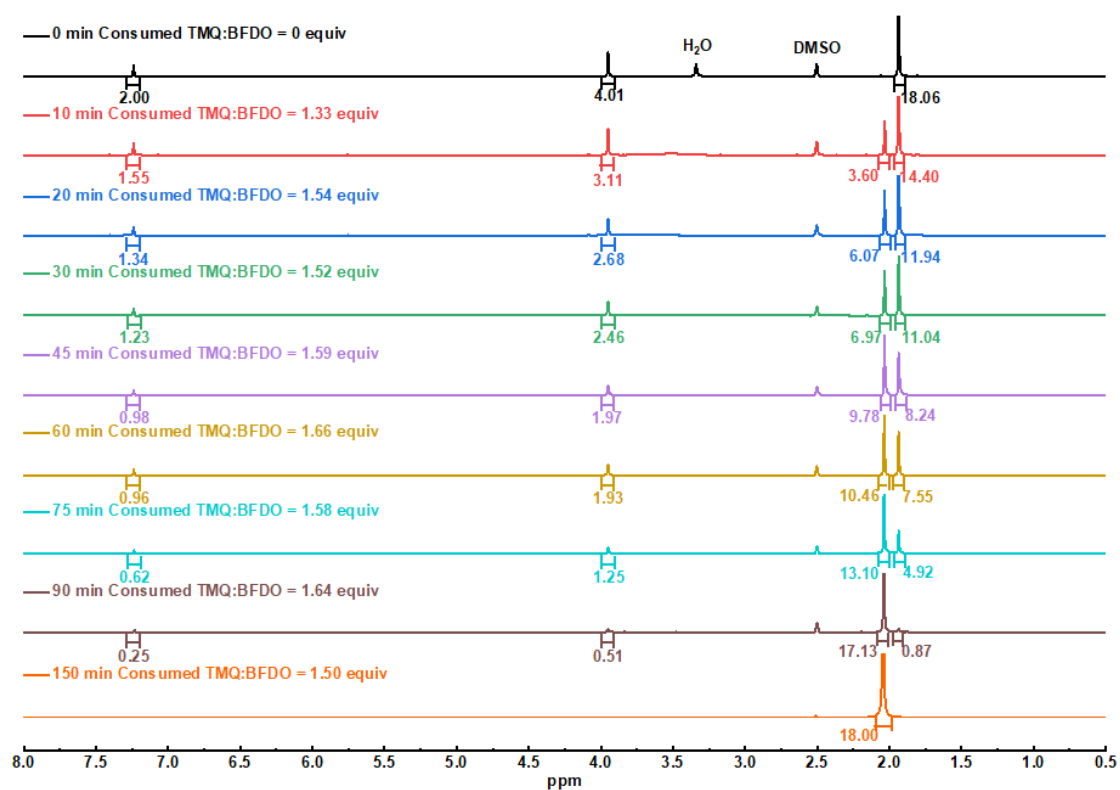


Fig. S31. *In situ* ^1H -NMR results of reactions with 1.5 equiv. TMQ. The average consumed ratio of TMQ:H-BFDO is ca. 1.57.

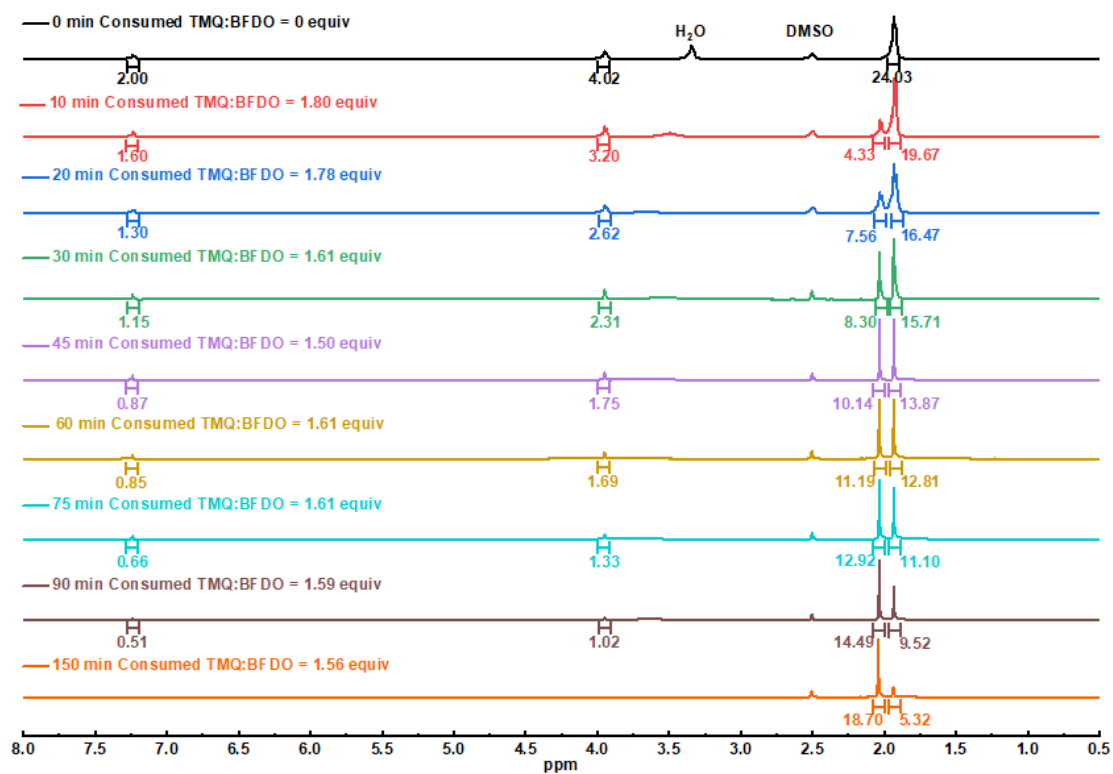


Fig. S32. *In situ* ^1H -NMR results of reactions with 2 equiv. TMQ. The average consumed ratio of TMQ:H-BFDO is ca. 1.56.

F. Interaction between PBFDO and solvents.

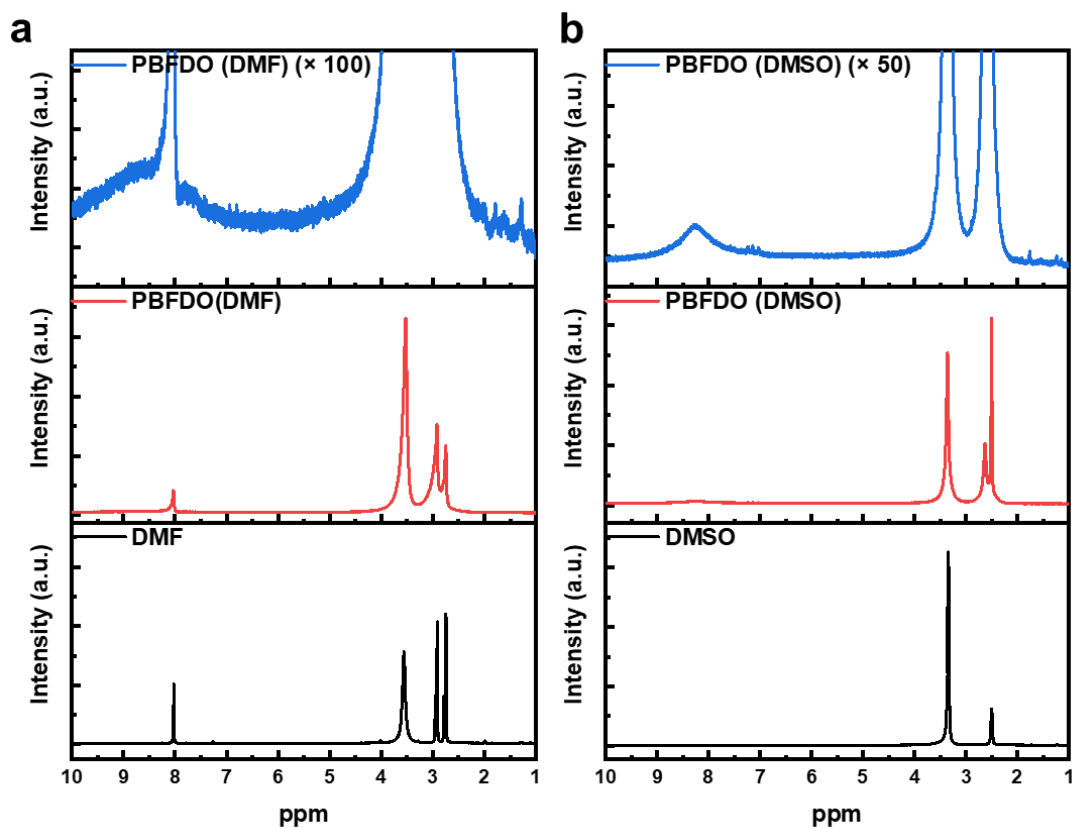


Fig. S33. ^1H -NMR spectra of PBFDO in deuterated DMF (left) /DMSO (right). The concentration is about 15 mg ml^{-1} . The bottom lines displayed the ^1H -NMR spectra of pure solvents. PBFDO exhibited weak and broad NMR signals located around 8.5 ppm, which could be observed in the enlarged ^1H -NMR spectra. The peaks belonging to the solvents broadened and slightly shifted after incorporating PBFDO because of the interaction between solvents and the polymer.

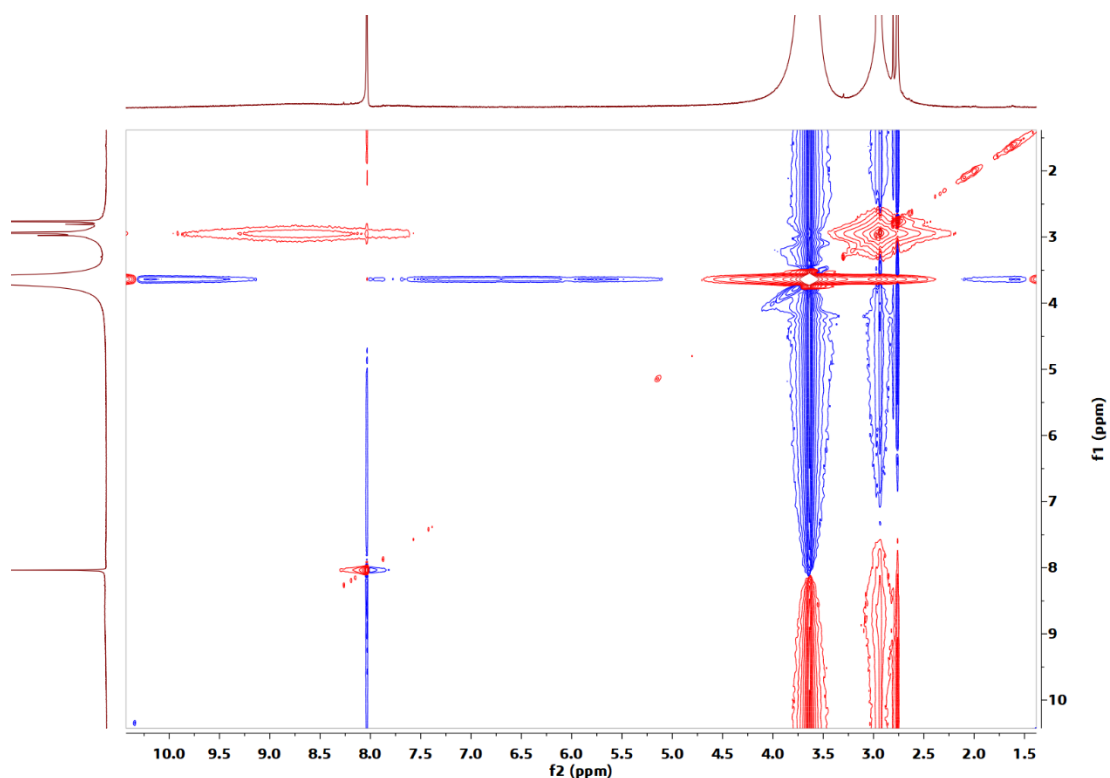


Fig. S34. 2D ^1H -NOESY of PBFDO in deuterated DMF. When two protons are spatially close, the dipolar cross-relaxation can be detected by the two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY). With this method, the interaction between different materials could be identified through the cross peak between protons^{10,11}. Here, cross peaks were observed between the hydrogen on methyl group of DMF (2.5~3.2 ppm) and the hydrogen on aromatic ring of PBFDO (7.6-9.5 ppm), indicating close proximity between the DMF molecule and the polymer due to the strong interactions between PBFDO and solvents.

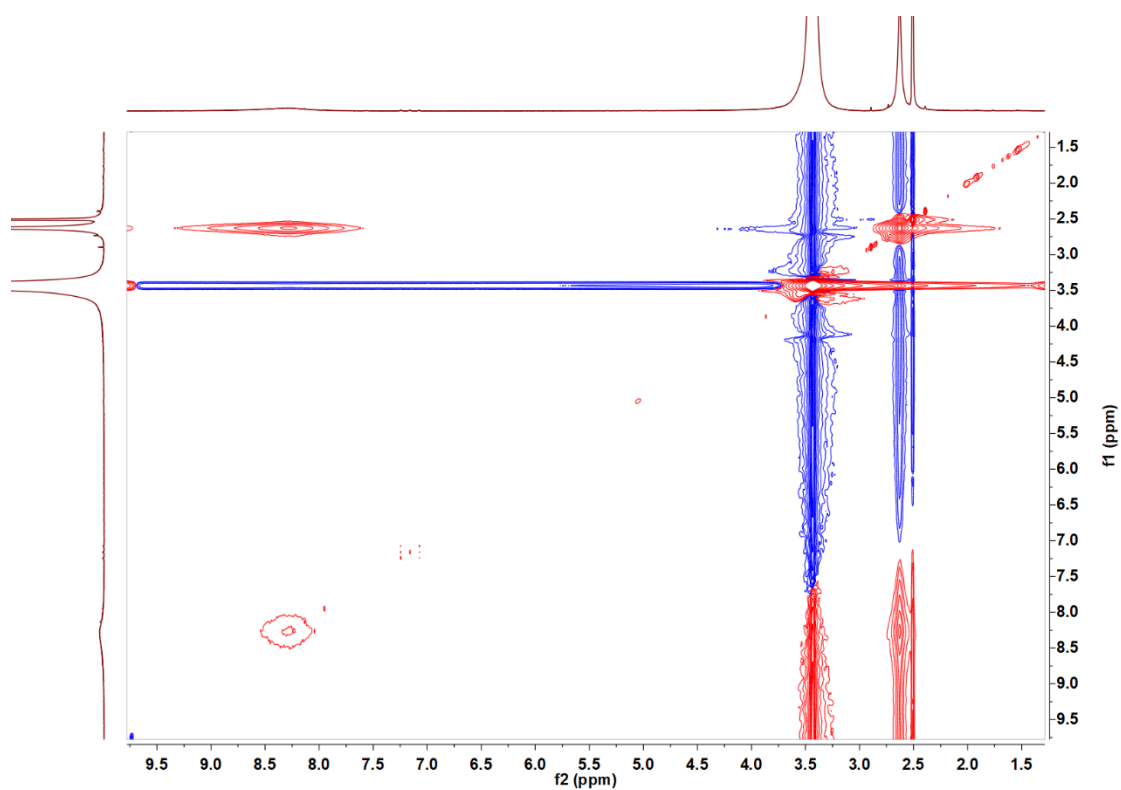


Fig. S35. 2D ^1H -NOESY of PBFDO in deuterated DMSO. Cross peaks were observed between the hydrogen on methyl group of DMSO (2.4~2.8 ppm) and the hydrogen on aromatic ring of PBFDO (7.5-9.0 ppm), suggesting the close distance between DMSO molecule and PBFDO because of the strong interaction.

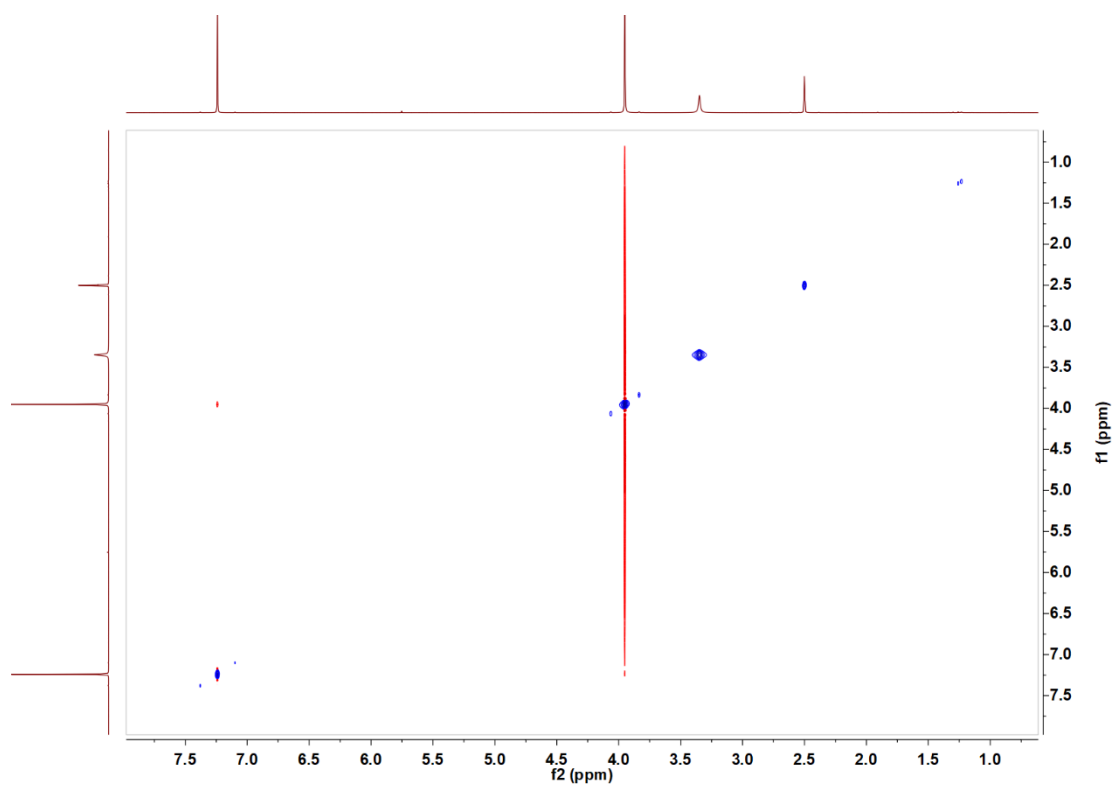


Fig. S36. 2D ^1H -NOESY of H-BFDO monomer in deuterated DMSO. No dipolar cross-relaxation between monomer and solvent can be observed.

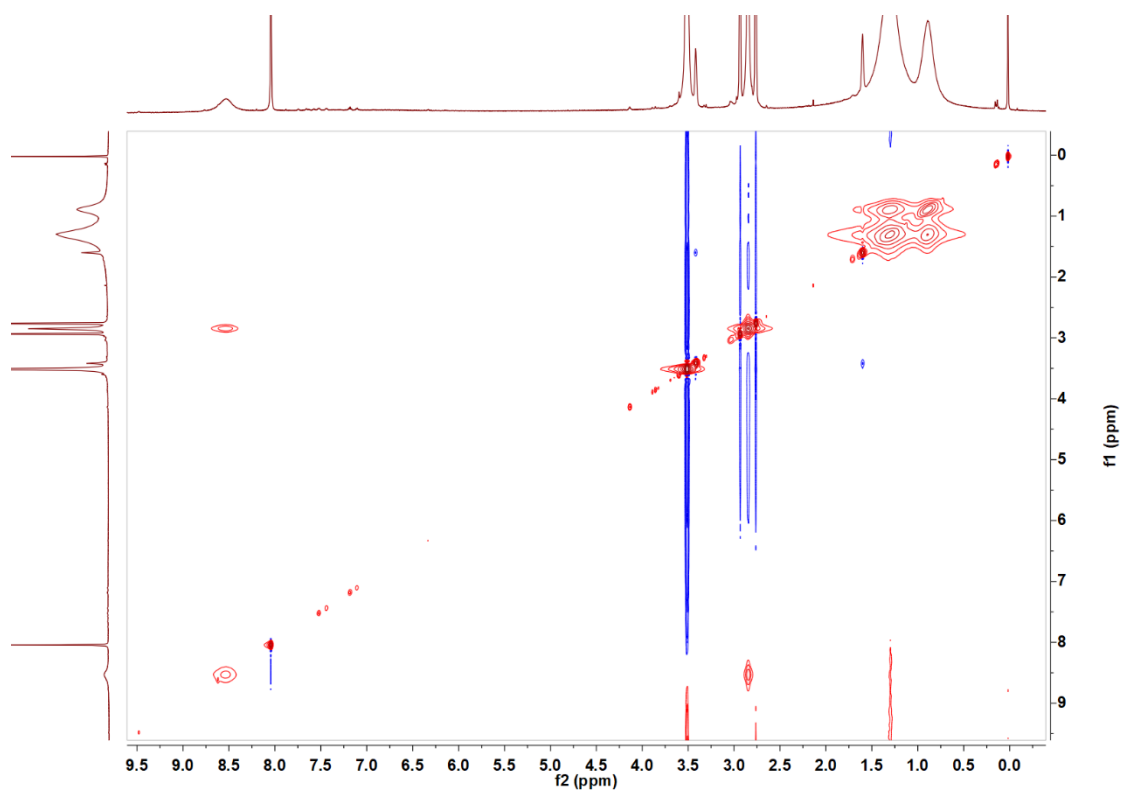


Fig. S37. 2D ^1H -NOESY of doped oligomers-C6C8Br (DMF) in deuterated DMF. Weak cross peaks were observed between the hydrogen on methyl group of DMF (2.8~3.1 ppm) and the hydrogen on aromatic ring of oligomers (8.3-8.6 ppm), indicating the existence of interaction between solvents and oligomers. We also tried to test the 2D ^1H -NOESY of oligomer $n = 1$, however, it does not dissolve well in DMF or DMSO probably due to the obstruction of the alkyl chain.

G. General characterisation of PBFDO.

Table S3 Elemental analysis of PBFDO.

Product	Experimental (%)				
	C	H	N	S	O
PBFDO ^a	63.93±0.15	1.63±0.02	0.03±0.02	0.12±0.04	33.99±0.16
PBFDO ^b	64.07±0.04	1.72±0.06	0.04±0.01	0.02±0.01	34.15±0.06
Simulated ^c	64.19	1.62	0.00	0.00	34.20

^a Sample prepared from DMSO. The solid was scratched from the deposited film for measurement. The small amount of element sulphur in the sample is mainly due to the low volatility of DMSO resulting in trace residues in the film.

^b The solid scratched from the deposited film was then washed with dichloromethane using Soxhlet apparatus. The element sulphur in the sample is greatly reduced due to the removal of DMSO.

^c The oligomer having 8 repeating units with 6 units doped with protons was adopted for theoretical estimation and the value was listed in the brackets.

The molecular weight of PBFDO was first evaluated by gel permeation chromatography (GPC) with DMSO as the eluent. To minimise the effect of aggregation on molecular weight estimation, the concentration for GPC measurements was adjusted to 1 mg mL⁻¹. The results exhibited a high molecular weight up to 42 kDa. Additionally, it was found that PBFDO had an adsorption effect on the chromatographic column, which may be related to its unique solubility properties and will lead to inaccurate estimation of molecular weight. We further checked the viscosity of PBFDO with different concentrations as a characterisation of its basic properties (**Table S4**). As the concentration increases, the viscosity of the polymer solution also increases, from 27 cp (5 mg mL⁻¹) to 250 cp (15 mg mL⁻¹). For comparison, the viscosity of the oligomer-C6C8Br solution was also tested. At the same concentration, the viscosity of the oligomer solution containing about 8 repeating units was much lower than that of the polymer solution, indicating stronger interactions with the solvent and a stronger chain entanglement effect in the polymer solution.

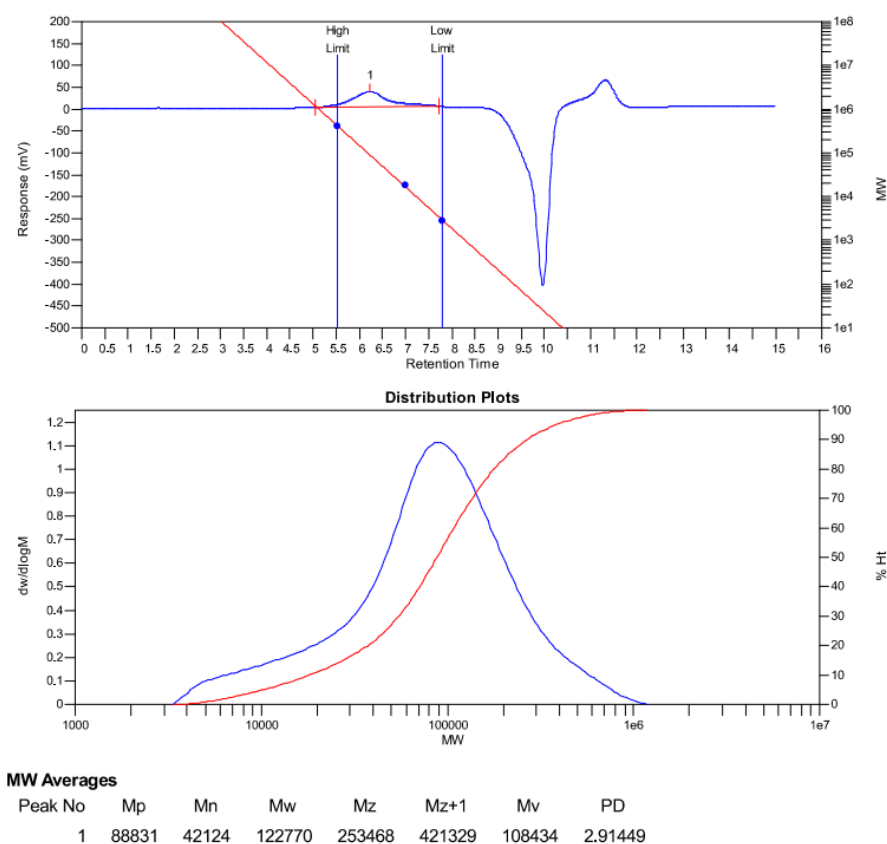


Fig. S38. Gel permeation chromatography traces of PBFDO in DMSO.

Table S4 Viscosity measurements.

Sample	Viscosity (cP)
DMSO	2.7 ~ 3.9
PBFDO (5 mg ml ⁻¹)	26.7 ~ 27.6
PBFDO (10 mg ml ⁻¹)	52.2 ~ 53.1
PBFDO (15 mg ml ⁻¹)	249.5 ~ 250.4
Oligomers-C6C8Br (5 mg ml ⁻¹)	5.8 ~ 6.0
Oligomers-C6C8Br (10 mg ml ⁻¹)	11.6 ~ 12.0

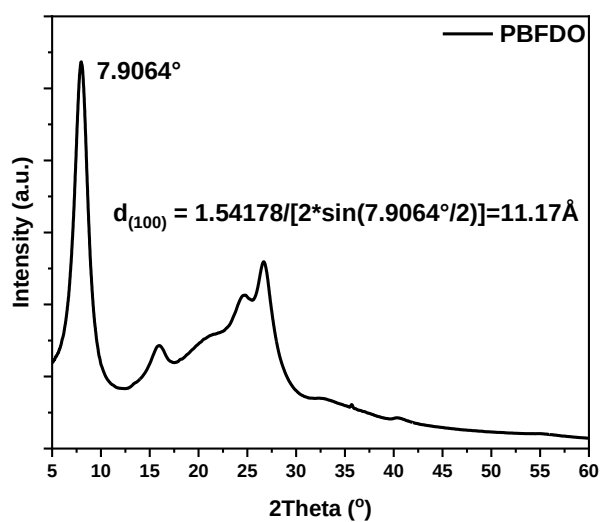


Fig. S39. Powder X-ray diffraction (PXRD) characterization of PBFDO. The sample exhibits a strong (100) peak with a distance of 11.17 Å and fine crystallinity, which is consistent with the GIWAXS characterisation and facilitates high mobility and conductivity of PBFDO.

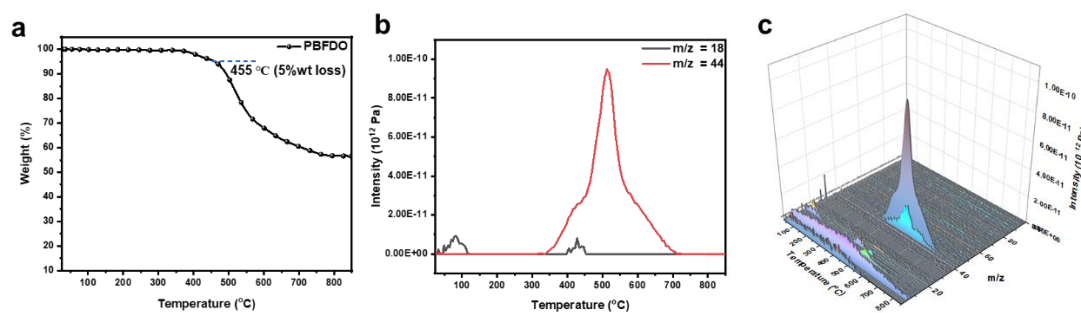


Fig. S40. TG-MS measurements of PBFDO films. The TG data proved that almost no solvent residues left in the film, which was in accordance with the XPS characterisation. PBFDO showed high thermal stability and its onset degradation over 400 °C could be attributed to the cleavage of ester group and decomposition of carbonyl groups, thus resulting in the emission of the carbon dioxide gas ($m/z = 44$).

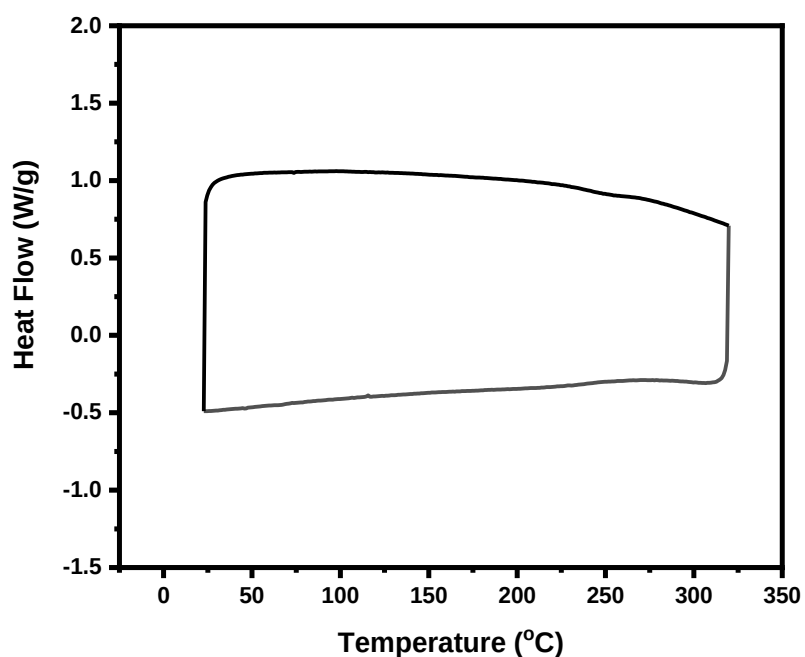


Fig. S41. DSC curve of PBFDO under nitrogen. PBFDO exhibited no obvious exothermic or endothermic behavior in the range of 25 ~ 320 °C at heating/cooling rates of 10/10 °C min⁻¹.

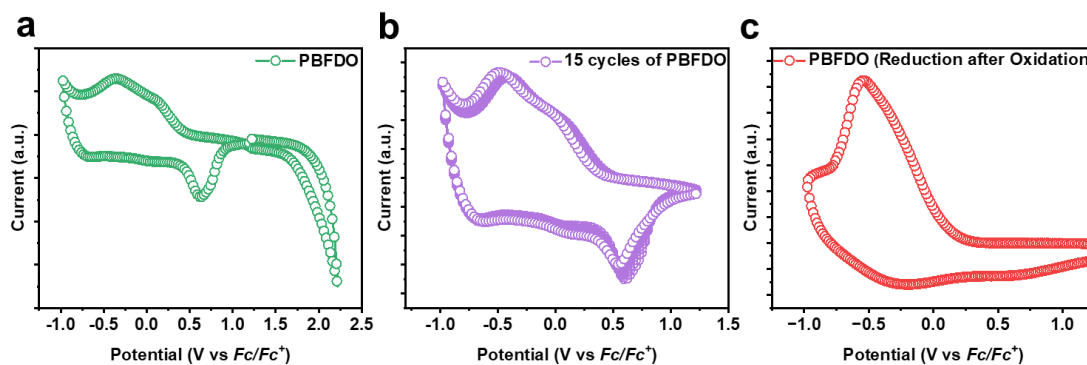


Fig. S42. Cyclic voltammetry curves of PBFDO. All results were calibrated using the ferrocene/ferrocenium (Fc/Fc^+ , $E_{re} = -4.8$ eV). **a**, A reduction peak around 0.38 V (vs Fc/Fc^+) was observed in PBFDO, indicating its extremely deep-lying onset reduction level at -5.18 eV. **b**, Only slight variation was observed for PBFDO operated around its LUMO level for 15 cycles, indicating that PBFDO featured high redox activity and reversibility. Over 85% conductivity was retained even after 15 cycles of redox measurements, which is in accordance with the excellent operation stability of organic electrochemical transistors in **Fig. 4c** (main text). **c**, Considering the heavily n-doped state of PBFDO, we tried to de-dope the polymer by electrochemical oxidation. Although we are not sure whether the PBFDO was fully de-doped or its conjugation structure changed after electrochemical oxidation since PBFDO does not show good reversibility around the oxidation potential, the onset reduction level of the polymer after electrochemical oxidation was measured to be -5.04 eV, which remains the extremely low level.

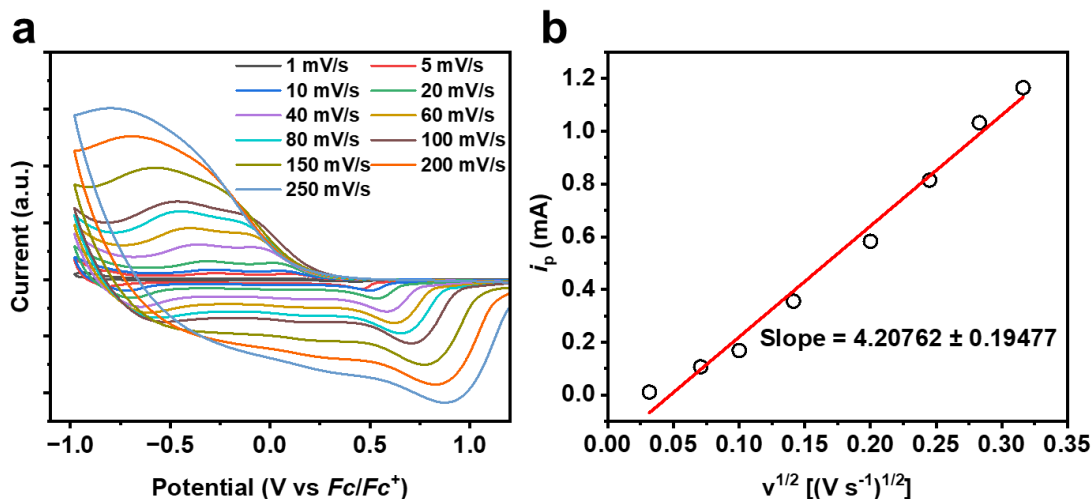


Fig. S43. **a**, Cyclic voltammetry curves of PBFDO measured at different scanning rates. **b**, Linear fitted spectrum of the peak current i_p and $v^{1/2}$ (v is the scanning rate). At high scan rates, PBFDO exhibits only one reduction peak at 0.5 V, but different reduction peaks at 0.1 V as well as 0.4 V can be distinguished at low scan rates, which may be related to the diffusion of the tetrabutylammonium ion in the film. According to the Randles-Sevcik equation: $i_p = 0.4463 \left(\frac{n^3 F^3}{RT} \right)^{1/2} AC(Dv)^{1/2}$, where n is the number of electrons transferred in a redox cycle, F is the faraday constant, R is the universal gas constant, T is the absolute temperature, A is the surface area of working electrode, C is the molar concentration of redox-active species, D is the diffusion coefficient, and v is the scan rate. At the room temperature of 298.15 K, the equation becomes: $i_p = (2.687 \times 10^5) n^{3/2} AC(Dv)^{1/2}$. Based on fitted slope of i_p - $v^{1/2}$, the diffusion coefficient was estimated as $1.53 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, which is less than that reported for Na, K and Mg¹². Based on Stocks-Einstein equation $D = \frac{k_B T}{6\pi\eta r}$, the diffusion coefficient of ions is related to the radius of hydrated ion. The CV data were obtained in the acetonitrile solution of tetrabutylammonium hexafluorophosphate. Compared with Mg, Zn, K, and Na, the hydrated ion radius of tetrabutylammonium is much bigger, which might account for its lower diffusion coefficient. Moreover, the compact micro-stacking structure of PBFDO would further limit the ion diffusion.

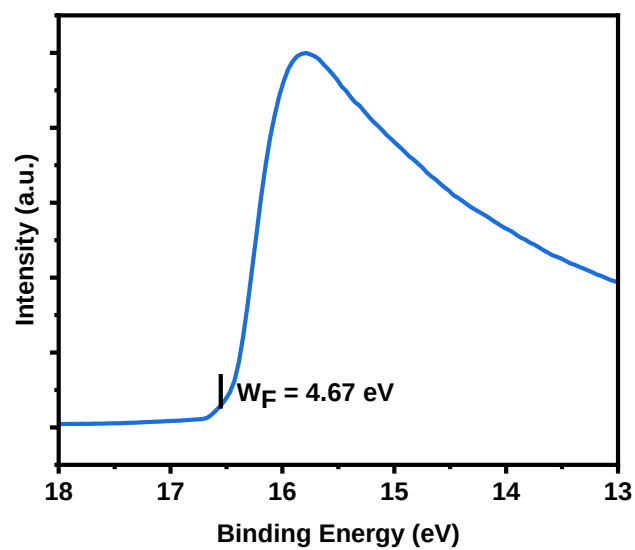


Fig. S44. UPS spectrum of PBFDO deposited on Si substrate. The Fermi level of PBFDO was measured as -4.67 eV , which locates higher than its reduction level, indicating PBFDO was under highly n-doped state.

H. Morphology analysis.

Scanning electron microscope (SEM) images were obtained by a cold field emission scanning electron microscope (Zeiss Gemini 300 with OXFORD Xplore Energy Dispersive Spectrometer (EDS)) operated at an accelerating voltage of 1.0 kV. The sample was treated by gold-sputtering before measurements. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai G2 f20 s-twin.

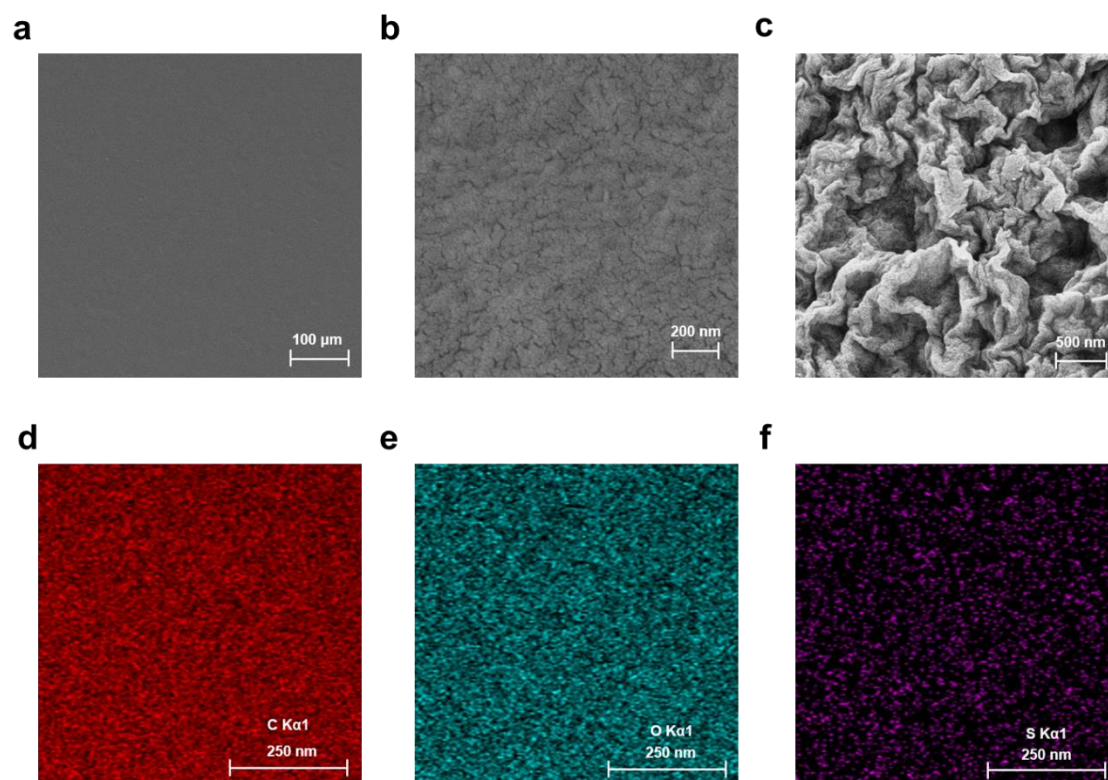


Fig. S45. **a**, SEM image of PBFDO film through drop-casting. Smooth and uniform film was observed without obvious leakage. **b**, Enlargement picture, exhibiting existence of fiber-like morphology in PBFDO film. **c**, The image of PBFDO fibers, which were obtained by precipitating the PBFDO (DMSO) solvent into tetrahydrofuran (THF). **d-f**, The energy mapping of PBFDO film. **d**, carbon element; **e**, oxygen element; and **f**, sulfur element.

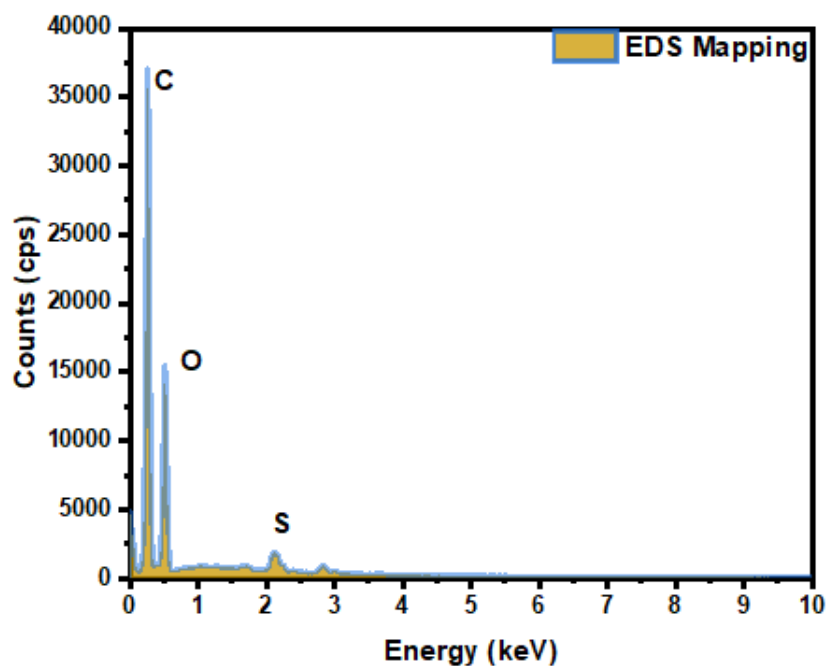


Fig. S46. Element analysis through EDS mapping for PBFDO.

Table S5 Summary of element analysis obtained from EDS measurement.

Element	Weight %	Weight % Sigma	Atom%
C	68.04	0.30	73.71
O	29.10	0.17	23.67
S	0.07 ^a	0.03	0.03

^aSmall amounts of elemental sulphur can be attributed to residues of DMSO due to its low volatility.

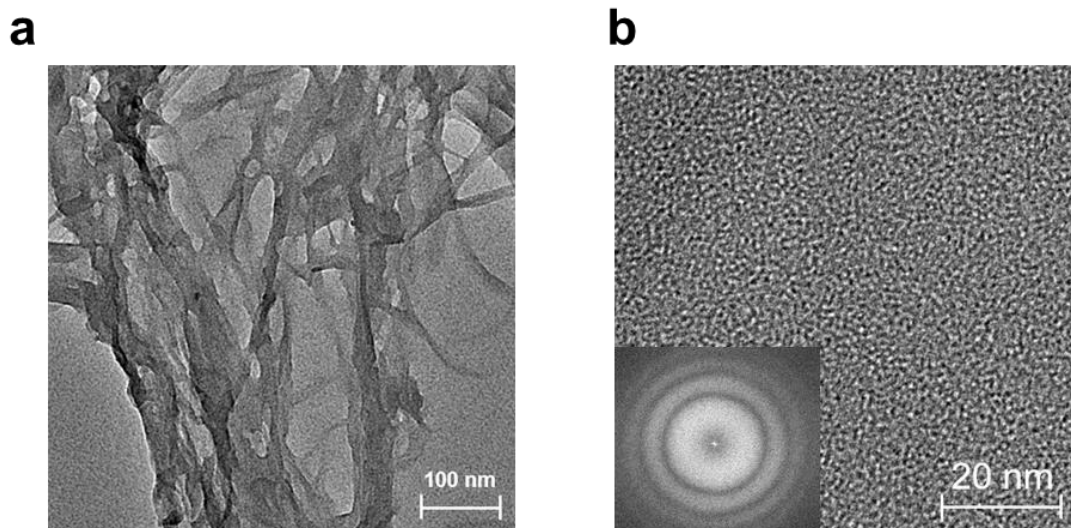


Fig. S47. **a**, TEM image of PBFDO fibers. **b**, High-resolution TEM of PBFDO film (spin-coating). The inset picture is selected area electron diffraction (SAED).

I. Temperature-dependent conductivity and Hall measurements.

The temperature-dependent conductivity and Hall measurements were conducted using Quantum Design PPMS9 under vacuum. The room temperature conductivity was measured by JouleYacht MRS-3RT. All the conductivity measurements were performed using the four-point probe structure as shown in **Fig. S48a**. The conductivity was calculated through the following equation: $\sigma = IL/VWd$, where W is the sample width, d is the thickness of the film, and L is the span of two voltage probes. For temperature-dependent conductivity measurement, the sample was first cooled to 10 K and the conductivities at different temperatures were recorded with a heating rate of 5 K min⁻¹.

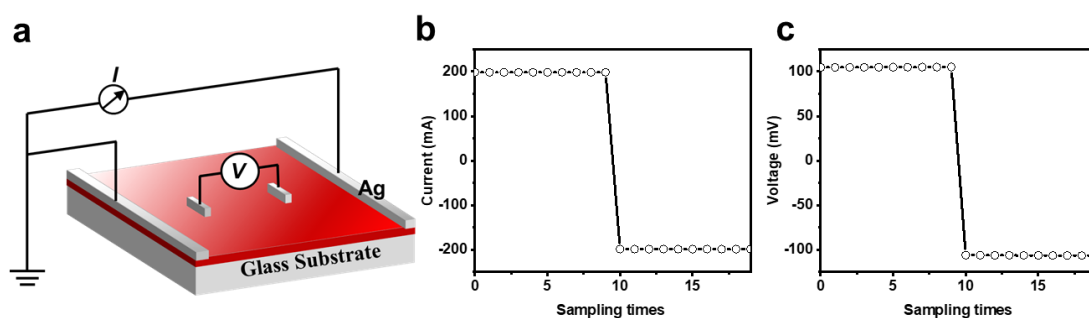


Fig. S48. **a**, Schematic illustration of the four-point probe measurement of conductivity. **b-c**, The applied current and corresponding voltage signal of PBFDO film measured under room temperature (here $W = 10$ mm, $L = 3.6$ mm, $d = 3342 \pm 156$ nm, the conductivity was calculated to be 2011 ± 94 S cm⁻¹. Six points in the film were chosen for film thickness measurements and error bar represents the standard deviation from the mean values).

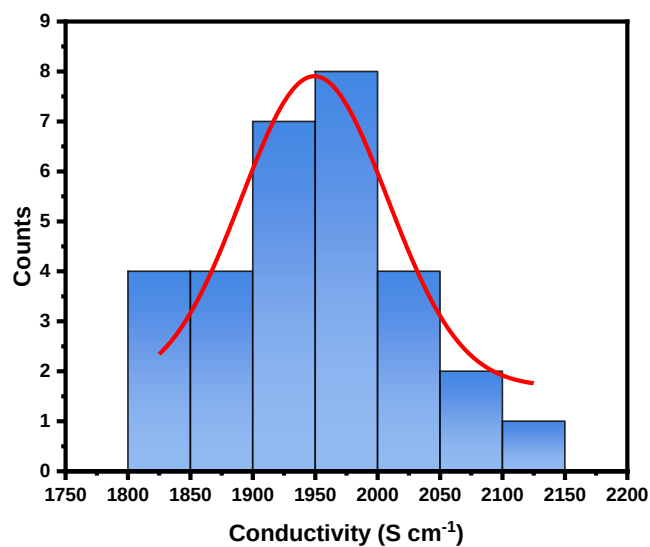


Fig. S49. Statistical graph of average conductivities based on 30 individual samples.

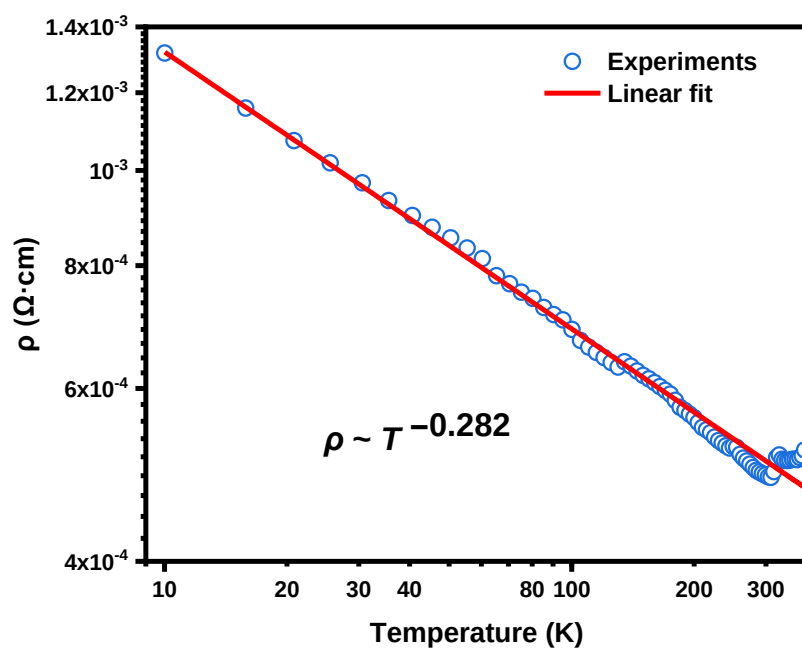


Fig. S50. Log-log plot of resistivity versus temperature at various temperatures. The linear fitting indicates that the conductivity follows the power law: $\rho \propto T^{-0.282}$.

For Hall measurements, the structure as shown in **Fig. 2c** in the main text was adopted, where an external magnetic field B was applied perpendicular to the sample plane. The uncertainty of magnetic field B was measured to be less than 1 %. The longitudinal voltage V_{xx} , and transverse voltage V_{xy} were recorded with a constant DC current, I applied, when B was ramped up and down from 8 T to -8 T with a sweeping rate of 0.5 T min^{-1} , and the resistance $R = V/I$ was calculated and recorded by the instrument. Prior to the Hall measurement, the ideal contact between electrode and the film was confirmed by conductivity measurements without applied field. The errors between conductivity from Hall measurement and results from above four-point measurement at various temperatures were less than 5%. It should be noted that the measured longitudinal voltage V_{xx} , and transverse voltage V_{xy} usually contains offset voltages due to a misalignment of electrodes, requiring additional corrections based on symmetry characteristics of the resistance with respect to the magnetic field, which are discussed as follows.

For longitudinal resistance $R_{xx} = V_{xx}/I$ in an ideal system, the value should be completely symmetrical about the “zero field”, $B = 0$ T. However, under different applied magnetic field, the extra deviation ΔR_{xy} was introduced by the transverse asymmetric voltage due to the Hall effect arising from the imperfect symmetry of the electrode position as exhibited in **Fig. S51**. The error caused by transverse voltage is dependent on the field, that is, $R_{xy}(B^+)$ and $R_{xy}(B^-)$ have the same absolute value but opposite signs. Therefore, the deviation $|\Delta R_{xy}|$ could be extracted from $|R_{xx}(B^+) - R_{xx}(B^-)|/2$ and the real longitudinal resistance could be calculated using following equation:

$$R_{xx}(B^+ \text{ or } B^-) = \max [R_{xx}(B^+), R_{xx}(B^-)] - |R_{xx}(B^+) - R_{xx}(B^-)|/2$$

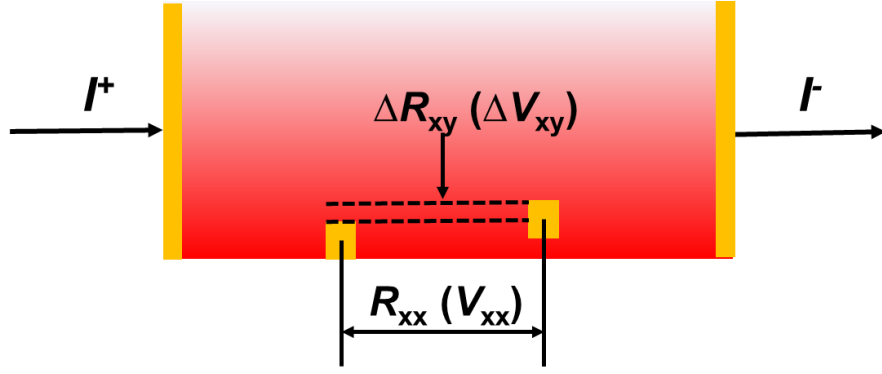


Fig. S51. A schematic diagram showing the deviation of longitudinal resistance R_{xx} caused by transverse asymmetric resistance R_{xy} .

Similarly, for transverse resistance $R_{xy} = V_{xy}/I$, the measured transverse voltage often contains the effect from longitudinal voltage due to a misalignment of transverse probes as shown in **Fig. S52a**. Because the longitudinal resistance R_{xx} does not change the sign with the change of the magnetic field direction, it introduces the same change to the Hall signals under magnetic field of different directions, increasing (**Fig. S52b**) or decreasing at both directions (**Fig. S52c**). The deviation value caused by longitudinal resistance could be extracted using the following equation:

$$|\Delta R_{xx}(B^+ \text{ or } B^-)| = |R_{xy}(B^+) - R_{xy}(B^-)|/2$$

The real Hall resistance V_H/I then can be corrected according to the above two different situations using the obtained value $|\Delta R_{xx}(B^+ \text{ or } B^-)|$.

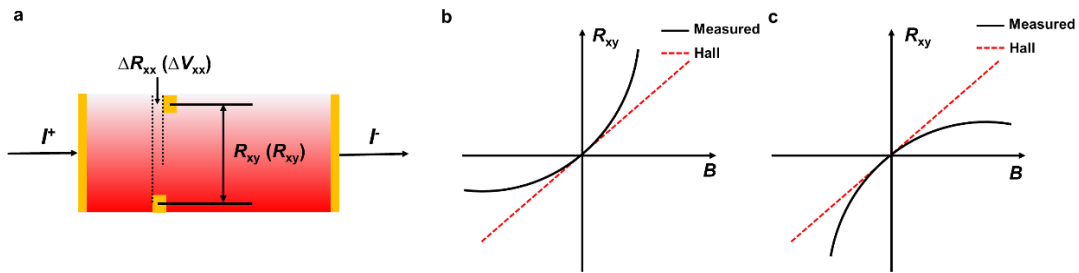


Fig. S52. a, Schematic diagram showing how longitudinal voltage offset influences the measurement of Hall signal. **b-c**, Two situations of the effect of ΔR_{xx} on Hall signal.

From the Hall measurements, the Hall coefficient, R_H , and Hall mobility, μ_H ,

were extracted using the following equation:

$$|R_H| = V_H d / IB,$$

$$|\mu_H| = |R_H| \sigma,$$

where d is the thickness of the conductive layer, and σ is the conductivity measured from $\sigma = L/R_{xx} Wd$. Practically, to minimize the experimental uncertainty, $|R_H|$ was extracted by taking a slope of Hall resistance versus B between 8 and -8 T and results were shown in **Fig. S53** and **Fig. 2d** (main text). The coherence factor, γ_H , represents degree of phase coherence and is defined as¹³

$$\gamma_H = ne / |R_H|^{-1},$$

where n is the charge concentration and e is the elemental charge. Assuming the transport is ideal which reproduces the ideal Hall effect formula, γ_H equals to 1, and the carrier concentration extracted from the Hall effect is $n_H = (|R_H| e)^{-1}$. The coherence factor also represents a finite deviation of Hall mobility from drift mobility, μ_D , as $\mu_H = \gamma_H \times \mu_D$.

Taking the coherence factor of around $0.5 \sim 0.9$ in a real system into account¹³, the Hall measurement may overestimate carrier concentration and underestimate mobility. Nevertheless, the Hall measurement could still act a power tool to evaluate the transport physics in conducting polymers and the observation of an ideal Hall effect can be interpreted as demonstration of coherent charge transport.

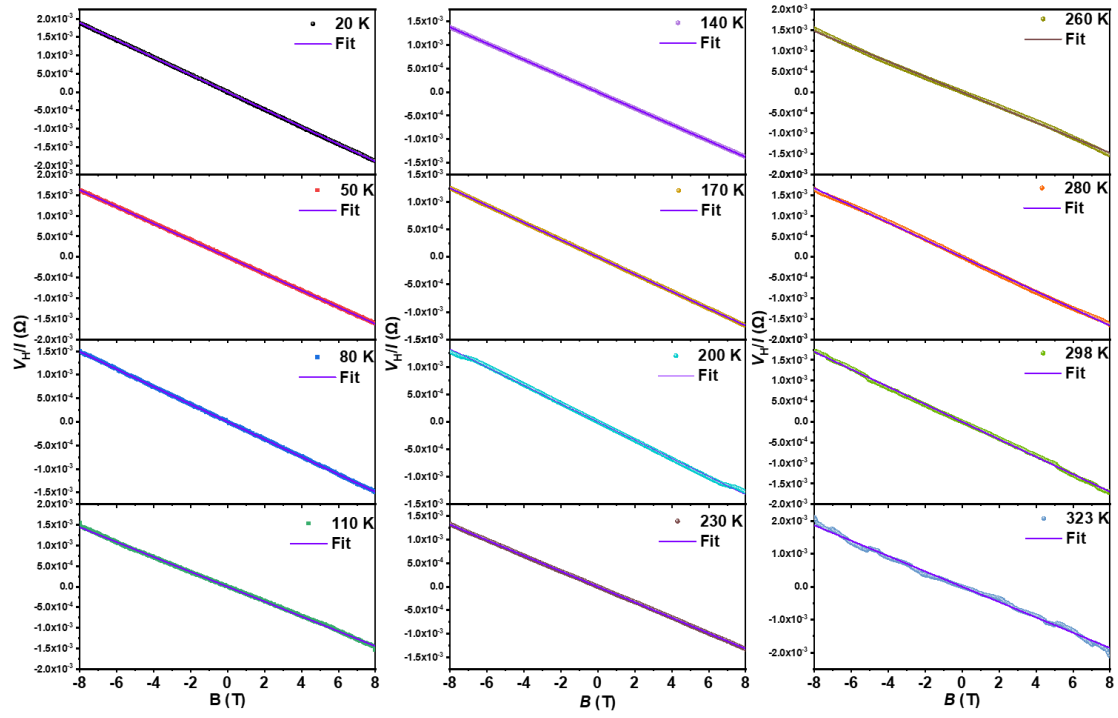


Fig. S53. Hall resistance V_H/I versus magnetic field B at various temperatures. By default, the left end of the current channel is positive, and the right end is negative while the upper end of the Hall channel is positive, and the lower end is negative. The $V_H/I - B$ curve locates in the second and fourth quadrants, indicating the n-type conduction in the PBFDO film.

J. Qualitative analysis of electron spin resonance (ESR) measurements.

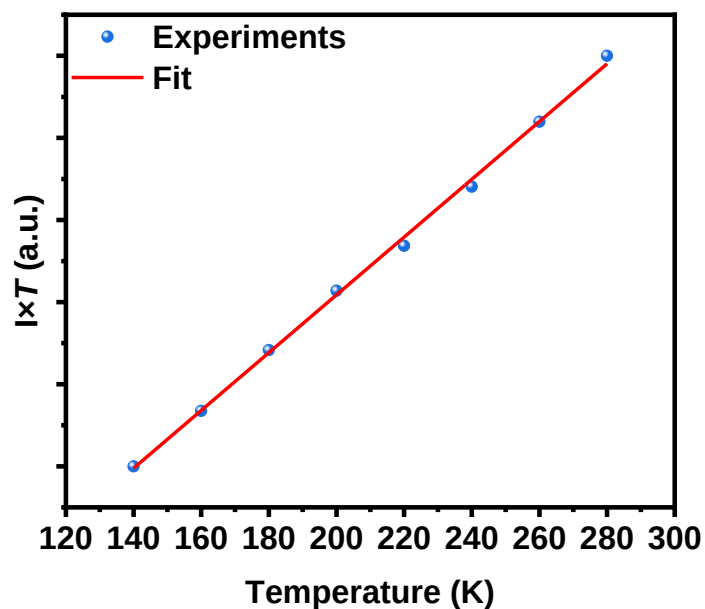


Fig. S54. The product of double integration of ESR signals (I) and temperature (T) versus T plot. Data were obtained at various temperatures using the spectrum in **Extended Data Fig. 3a**. The qualitative analysis of ESR indicates the spin susceptibility follows the relationship: $\chi_{\text{total}}T = \chi_{\text{Pauli}}T + C$, which is in accordance with the SQUID results.

K. Organic electrochemical transistors (OECTs) with different thicknesses.

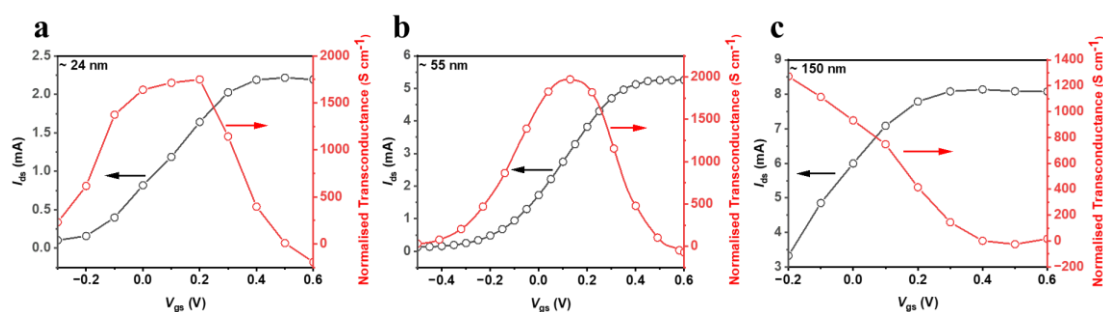


Fig. S55. OECTs performance with different PBFDO thicknesses. PBFDO can show very good reproducibility as well as high transconductance in the case of thin films (**a** and **b**). However, the reproducibility becomes extremely poor in the case of thick films (**c**), probably due to the strong hydrophobicity of the PBFDO which prevents the entry of ions from aqueous solutions to the film. In addition, OECT devices in this work were performed under the accumulation mode. The inherent high conductivity of the thick film sample makes the change of transconductance induced by further doping relatively smaller, which further limits the device performance. Therefore, the optimal thickness of PBFDO for OECTs was determined as about 55 nm.

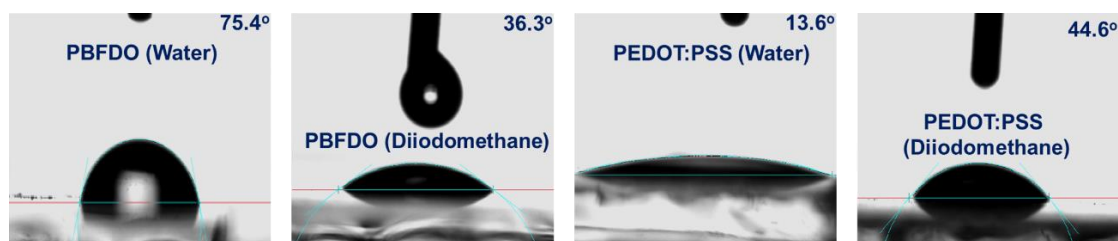


Fig. S56. The contact angle characterization of PBFDO. Compared to PEDOT:PSS, PBFDO has a very high contact angle with water, which prevents ions entering the film from the aqueous solution and limits the performance of the OECT devices.

L. Integrated thermoelectric devices.

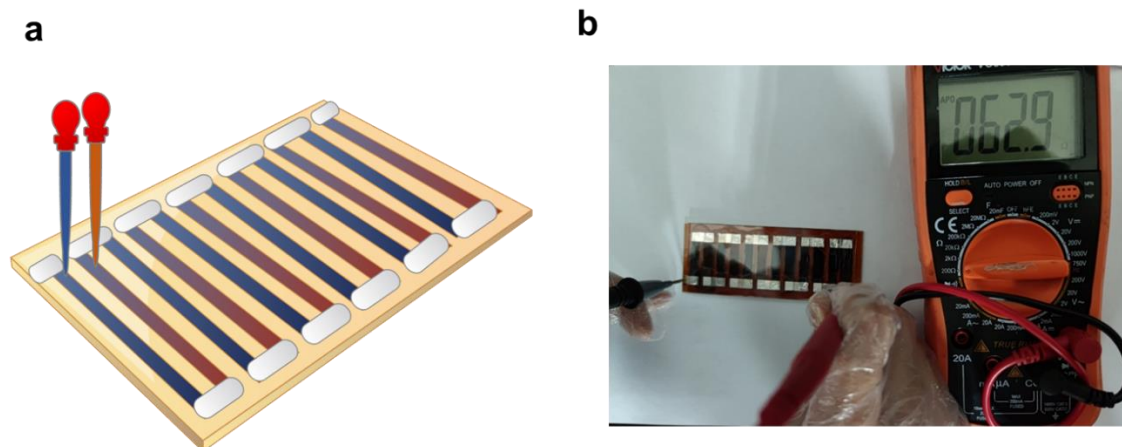


Fig. S57. Integrated thermoelectric device prepared by printing PEDOT:PSS (CLEVIOSTM PH1000, 5vol% DMSO) and PBFDO on a polyimide (PI) substrate. **a**, Schematic illustration of the device fabricating process. **b**, The resistance of the whole device is ca. 63 Ω .

M.Summary of conductivities of reported n-type conducting materials.

Table S6. Summary of electrical conductivities of solution-processed n-type conducting materials.

Materials	Conductivity (S cm ⁻¹)	Year	Reference
PBFDO	2011	2021	This work
C ₆₀ : (o-MeO-DMBI-I)	5.5	2012	[14]
P(NDI2OD-T ₂): (2-Rc-DMBI) ₂	3×10^{-3}	2014	[15]
C ₆₀ : (2-Cyc-DMBI-H)	0.1	2014	[15]
P(NDIOD-T ₂): (N-DMBI)	8×10^{-3}	2014	[16]
ClBDPPV: (N-DMBI)	4	2015	[17]
FBDPPV: (N-DMBI)	14	2015	[17]
BBL: (TDAE)	2.4	2016	[18]
Poly (Ni-ett)	227	2016	[19]
P(PDI2OD-A): (2-Cyc-DMBI) ₂	0.27	2016	[20]
PNDTI-BBT-DP: (N-DMBI)	5	2017	[21]
P(BTP-DPP): (RuCp*mes) ₂	0.45	2017	[22]
ClBDPPV: (TBAF)	0.62	2017	[23]
2Strans-PNDIT ₂ : (N-DPBI)	6×10^{-3}	2018	[24]
PNDI2TEG-2Tz: (N-DMBI)	1.8	2018	[25]
TEG-N2200: (N-DMBI)	0.17	2018	[26]
P(NDI2OD-Tz ₂): (TDAE)	0.1	2018	[27]
p(gNDI-gT ₂): (N-DMBI)	0.3	2018	[28]
LPPV-1: (N-DMBI)	1.1	2019	[29]
PDTzTI: (TDAE)	4.6	2019	[30]
P(PzDPP-CT2): (N-DMBI)	8.4	2019	[31]
FBDPPV: (N-DMBI) ₂	7.9	2019	[32]
2DQQT-Se	0.29	2019	[33]
FBDPPV: (TAM)	21	2020	[34]
TBDPPV: (N-DMBI)	85	2020	[35]
TBDOPV-T: (N-DMBI)	59	2020	[35]
BBL:P(g ₄ 2T-T)	2	2020	[36]
P(NDI2OD-T ₂): PEI	2×10^{-3}	2020	[37]
UFBDPPV: (TAM)	22.5	2020	[38]
UFBDPPV: (N-DMBI)	16	2020	[38]
QTICN	0.34	2020	[39]
N-N: (N-DMBI)	0.65	2021	[40]
P(PzDPP-CT2): (N-DMBI)(New)	32.1	2021	[41]
PCICITVT: (N-DMBI)	38.3	2021	[42]
PFCITVT: (N-DMBI)	16.1	2021	[42]
PCNI-BTI: (N-DMBI)	23.3	2021	[43]
BBL:PEI	8	2021	[44]
f-BTI2TEG-FT: (N-DMBI)	104	2021	[45]

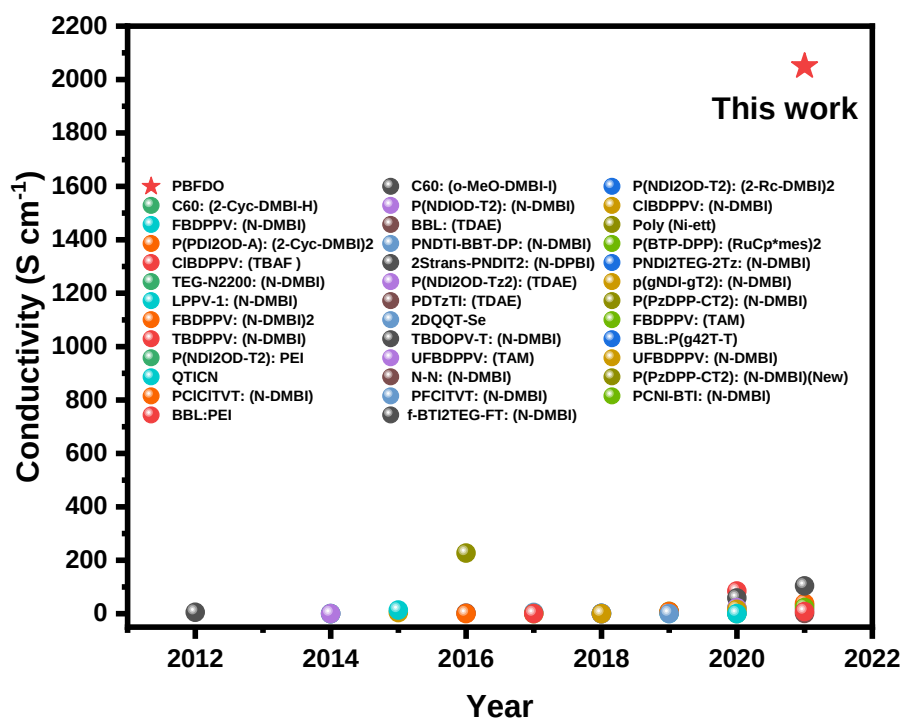


Fig. S58. Summary of electrical conductivities of state-of-the-art solution-processed n-type conducting materials.

N. References.

- 1 J. H. Wood, L. C. 2,5-Dihydroxy-p-benzenediacetic acid. *Org. Synth.* **26**, 24 (1946).
- 2 Lei, T., Dou, J.-H., Cao, X.-Y., Wang, J.-Y. & Pei, J. Electron-deficient poly(p-phenylene vinylene) provides electron mobility over $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions. *J. Am. Chem. Soc.* **135**, 12168-12171 (2013).
- 3 Hu, W., Lin, J.-P., Song, L.-R. & Long, Y.-Q. Direct synthesis of 2-Aryl-4-quinolones via transition-metal-free intramolecular oxidative C(sp³)-H/C(sp³)-H Coupling. *Org. Lett.* **17**, 1268-1271 (2015).
- 4 An, G., Wang, L. & Han, J. Palladium catalyzed regioselective cyclization of arylcarboxylic acids via radical intermediates with diaryliodonium salts. *Org. Lett.* **23**, 8688-8693 (2021).
- 5 Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).
- 6 Jia, H. *et al.* Formation and stabilization of environmentally persistent free radicals induced by the interaction of anthracene with Fe(III)-modified clays. *Environ. Sci. Technol.* **50**, 6310-6319 (2016).
- 7 Christoforidis, K. C., Un, S. & Deligiannakis, Y. High-field 285 GHz electron paramagnetic resonance study of indigenous radicals of humic acids. *J. Phys. Chem. A* **111**, 11860-11866 (2007).
- 8 Hales, B. J. Immobilized radicals. I. Principal electron spin resonance parameters of the benzosemiquinone radical. *J. Am. Chem. Soc.* **97**, 5993-5997 (1975).
- 9 Lu, J. *et al.* 3,7-Bis(2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6-dione dicyanides with engineered side chains for unipolar n-type transistors. *ACS Appl. Electron. Mater.* **2**, 103-110 (2020).
- 10 Oh, S., Morales-Collazo, O., Keller, A. N. & Brennecke, J. F. Cation-anion and anion-CO₂ interactions in triethyl(octyl)phosphonium ionic liquids with

- aprotic heterocyclic anions (AHAs). *J. Phys. Chem. B* **124**, 8877-8887 (2020).
- 11 Wang, Y., Lu, R., Yao, J. & Li, H. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene enhances activity of peroxide intermediates in phosphine-free α -hydroxylation of ketones. *Angew. Chem. Int. Ed.* **60**, 6631-6638 (2021).
 - 12 Coppedè, N., Villani, M. & Gentile, F. Diffusion driven selectivity in organic electrochemical transistors. *Sci. Rep.* **4**, 4297 (2014).
 - 13 Uemura, T. *et al.* Temperature dependence of the Hall effect in pentacene field-effect transistors: Possibility of charge decoherence induced by molecular fluctuations. *Phys. Rev. B* **85**, 035313 (2012).
 - 14 Wei, P. *et al.* 2-(2-Methoxyphenyl)-1,3-dimethyl-1H-benzoimidazol-3-ium iodide as a new air-stable n-type dopant for vacuum-processed organic semiconductor thin films. *J. Am. Chem. Soc.* **134**, 3999-4002 (2012).
 - 15 Naab, B. D. *et al.* Effective solution- and vacuum-processed n-doping by dimers of benzimidazoline radicals. *Adv. Mater.* **26**, 4268-4272 (2014).
 - 16 Schlitz, R. A. *et al.* Solubility-limited extrinsic n-type doping of a high electron mobility polymer for thermoelectric applications. *Adv. Mater.* **26**, 2825-2830 (2014).
 - 17 Shi, K. *et al.* Toward high performance n-type thermoelectric materials by rational modification of BDPPV backbones. *J. Am. Chem. Soc.* **137**, 6979-6982 (2015).
 - 18 Wang, S. *et al.* Thermoelectric properties of solution-processed n-doped ladder-type conducting polymers. *Adv. Mater.* **28**, 10764-10771 (2016).
 - 19 Sun, Y. *et al.* Flexible n-type high-performance thermoelectric thin films of poly(nickel-ethylenetetrathiolate) prepared by an electrochemical method. *Adv. Mater.* **28**, 3351-3358 (2016).
 - 20 Naab, B. D. *et al.* Role of polymer structure on the conductivity of n-doped polymers. *Adv. Electron. Mater.* **2**, 1600004 (2016).
 - 21 Wang, Y. *et al.* Naphthodithiophenediimide-benzobisthiadiazole-based polymers: Versatile n-type materials for field-effect transistors and

- thermoelectric devices. *Macromolecules* **50**, 857-864 (2017).
- 22 Perry, E. E. *et al.* High conductivity in a nonplanar n-doped ambipolar semiconducting polymer. *Chem. Mater.* **29**, 9742-9750 (2017).
- 23 Zhao, X. *et al.* High conductivity and electron-transfer validation in an n-type fluoride-anion-doped polymer for thermoelectrics in air. *Adv. Mater.* **29**, 1606928 (2017).
- 24 Nava, D. *et al.* Drastic improvement of air stability in an n-type doped naphthalene-diimide polymer by thionation. *ACS Appl. Energy Mater.* **1**, 4626-4634 (2018).
- 25 Liu, J. *et al.* N-type organic thermoelectrics of donor–acceptor copolymers: Improved power factor by molecular tailoring of the density of states. *Adv. Mater.* **30**, 1804290 (2018).
- 26 Liu, J. *et al.* Enhancing molecular n-type doping of donor–acceptor copolymers by tailoring side chains. *Adv. Mater.* **30**, 1704630 (2018).
- 27 Wang, S. *et al.* A chemically doped naphthalenediimide-bithiazole polymer for n-type organic thermoelectrics. *Adv. Mater.* **30**, 1801898 (2018).
- 28 Kiefer, D. *et al.* Enhanced n-doping efficiency of a naphthalenediimide-based copolymer through polar side chains for organic thermoelectrics. *ACS Energy Lett.* **3**, 278-285 (2018).
- 29 Lu, Y. *et al.* Rigid coplanar polymers for stable n-type polymer thermoelectrics. *Angew. Chem. Int. Ed.* **58**, 11390-11394 (2019).
- 30 Liu, J. *et al.* Overcoming coulomb interaction improves free-charge generation and thermoelectric properties for n-doped conjugated polymers. *ACS Energy Lett.* **4**, 1556-1564 (2019).
- 31 Yan, X. *et al.* Pyrazine-flanked diketopyrrolopyrrole (DPP): A new polymer building block for high-performance n-type organic thermoelectrics. *J. Am. Chem. Soc.* **141**, 20215-20221 (2019).
- 32 Un, H.-I. *et al.* Understanding the effects of molecular dopant on n-type organic thermoelectric properties. *Adv. Energy Mater.* **9**, 1900817 (2019).

- 33 Yuan, D. *et al.* Air-stable n-type thermoelectric materials enabled by organic diradicaloids. *Angew. Chem. Int. Ed.* **58**, 4958-4962 (2019).
- 34 Yang, C.-Y. *et al.* A thermally activated and highly miscible dopant for n-type organic thermoelectrics. *Nat. Commun.* **11**, 3292 (2020).
- 35 Lu, Y. *et al.* Persistent conjugated backbone and disordered lamellar packing impart polymers with efficient n-doping and high conductivities. *Adv. Mater.* **33**, 2005946 (2021).
- 36 Xu, K. *et al.* Ground-state electron transfer in all-polymer donor–acceptor heterojunctions. *Nat. Mater.* **19**, 738-744 (2020).
- 37 Seidel, K. F. *et al.* Single-step formation of a low work function cathode interlayer and n-type bulk doping from semiconducting polymer/polyethylenimine blend solution. *ACS Appl. Mater. Interfaces* **12**, 28801-28807 (2020).
- 38 Lu, Y. *et al.* The critical role of dopant cations in electrical conductivity and thermoelectric performance of n-doped polymers. *J. Am. Chem. Soc.* **142**, 15340-15348 (2020).
- 39 Yang, K. *et al.* Stable organic diradicals based on fused quinoidal oligothiophene imides with high electrical conductivity. *J. Am. Chem. Soc.* **142**, 4329-4340 (2020).
- 40 Chen, H. *et al.* Acene ring size optimization in fused lactam polymers enabling high n-type organic thermoelectric performance. *J. Am. Chem. Soc.* **143**, 260-268 (2021).
- 41 Xiong, M. *et al.* Efficient n-doping of polymeric semiconductors through controlling the dynamics of solution-state polymer aggregates. *Angew. Chem. Int. Ed.* **60**, 8189-8197 (2021).
- 42 Han, J. *et al.* Dichlorinated dithienylethene-based copolymers for air-stable n-type conductivity and thermoelectricity. *Adv. Funct. Mater.* **31**, 2005901 (2021).
- 43 Feng, K. *et al.* Cyano-functionalized bithiophene imide-based n-type polymer

- semiconductors: Synthesis, structure–property correlations, and thermoelectric performance. *J. Am. Chem. Soc.* **143**, 1539-1552 (2021).
- 44 Yang, C.-Y. *et al.* A high-conductivity n-type polymeric ink for printed electronics. *Nat. Commun.* **12**, 2354 (2021).
- 45 Guo, H. *et al.* Transition metal-catalysed molecular n-doping of organic semiconductors. *Nature* **599**, 67-73 (2021).