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Abstract

Poly(benzodifurandione) (PBFDO) is the benchmark n-type polymer, yet no route delivers ultrahigh conductivity, benign conditions and scalability together: high-conductivity syntheses require weeks of dimethyl sulfoxide (DMSO) dialysis, whereas dialysis-free alternatives use toxic or corrosive mediators or sacrifice performance. Elemental sulfur — abundant and non-toxic — resolves this trilemma in one metal-free pot through a non-radical polycondensation: the BFDO enol opens the S₈ ring to give a thione intermediate that undergoes aldol-type condensation with further enol, while the liberated H₂S and dimethyl sulfide n-dope the chain. Sulfur turns over in a recyclable redox cycle, so 0.1 eq. S suffices. Filtered crude serves directly as a conductive ink. Optimized PBFDO reaches 2059 S cm⁻¹ and scales to 500 mL gram-scale batches (1366 S cm⁻¹ mean); thermoelectric and organic electrochemical transistor devices deliver 245 ± 20 μW m⁻¹ K⁻² and μC* = 460 F cm⁻¹ V⁻¹ s⁻¹.

Introduction

High-performance *n*-type conjugated conductive polymers remain a long-standing bottleneck for complementary organic electronic systems^{1–5}, as their charge transport, ambient stability and scalable manufacturability consistently lag far behind *p*-type analogues. Discovered in 2022, poly(benzodifurandione) (PBFDO) has emerged as a transformative *n*-type conducting polymer that bridges this performance gap, delivering record electrical conductivities exceeding 2000 S cm⁻¹—comparable to the benchmark *p*-type analogues poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).⁶ PBFDO also shows outstanding ambient stability, retaining ~95% of its native conductivity after 35 days in air, and favorable solution processability without insulating alkyl side chains. Notably, the conductivity ceiling of this material system continues to rise: polymerization-driven spontaneous assembly has recently produced aligned PBFDO nanoribbons with metallic-level conductivity exceeding 10⁴ S cm⁻¹ along the chain direction (1800 S cm⁻¹ perpendicular to the chain direction).⁷ These superior electronic properties—most notably its ultrahigh electrical conductivity—collectively empower PBFDO to deliver cutting-edge performance across diverse device platforms, including organic thermoelectric (OTE) modules with power factors (PF) > 300 μW m⁻¹ K⁻²,^{8,9} organic electrochemical transistors (OECTs) with normalized transconductance ($g_{m, \text{norm}}$) above 200 S cm⁻¹,^{10–13} and lithium–organic batteries achieving 255 Wh kg⁻¹ in 2.5 Ah pouch cells.¹⁴ These merits make PBFDO a promising candidate for wearable electronics, bioelectronic interfaces and next-generation printed circuitry.^{15,16}

Despite these advantages, translational progress toward practical PBFDO devices is hindered by synthetic limitations rather than by intrinsic material performance. All established workflows impose a three-way trade-off between ultrahigh conductivity, benign reaction conditions, and scalable, straightforward purification, forcing a compromise on at least one metric. Early high-conductivity protocols using tetramethylquinone (TMQ)⁶ or copper acetate¹⁷ mediators reach conductivities approaching 2000 S cm⁻¹ (Fig. 1a), but require weeks of exhaustive dialysis in dimethyl sulfoxide

(DMSO) and massive solvent consumption, restricting synthesis to milligram lab-scale batches at prohibitive cost. Alternative catalytic strategies rely on toxic or corrosive additives—selenium dioxide (SeO_2)¹⁸, molybdenum trioxide (MoO_3)¹⁹ and acetic anhydride (Ac_2O)²⁰—raising major safety and environmental concerns for scale-up. Greener metal-free routes using α -tocopherylquinone (α -TQ) enable aqueous polymerization without toxic catalysts or dialysis, yet suffer drastic conductivity losses, forfeiting PBFDO's defining characteristic.^{21,22} Thus every existing route falls into an intractable trilemma: none simultaneously satisfies all three industrial requirements—ultrahigh conductivity, non-toxic mild media, and scalable production with minimal post-processing—and at best only two can be realized at once.

Herein, we report a metal-free, elemental sulfur (S_8)-mediated one-pot oxidative polycondensation that resolves this trilemma (**Fig. 1b**). Distinct from all previously reported radical-mediated routes to PBFDO^{6,17,20}, our protocol proceeds via an unprecedented non-radical aldol-type polycondensation centered on a key thione intermediate **A**. Earth-abundant, non-toxic sulfur²³ acts as a dual-function mediator: it drives oxidative C=C coupling of BFDO monomers along this non-radical pathway, while simultaneously generating in situ *n*-type dopants (hydrogen sulfide, H_2S ; dimethyl sulfide, DMS) via redox cycling. The crude ink requires only simple filtration to remove macroscopic aggregates, eliminating time-consuming DMSO dialysis. Under optimized conditions PBFDO reaches a peak conductivity of 2059 S cm^{-1} , matching the literature benchmarks, and retains a mean conductivity of 1366 S cm^{-1} upon direct scale-up to 500 mL gram-scale batches; the scaled ink keeps 92% of its conductivity after 60 days in air. This sustainable, scalable paradigm avoids toxic metal catalysts, corrosive additives and multi-day purification, establishing a manufacturable route to high-performance *n*-type conjugated polymers and unlocking PBFDO's potential for industrial organic electronics.

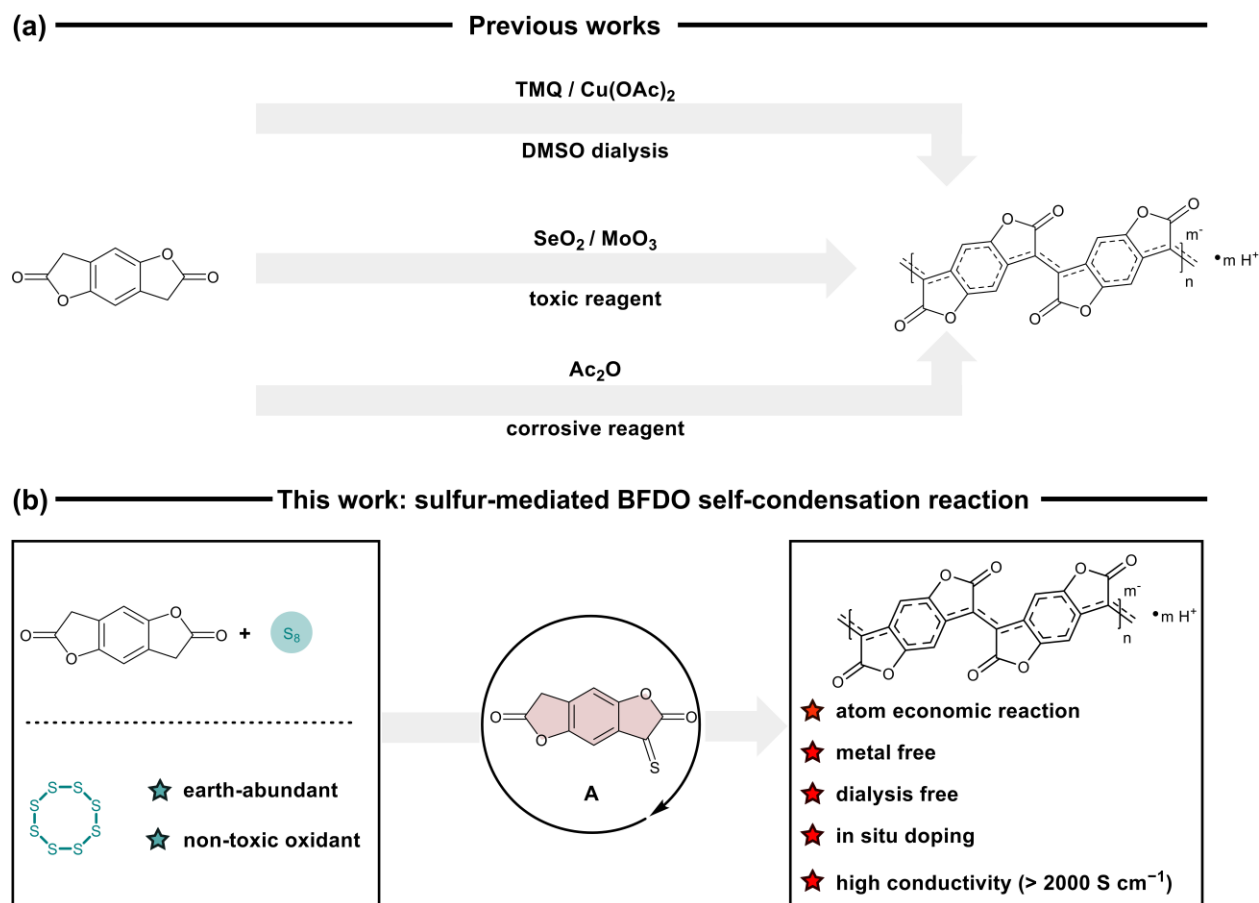


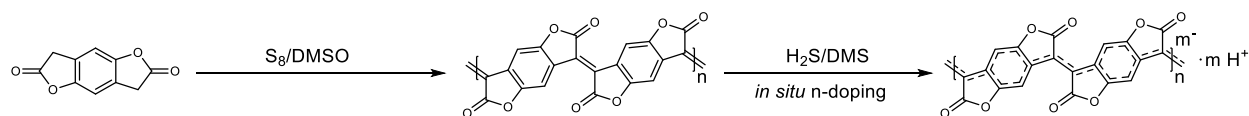
Fig. 1 | **Overview of synthetic strategies for poly(benzodifurandione) (PBFDO).** (a) Limitations of previously reported PBFDO synthetic protocols: high-conductivity routes demand prolonged DMSO dialysis, while dialysis-free alternatives rely on toxic/corrosive additives or suffer severely suppressed electrical conductivity. (b) This work: metal-free elemental sulfur (S₈)-mediated one-pot self-condensation of BFDO monomers. Earth-abundant, non-toxic S₈ acts as both oxidant and precursor for in situ *n*-type dopants. The procedure avoids dialysis and toxic catalysts, directly producing high-conductivity PBFDO with maximum conductivity exceeding 2000 S cm⁻¹.

Results and Discussion

S₈-Mediated PBFDO Polymerization

Molecules with reactive benzylic C–H bonds are known to be oxidatively coupled by S₈ in the presence of organic bases, forming dimers via C=C bonds at benzylic methylene sites²⁴; a representative case is the 1,4-diazabicyclo[2.2.2]octane (DABCO)/S₈-mediated condensation of 2-oxoindole in DMSO to isoindigo²⁵. Inspired by these sulfur-promoted C=C forming reactions, we hypothesized that BFDO monomers could undergo analogous oxidative polycondensation to afford PBFDO. Prior work demonstrates that amines enable this coupling by deprotonating substrates. We therefore screened a library of organic amine catalysts—DABCO, pyridine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (Et₃N), 4-dimethylaminopyridine (DMAP), quinuclidine and diisopropylamine (DIPA)—for the S₈-mediated polymerization of BFDO, with a base-free reaction as control (**Supplementary Table 1**). All reactions used 1 eq. S (as S₈) and 10 mg mL⁻¹ BFDO in DMSO at 100 °C for 6 h, with 0.1 eq. amine added to the catalyst-containing reactions. Ultraviolet–visible–near-infrared (UV–Vis–NIR) spectra of the crude mixtures (**Supplementary Fig. 1**) showed the near-infrared polaron and bipolaron bands (1200 to 1600 nm) diagnostic of PBFDO²⁶, and conductivities for every condition are summarized in **Supplementary Table 1**. Notably, the base-free system, in which oxidation was driven solely by S₈, delivered the highest conductivity of 1305 S cm⁻¹.

To rationalize this result, benzofuranone (BFO) was used as a simplified model substrate for oxidative condensation dimerization assays. Two parallel controls were run under identical conditions: one with elemental sulfur alone, the other with added DABCO as an exogenous base. The results showed that DABCO accelerated the kinetics but also promoted isomerization of the primary dimer (*E*)-2H,2'H-[3,3'-bibenzofuranylidene]-2,2'-dione (BFD, isoxindigo) to chromeno[4,3-c]chromene-5,11-dione (CCD, dibenzonaphthyrone) (**Supplementary Table 2**), whose conjugated backbone is known to impair charge transport along the chain²⁷. We therefore infer that catalytic bases speed monomer conversion but generate CCD defects that embed in the PBFDO backbone, lowering the bulk conductivity.

Table 1 | Optimization of elemental sulfur-mediated polymerization conditions for PBFDO.

Entry	S_8 (eq. S)	Monomer concentration (mg mL ⁻¹)	Time (h) ^[a]	Temperature (°C)	Appearance	Monomer conversion (%) ^[b]	Conductivity (S cm ⁻¹) ^[c]
1	1	5	15	100	solution	> 99	1600 ± 251
2	1	5	5	120	solution	> 99	2059 ± 166
3	1	5	2	150	solution	> 99	403 ± 4
4	1	10	5	120	gel	> 99	2108 ± 211
5	0.1	10	12	120	gel	75.6	1333 ± 213
6	2	10	3	120	gel	87.7	1772 ± 174
7	0.1	5	25	120	solution	> 99	1663 ± 233
8	2	5	5	120	solution	> 99	1379 ± 124

^[a] Reaction time recorded at the onset of gelation or full monomer conversion, whichever occurs first. ^[b] Monomer conversion calculated from ¹H NMR integral analysis. ^[c] Conductivity measured using four-probe electrodes with a width/length aspect ratio (W/L) of 1000 μm / 200 μm; filtration removes only macroscopic aggregates and insoluble impurities. Values are mean ± standard deviation (SD) from at least three independent measurements (n ≥ 3).

Given the superior conductivity of the base-free system and the mechanistic insights above, we optimized the sulfur-only protocol (**Table 1**). We first varied reaction temperature at a fixed monomer loading of 5 mg mL⁻¹ with 1 eq. S (**Table 1, entries 1–3**). ¹H NMR tracking (**Supplementary Figs. 2–5**) revealed a marked acceleration with temperature: full conversion (>99%) required 15 h at 100 °C, 5 h at 120 °C and only 2 h at 150 °C. The polymer synthesized at 120 °C exhibited the highest

conductivity, reaching 2059 S cm⁻¹. Raising the concentration to 10 mg mL⁻¹ induced gelation within 5 h (**Table 1, entry 4; Supplementary Fig. 6**); despite gelation, its conductivity rose further to 2108 S cm⁻¹, exceeding the 5 mg mL⁻¹ system.

Since **entry 4** gave the highest conductivity, we next varied the sulfur loading at a fixed monomer loading of 10 mg mL⁻¹ (**Table 1, entries 5–6; Supplementary Figs. 7–8**). Even a catalytic 0.1 eq. S and a stoichiometric excess of 2 eq. S both gave conductivities above 1300 S cm⁻¹ at the 10 mg mL⁻¹ screening scale, although both conditions led to gelation; with 2 eq. S gelation occurred after only 3 h, restricting chain growth and leaving the conversion incomplete. Notably, efficient polymerization proceeds with only a catalytic 0.1 eq. S (**Table 1, entries 5, 7**)—far below stoichiometric—indicating that sulfur operates in a recyclable redox cycle, which we dissect in the following mechanistic section.

Although the 10 mg mL⁻¹ condition (**Table 1, entry 4**) gave the highest conductivity (2108 S cm⁻¹), spontaneous gelation yields a non-flowable mixture incompatible with solution-based device fabrication. After screening different S loadings (0.1, 1 and 2 eq. S) at 5 mg mL⁻¹ (**Table 1, entries 2, 7 and 8; Supplementary Figs. 3, 9 and 10**), we set the optimal parameters as 5 mg mL⁻¹ monomer, 1 eq. S and 120 °C, affording PBFDO with a peak conductivity of 2059 S cm⁻¹ and full conversion after 5 h. Crucially, this optimized protocol requires no dialysis or post-synthetic purification: the crude reaction mixture is simply filtered through a 0.22 µm PTFE syringe filter to afford a ready-to-use conductive ink, in contrast to the weeks of DMSO dialysis demanded by conventional high-conductivity routes.^{6, 17} A proton resonance at 2.01 ppm (¹H NMR, **Supplementary Fig. 12**), assigned to DMS—a reduced byproduct of DMSO—confirms DMSO's participation in the reaction²⁸. Elemental analysis gave a residual sulfur content of 3.01 wt% in the isolated solids (**Supplementary Table 3**), and X-ray photoelectron spectroscopy (XPS) showed this sulfur to be predominantly zero-valent elemental sulfur, with a minor S=O contribution from residual DMSO (**Supplementary Fig. 13**)²⁹. These results suggest that this residual sulfur is most likely present as submicron nanoparticles encapsulated within PBFDO

aggregates, which would render them inaccessible to removal by simple filtration. Even so, the polymer retains excellent electrical performance.

Based on the above experimental evidence supporting sulfur's recyclable catalytic cycle, we systematically characterized key reactive intermediates to decipher the underlying polymerization pathway. Upon mixing elemental sulfur with BFO in DMSO, the solution slowly turned intensely blue at room temperature (**Supplementary Fig. 14**), a signature of the trisulfur radical anion ($S_3^{\bullet-}$)³⁰, with a diagnostic UV–Vis–NIR band at 595 nm³¹ that vanished completely on heating (**Supplementary Fig. 15**). The $S_3^{\bullet-}$ radical anion thus acts only as a spectator species generated during S_8 ring opening and electron transfer, and does not participate in chain growth, consistent with the negligible effect of radical scavengers described below. Adding the radical scavengers 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and N-tert-butyl- α -phenylnitrone (PBN) caused negligible perturbation of the polymerization (**Supplementary Figs. 16–18**). Together these results establish a non-radical route; radical scavengers severely suppress or even terminate polymerization in all previously reported radical-mediated PBFDO synthetic routes^{6,17,20}.

To further probe the sulfur redox cycle and capture intermediates, we performed complementary characterization. Bubbling the reaction off-gas into aqueous silver nitrate ($AgNO_3$) solution produced a black precipitate, confirming H_2S evolution (**Supplementary Fig. 19**), and DMS was identified by gas chromatography–mass spectrometry (GC-MS) (**Supplementary Fig. 20**), consistent with the 2.01 ppm resonance in the crude ^1H NMR (Supplementary Fig. 12). The in situ H_2S and DMS act as reducing agents that spontaneously n-dope PBFDO and are then re-oxidized to regenerate sulfur and DMSO, respectively. High-resolution mass spectrometry (HR-MS) tracking of the BFO model reaction with S_8 directly detected the C=S thione and C=O carbonyl intermediates (**Supplementary Fig. 21**), and the thione was further corroborated chemically: adding 2.0 eq. 2,3-dimethyl-1,3-butadiene to the same BFO dimerization intercepted the transient C=S species as the thio-Diels–Alder cycloadduct in 75% yield (**Supplementary Figs. 22–25**). Since BFO is a simplified model substrate for the BFO

coupling, these experiments give direct evidence for the thione intermediate in the model system and indirect support for the same thione-mediated pathway operating during polycondensation.

From these characterizations and literature precedents^{19,25,32,33}, we propose the pathways in **Fig. 2**. The enol tautomer of BFDO opens cyclic S₈ to furnish the pivotal thione intermediate **A**. Given the detected H₂S and DMS, two routes are proposed. In Path A, the enol of BFDO undergoes aldol-type condensation with **A**, extruding H₂S to give the conjugated dimer. In Path B, the oxygen atom of activated DMSO (a Swern/Pummerer-type process) reacts with **A**, releasing DMS^{19,33} and forming the carbonyl intermediate **B**, which then undergoes aldol condensation with the BFDO enol to give the same dimer. These dimers polycondense further by the same modes (Path A or B) to build the PBFDO backbone, while the *in situ* H₂S and DMS^{19,20} act as *n*-type dopants, yielding highly conductive PBFDO.

To further validate the mechanism, high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) of the early-stage mixture (30 min) (**Supplementary Fig. 26**) identified the BFDO monomer ([M-H]⁻ calcd. for C₁₀H₅O₄⁻, m/z 189.0193; found, 189.0200), the dimer ([M-H]⁻ calcd. for C₂₀H₇O₈⁻, m/z 375.0146; found, 375.0187) and **A** ([M-H]⁻ calcd. for C₁₀H₃O₄S⁻, m/z 218.9758; found, 218.9775). Direct observation of thione intermediate **A** confirms the core step in which the BFDO enol tautomer initiates ring-opening of cyclic S₈.

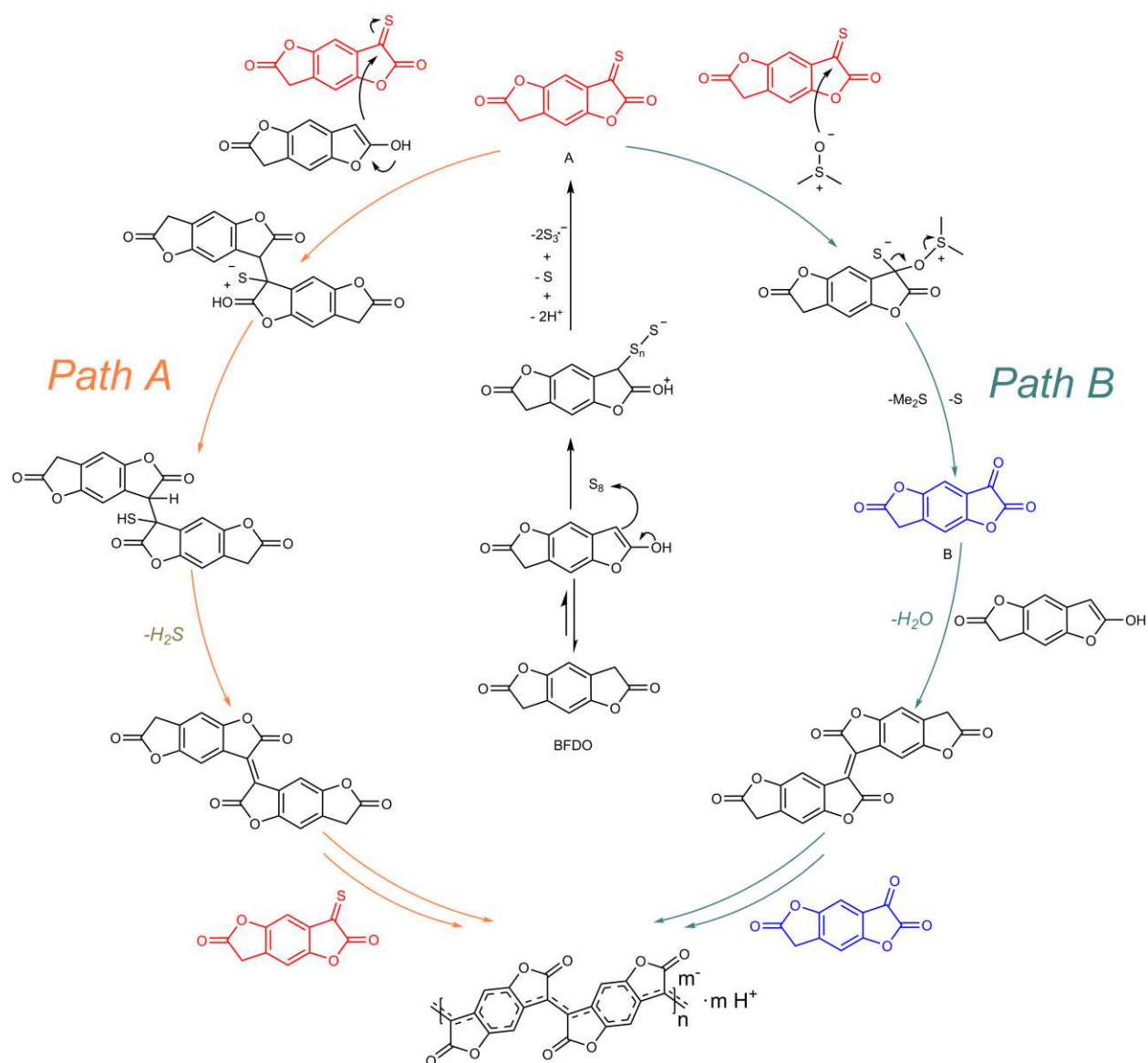


Fig. 2 | Proposed dual polycondensation pathways initiated by ring-opening of S₈ by the enol tautomer of BFDO. In situ produced H₂S and dimethyl sulfide (DMS) act as intrinsic *n*-type dopants to spontaneously dope PBFDO, while sulfur species circulate in a recyclable redox catalytic cycle to sustain polycondensation.

Polymerization Kinetics

To dissect the kinetics, we tracked the reaction in real time by ¹H NMR, dynamic light scattering (DLS) and UV–Vis–NIR spectroscopy. ¹H NMR showed that full conversion was reached within 5 h for 1 eq.

or 2 eq. S at 5 mg mL⁻¹, but much longer times with only 0.1 eq. S (**Fig. 3a–b, Supplementary Fig. 11**). Reliable DLS readings were unavailable at early times, when low-molecular-weight dimers and oligomers fall below the detection threshold (**Fig. 3c, Supplementary Figs. 27–28, Supplementary Tables 4–5**); the hydrodynamic diameter first became measurable at 4 h for the 2 eq. S system and at 5 h for the 1 eq. S system, followed by a slow increase thereafter. Notably, the 2 eq. S system consistently exhibited larger hydrodynamic diameters (85–94 nm) than the 1 eq. S system (46–69 nm), suggesting that excess sulfur accelerates nucleation and promotes aggregation of the growing polymer chains. UV–Vis–NIR spectra showed the signatures of doped PBFDO: progressive growth of the near-infrared polaron and bipolaron bands (**Fig. 3d**), directly reflecting PBFDO formation.

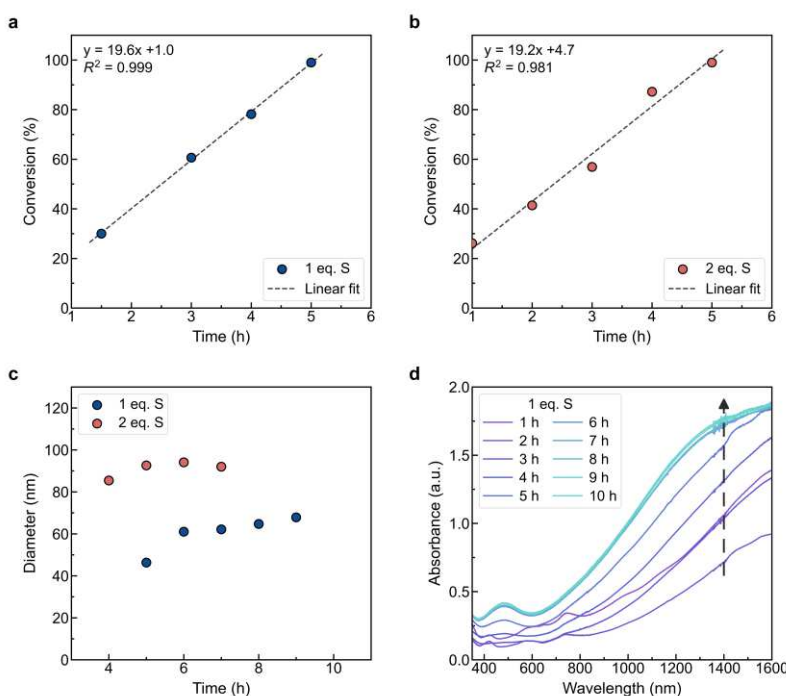


Fig. 3 | Time-resolved kinetic characterization of S₈-mediated PBFDO polymerization. (a,b) Time-dependent monomer conversion curves quantified by ¹H NMR for reactions with 1 eq. and 2 eq. S, respectively. (c) Dynamic light scattering (DLS) tracking the evolution of polymer hydrodynamic diameter over the course of polymerization. (d) Time-series UV–Vis–NIR absorption spectra of PBFDO

synthesized with 1 eq. S, recorded after 1–10 h of reaction. The dashed arrow marks the increase of the near-infrared absorption with reaction time, reflecting the progressive growth of polaron/bipolaron bands.

Structural and Electronic Characterization

Spectroscopic and electrochemical measurements further confirm the structure and electronic state of our PBFDO. Fourier-transform infrared (FTIR) shows an intense carbonyl (C=O) band at 1791 cm^{-1} and a conjugated C=C band at 1658 cm^{-1} , verifying inter-unit C=C linkages and a fully conjugated backbone (**Supplementary Fig. 29**). Cyclic voltammetry (CV) gives a lowest unoccupied molecular orbital (LUMO) of -5.05 eV with negligible drift over successive cycles, indicating robust electrochemical stability (**Supplementary Fig. 30**). Ultraviolet photoelectron spectroscopy (UPS) gives a work function of -3.01 eV , which lies above the reduction potential, confirming a heavily n-doped state (**Supplementary Fig. 31**). Thermogravimetric analysis (TGA, N_2 , $10\text{ }^\circ\text{C min}^{-1}$) shows a 5% mass loss at $295\text{ }^\circ\text{C}$, mainly from residual DMSO and partial sublimation of the trapped zero-valent sulfur in the aggregates (**Supplementary Fig. 32**).

XPS spectra of the BFDO monomer and PBFDO are summarized in **Fig. 4a–f**. Relative to the pristine monomer, PBFDO shows an emergent O 1s component at 535.35 eV and slight attenuation of the carbonyl O 1s signal at 531.43 eV . The 535.35 eV peak is assigned to proton-coordinated carbonyls, where proton binding raises the oxygen binding energy; it accounts for 42% of the total carbonyl O 1s area, corresponding to a doping density of 0.84 electrons per repeat unit. Grazing incidence wide-angle X-ray scattering (GIWAXS) was employed to characterize the microstructure of PBFDO films. The films predominantly exhibited edge-on orientation, with a pronounced lamellar (100) peak at $q_z = 0.473\text{ \AA}^{-1}$ ($d = 13.28\text{ \AA}$) and a π – π (010) peak at $q_{xy} = 1.783\text{ \AA}^{-1}$ ($d = 3.52\text{ \AA}$), indicating tight packing (**Fig. 4g,h**). Atomic force microscopy (AFM) gave a low root-mean-square roughness of 2.807 nm , demonstrating uniform film formation and excellent solution processability (**Fig. 4i**).

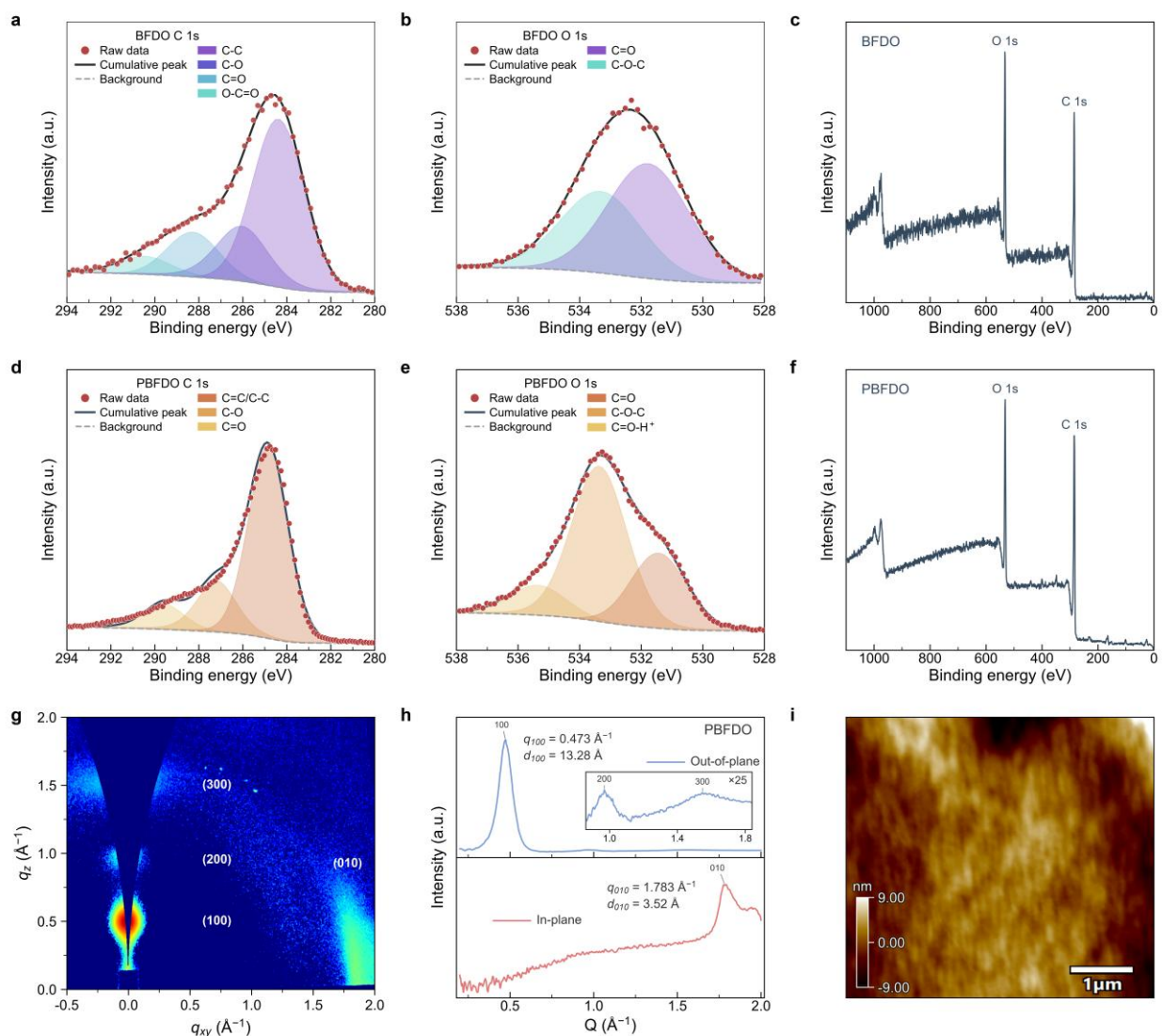


Fig. 4 | Chemical and microstructural characterizations of sulfur-synthesized PBFDO films. (a–c) X-ray photoelectron spectroscopy (XPS) spectra of pristine BFDO monomer, including C 1s and O 1s core-level signals. (d–f) Corresponding C 1s and O 1s XPS spectra of PBFDO. The new O 1s peak at 535.35 eV originates from protonated carbonyl groups, enabling quantitative calculation of *n*-doping efficiency. (g,h) Two-dimensional grazing-incidence wide-angle X-ray scattering (2D-GIWAXS) pattern of PBFDO film and corresponding in-plane/out-of-plane line-cut profiles, revealing dominant edge-on molecular stacking with tight π – π interchain packing. (i) Atomic force microscopy (AFM) height

topography of PBFDO thin film, demonstrating smooth surface morphology with low root-mean-square roughness.

Thermoelectric and OECT Performance

Given its ultrahigh conductivity and excellent electron transport, PBFDO is promising for diverse organic electronic devices^{9,13,34,35}; we therefore fabricated OTE devices and OECTs from PBFDO made by our method. For the OTE devices, the negative Seebeck coefficient confirms n-type behavior (**Fig. 5a–c**; **Supplementary Fig. 33**). PBFDO synthesized with 0.1, 1 and 2 eq. S gave Seebeck coefficients of -24.9 ± 0.2 , -34.5 ± 0.1 and -39.8 ± 0.3 $\mu\text{V K}^{-1}$, corresponding to power factors of 103 ± 14 , 245 ± 20 and 218 ± 20 $\mu\text{W m}^{-1} \text{K}^{-2}$ (**Fig. 5a**), among the highest reported for n-type thermoelectric polymers^{8,9,21}.

We next evaluated OECTs fabricated from polymers made with different S loadings (**Fig. 5d,e**; **Supplementary Figs. 34–35**; **Supplementary Table 6**). At a 0.6 V source–drain voltage, the 1 eq. S material reached a peak normalized transconductance of 248 S cm^{-1} , and a peak μC^* (μ , electron mobility; C^* , volumetric capacitance) of $460 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ —the highest of six independent devices (values outside parentheses are maxima; means are given in parentheses in **Supplementary Table 6**) and among the highest reported for n-type OECT materials (**Supplementary Fig. 36**)^{12,13}. With transient response times of 3.09/3.82 ms (**Fig. 5e**), the device showed excellent stability for small pulse amplitudes (0–0.2 V) in aqueous electrolyte, losing only ~1% after 1000 cycles (**Fig. 5e**). Spectroelectrochemistry linked doping-level changes to the electronic bands (**Fig. 5f**): after dedoping at 0.6 V, two features intensified—a high-energy band at 450–550 nm from the π – π^* transition and an extended band at 650–950 nm from intramolecular charge transfer (ICT). At –0.6 V the neutral absorption nearly vanished, indicating a fully n-doped, electron-rich state. Electrochemical impedance spectroscopy (EIS) (**Supplementary Fig. 37**) gave a volumetric capacitance (C^*) of 300 F cm^{-3} and an electron mobility (μ) of $1.53 (1.31) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, well above most reported n-type conjugated polymers owing to the highly planar backbone.

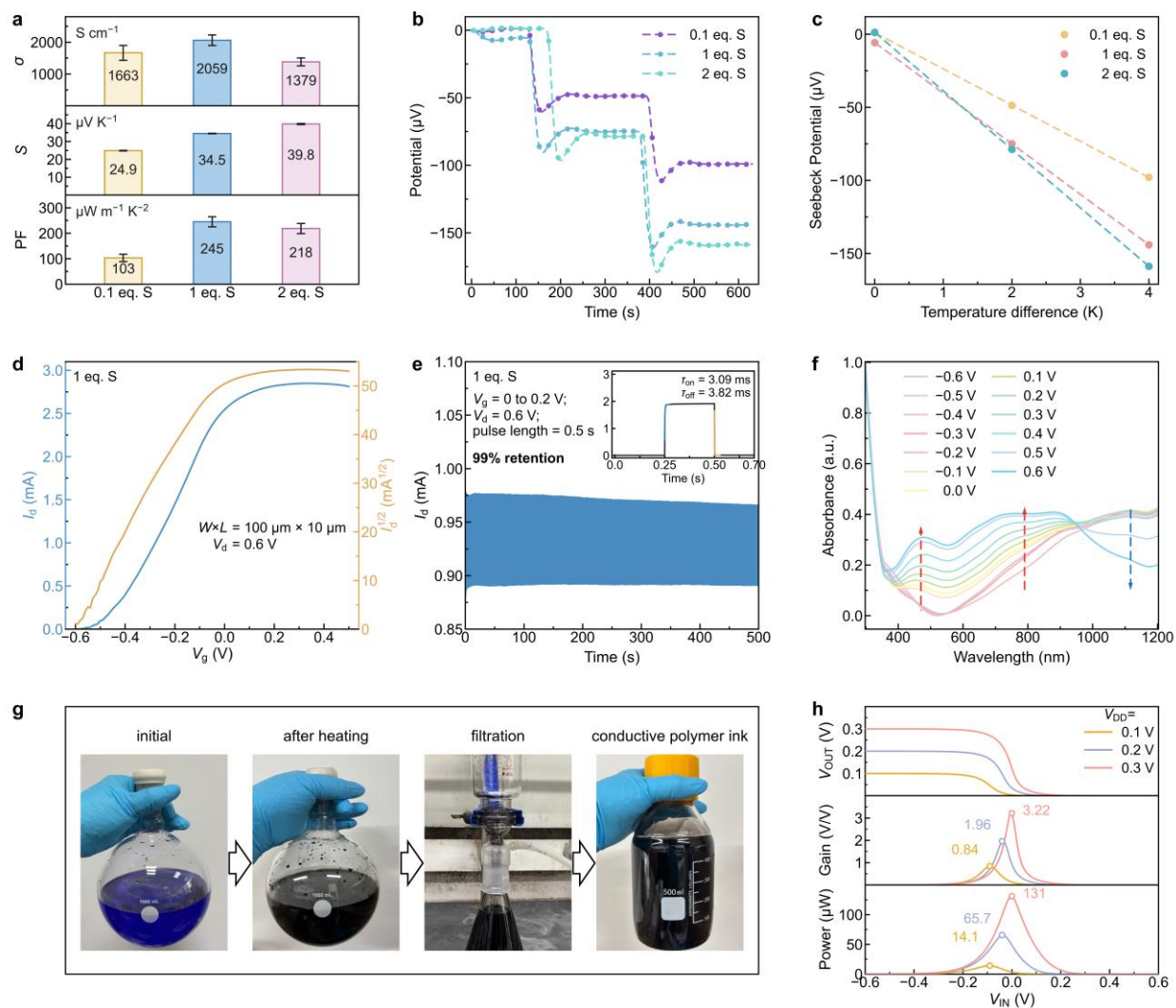


Fig. 5 | Thermoelectric and organic electrochemical transistor (OECT) performance of S_8 -synthesized PBFDO. (a) Summary of thermoelectric parameters including electrical conductivity, Seebeck coefficient and power factor for PBFDO prepared with 0.1 eq., 1 eq. and 2 eq. S. (b,c) Thermovoltage transient curve and fitting for Seebeck coefficient measurement. (d) Transfer characteristic curves of PBFDO-based OECTs ($W \times L = 100 \mu\text{m} \times 10 \mu\text{m}$; $V_d = 0.6 \text{ V}$); the right axis shows $I_d^{1/2}$, from which the threshold voltage is extracted by fitting the $I_d^{1/2}$ - V_g profile. (e) Long-term cycling stability of the OECT measured under repeated 0.5 s gate-voltage pulses in aqueous NaCl electrolyte (99% current retention after 500 s); inset, transient turn-on (τ_{on}) and turn-off (τ_{off}) responses

time. (f) Potential-dependent UV–Vis–NIR spectroelectrochemistry of PBFDO thin film, illustrating reversible n-type doping/dedoping behaviour; dashed arrows mark the potential-induced changes of the 450–550 nm π – π^* and 650–950 nm intramolecular charge-transfer bands. (g) Photographs of the 500 mL large-batch polymerization setup for sulfur-mediated PBFDO production (initial, after heating, filtration, and the final conductive polymer ink). (h) Inverter performance metrics measured at supply voltages $V_{DD} = 0.1$ V, 0.2 V and 0.3 V (key in the top-right of the panel), including voltage transfer curve, voltage gain (peaking at 3.22 V/V at $V_{DD} = 0.3$ V) and power consumption (up to 131 μ W).

Gram-Scale Synthesis and Complementary Logic Circuits

To advance practical application, we performed a 500 mL scale-up based on the optimized sulfur-mediated polymerization with 1 eq. S (**Fig. 5g**; **Supplementary Fig. 38**). The 500 mL solution reached complete monomer conversion after 7 h stirring at 120 °C, confirmed by ^1H NMR (**Supplementary Fig. 39**). The mixture was initially blue and turned black after 7 h, indicating extensive polymerization; it was then filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane to give the conductive polymer ink.

We then assessed the conductivity and stability of the 500 mL batch. Although conductivity decreased on scale-up—from 2059 ± 166 S cm^{-1} (10 mL batch) to 1366 ± 279 S cm^{-1} (500 mL batch)—the ink still performed well, retaining 92% of its conductivity (1257 ± 20 S cm^{-1}) after 60 days in air (**Supplementary Fig. 40**). The scaled-up PBFDO thus preserves excellent conductivity and stability, meeting the requirements of conductive polymers for electronic devices and supporting its feasibility for large-scale production and industrial use in fields such as printed electronics.

We then paired scaled PBFDO with the p-type polymer P(g42T-TT) to build a p–n complementary inverter (**Supplementary Fig. 41**). Transfer curves of P(g42T-TT) and PBFDO in 0.1 M NaCl were recorded (**Supplementary Fig. 42**), and the inverter’s switching response is shown in Fig. 5h. At a supply voltage (V_{DD}) of 0.3 V it delivered a voltage gain of 3.22 V/V and a power consumption of 131

μW . The peak gain near $V_{\text{in}} = 0\text{ V}$ means a small offset suffices to record biological signals, reducing power draw³⁶, suggesting PBFDO can enable high-performance complementary logic circuits.

Conclusion

In summary, we present a green one-pot synthesis of the *n*-type conducting polymer PBFDO that exploits the dual role of S_8 as both oxidant and in situ *n*-dopant. Mechanistic studies identified the thione intermediate—formed when the BFDO enol opens the S_8 ring—as the crucial species enabling aldol-type condensation and oxidative polymerization, while in situ H_2S and DMS dope PBFDO. The strategy avoids toxic catalysts and cumbersome post-purification such as dialysis. The resulting PBFDO reaches conductivities up to 2059 S cm^{-1} under the optimized, solution-processable conditions and retains high performance ($1366 \pm 279\text{ S cm}^{-1}$) and ambient stability even at the 500 mL scale. In devices, PBFDO OTEs reach a power factor of $245 \pm 20\text{ }\mu\text{W m}^{-1}\text{ K}^{-2}$ and OECTs a high μC^* of $460\text{ F cm}^{-1}\text{ V}^{-1}\text{ s}^{-1}$ with excellent operational stability. This protocol markedly improves the efficiency, sustainability and scalability of PBFDO synthesis, laying a foundation for its industrial application in organic electronics.

Methods

Polymerization Procedures

General procedure for PBFDO polymerization. BFDO monomer ($5\text{--}10\text{ mg mL}^{-1}$) and sulfur ($0.1\text{--}2\text{ eq. S}$) were first dissolved in DMSO under nitrogen atmosphere. Sulfur loadings are expressed as equivalents of sulfur atoms (eq. S) relative to BFDO, irrespective of speciation; because elemental sulfur is supplied as the S_8 ring, 1 eq. S corresponds to 0.125 eq. of S_8 molecules (8.4 mg of S_8 per 50 mg of BFDO). The resulting mixture was then heated to $100\text{--}150\text{ }^\circ\text{C}$ and stirred for several hours until gelation occurred or the monomer was fully converted, as confirmed by $^1\text{H NMR}$. After cooling to room temperature, the solution was filtered through a $0.22\text{ }\mu\text{m}$ polytetrafluoroethylene (PTFE) filter. This step removed only aggregates and insoluble impurities, and

no dialysis was required. The electrical conductivity of the polymer solution was measured by the four-probe method. The polymerization conditions and conductivity results are summarized in **Table 1**.

Detailed experimental example: Under nitrogen, BFDO (50 mg, 0.26 mmol, 1 eq.) and S₈ (8.4 mg, 0.26 mmol S, 1 eq. S) were dissolved in 10 mL DMSO (5 mg mL⁻¹). The mixture was heated to 120 °C for 5 h, gradually turning from light blue to dark black. After cooling to room temperature, the mixture was filtered through a 0.22 µm PTFE syringe filter to afford the PBFDO ink.

Substrate and Film Preparation

Substrate and film preparation. Glass and silicon substrates were cleaned by sequential ultrasonication in deionized water, acetone, and isopropanol for 5 min each, followed by 1 min of plasma treatment. The polymer solution was then drop-cast onto the substrate, preheated at 60 °C for 5 min, spin-coated at 2000 rpm, and dried under nitrogen to remove residual solvent.

Thermoelectric Measurements

The conductivity was measured using the four-probe method on a Keithley 4200 SCS semiconductor analyzer. The aspect ratio (W/L) of the four parallel electrodes is 1000 µm/200 µm. The Seebeck coefficient (S) was determined through the equation , where ΔV_{therm} represents the thermoelectric voltage between the hot and cold junctions under a temperature gradient of ΔT . ΔT was varied over 5–20 K, and S was obtained from the slope of ΔV_{therm} versus ΔT (linear fit, $R^2 > 0.99$); the reported uncertainty is the standard deviation of two parallel runs on independently prepared films ($n = 2$). The thermoelectric voltage ΔV_{therm} was collected via the Keithley 4200 SCS system. The power factor and its uncertainty were propagated from the standard deviations of σ and S via $\delta PF/PF = \sqrt{(2\delta S/S)^2 + (\delta\sigma/\sigma)^2}$. The power factor (PF) is calculated using the formula $S = \frac{\Delta V_{therm}}{\Delta T} PF = \sigma S^2$

OECT Fabrication and Characterization

The OECT device with a W/L ratio of $100\text{ }\mu\text{m}/10\text{ }\mu\text{m}$ was fabricated through photolithography, vapor deposition of gold, parylene sacrificial layer deposition, etching, and spin-coating of channel material. The PBFDO solution was first applied as a droplet onto the substrate and preheated at $60\text{ }^{\circ}\text{C}$ for 5 minutes. Subsequently, spin-coating was performed at 2000 rpm onto the substrate, followed by drying in nitrogen at $60\text{ }^{\circ}\text{C}$ to form the channel. After completing the exfoliation of the second sacrificial parylene layer, measurements were conducted. OECT performance characterization was performed using the FSA Pro semiconductor analyzer. All measurements were carried out in air with 0.1 M sodium chloride solution as the electrolyte and an Ag/AgCl electrode as the gate electrode. The μC^* product was extracted using the equation (where W , L , and d represent the width, length, and depth of the organic channel, and V_{th} is the threshold voltage). The film thickness was determined in the dry state using a DEKTAK profiler (Bruker).

$$g_m = \frac{\partial I_D}{\partial V_G} = \frac{Wd}{L} \times \mu C^* \times (V_G - V_{Th})$$

Supplementary Information

Supplementary Information is available for this paper, including detailed synthetic procedures, additional spectroscopic and structural characterization, and supplementary device data (Supplementary Figs. 1–42 and Supplementary Tables 1–6).

Data availability

All data supporting the findings of this study are available within the paper and its Supplementary Information. Further data are available from the corresponding authors upon reasonable request.

Competing interests

The authors declare no competing interests.

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y. L.: investigation and writing – original draft; J. L., X. W., T. D., S. W., X. L., S. C., F. Y., R. Z., R. D., J.-T. L., S. T., M. S.: analysis and supervision; L. F., Y. M., Q. J., and Z.-H. G.: conceptualization, supervision, funding acquisition and writing – review & editing.

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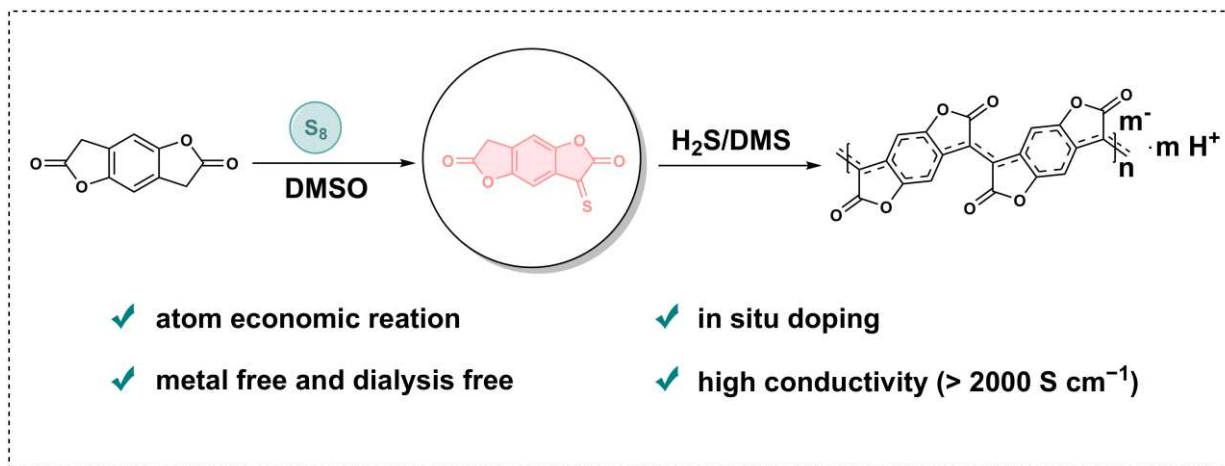
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