

Supporting Information

A pyridine-capped quaterthiophene as an alternative to PEDOT:PSS, processable from organic solvents and without acidity, for more stable electronic devices

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Materials and Methods.

4,7-Dibromo-2,1,3-benzothiadiazole (1) was purchased from Sigma-Aldrich. n-BuLi used in the reactions was titrated against diphenylacetic acid before use in reactions. The palladium tetrakis catalyst (tetrakis(triphenylphosphane)palladium(0)) used in the Stille coupling reaction was synthesised in-house before being used in synthesis. It had the appearance of a yellow, crystalline solid when produced.

Electrochemical Measurements.

Cyclic Voltammetry (CV): Cyclic voltammetry measurements were performed on a CH Instruments 660E Electrochemical workstation at a scan rate of 0.1 V/s. A blank cell was performed as an initial and final cleaning step before measuring. Three electrodes were used in these experiments:

1. Working electrode (WE): gold/ platinum (Au/Pt) disk or indium tin oxide (ITO) glass.
2. Counter electrode (CE): platinum (Pt) wire.
3. Reference electrode (RE): silver (Ag) wire.

Tetrabutylammonium hexafluorophosphate (TBAPF₆) (Sigma Aldrich) was used as an electrolyte (0.1 M) in dry DCM or acetonitrile. Solvents were obtained from an in-house solvent purification system. All glassware was cleaned, rinsed with DCM and dried at 120 °C in an oven overnight prior to use. The experiment was performed under Ar gas flow. Each value is corrected to the redox potential of ferrocene (Fc/Fc⁺).

Spectroelectrochemistry Measurements: Cyclic voltammetry and UV-Vis were linked together in this experiment by placing the electrodes in the cuvette in electrolyte solution using dry solvent acetonitrile/DCM for the formed thin film on the ITO glass electrode.

Bulk Electrolysis: Bulk electrolysis with three-party experiments were performed on a CH Instruments 660E Electrochemical workstation using a three-part cell, a large surface area gauze platinum working electrode, a silver wire reference electrode, and an isolated coiled platinum counter electrode in a glass tube with a porous frit at the bottom.

Column chromatography was performed with commercially available solvents, using silica gel Zeoprep 60 Hyd (40-63 μm mesh). Commercial TLC plates (Silica gel 60 F254) were used for thin-layer chromatography. Visualisation was performed by ultra-violet light and/or iodine vapour.

Mass Spectrometry: The mass spectrometry utilises Jeol M-STATION and Bruker microTOF-Q Mass Spectrometers to produce quality Low- and High-Resolution spectra using the electrospray (ESI) technique.

Spectroscopic Measurements

UV-Vis-NIR Spectroscopy: UV-Vis and transmittance spectra were recorded using a Shimadzu UV-2600 Spectrophotometer in the range 200-1200 nm, using a 1 cm path length quartz cell. Solution state measurements were performed using dry solvent. The measurements of the films were performed using an ITO glass electrode covered with a thin film of the dimer and placed in a cuvette in acetonitrile.

NMR Spectroscopy: NMR analysis was conducted on both a Bruker AVIII 500MHz and a Bruker AVIII 400MHz NMR Spectrometer.

IR Spectroscopy: Infra-red spectroscopy was carried out using a JASCO FTIR-4100 spectrometer with attenuated total reflectance.

Thermal Analysis

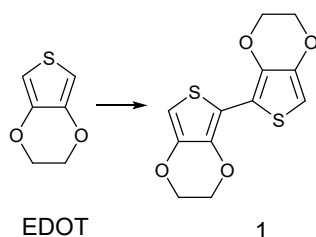
Thermal analysis was measured using a TGA instrument and DSC Polyma Differential Scanning Calorimeter and are uncorrected.

Melting points were obtained on a Cole-Parmer Stuart SMP50 automatic melting point apparatus.

Elemental Analysis was conducted on an Exeter CE-440 Elemental Analyser.

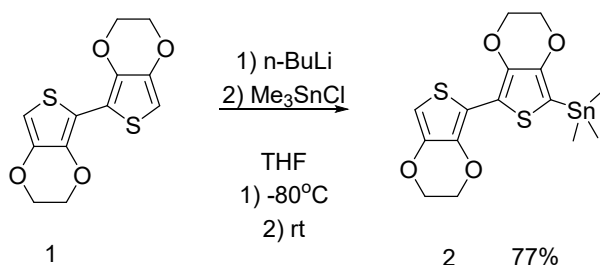
Synthesis of BEDOTPy

2,2'-Bi(3,4-ethylenedioxythiophene) (**1**)



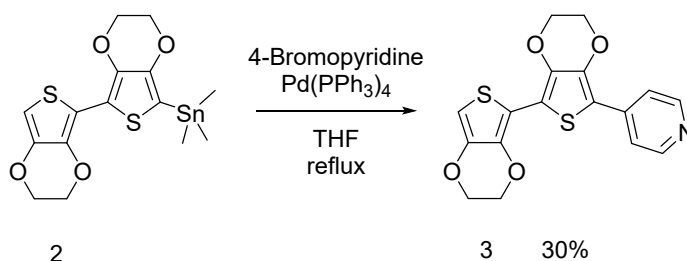
2,2'-Bi(3,4-ethylenedioxythiophene) (**1**) was prepared following a modified literature procedure.¹⁻⁷ 3,4-Ethylenedioxythiophene (EDOT) (10.13 g, 71 mmol, 1.0 eq) was dissolved in dry tetrahydrofuran (THF) (120 ml) under an ar atmosphere. n-Butyllithium (n-BuLi) solution (2.3 M in hexanes, 33 ml, 1.05 eq) was added dropwise and under stirring, cooled to -80 °C and the solution was left stirring for one hour, over which the temperature of the reaction mixture rose to -10 °C. The reaction vessel was cooled in a salt ice bath and anhydrous copper (II) chloride (9.27 g, 0.69 mmol, 0.95 eq) was added quickly, causing a temperature rise to around 40 °C, before the reaction was left for sixteen hours stirring at room temperature. Deionised water was added to quench the reaction and the reaction mixture was decanted and filtered over celite to remove the cuprous precipitate. The celite was washed and the filtrate extracted, both with dichloromethane (DCM), and the organic phases were combined, dried with sodium sulfate, filtered over cotton wool, and evaporated to yield a wet, greenish residue. Trituration in hexane for twenty-four hours yielded (**1**) (6.16 g, 61%) as a greenish brown powder. ¹HNMR (500 MHz, CDCl₃): 4.28 (m, 8H), 6.27 (s, 2H).

5-Trimethylstannyl-2,2'-bi(3,4-ethylenedioxythiophene) (**2**)



2,2'-bi(3,4-ethylenedioxythiophene) (**1**) (3.82 g, 13.5 mmol, 1.0 eq) was dissolved in dry THF (100 ml) under an argon atmosphere. n-BuLi (2.5 M in hexanes, 5.5 ml, 1.05 eq) was added dropwise at -80 °C and under stirring and afterwards, cooling was removed. The reaction was left to stir until it returned to room temperature and trimethyltin chloride solution (1 M in THF, 16 ml, 16 mmol, 1.2 eq) was added slowly. The reaction mixture was left to stir for sixteen hours, then deionised water was added to the reaction mixture, which was then extracted with DCM before being dried over sodium sulfate, filtered, and concentrated to a dark brown gum. (5.20 g). Due to the toxicity and instability of organotin complexes, this material was used in subsequent synthesis without further purification. ¹H NMR analysis confirmed that 70%-80% conversion from (**1**) to (**2**) occurred.

4-(2,2'-Bi(3,4-ethylenedioxythiophene)-5-yl)pyridine (**3**)



Bromopyridine hydrochloride (3.42 g, 16.9 mmol, 1.5 eq) was dissolved in deionised water. Potassium carbonate (2.45 g, 17 mmol, 1.5 eq) was dissolved in deionised water and mixed with the bromopyridine hydrochloride solution, before the resulting solution was extracted with toluene. The organic phases from the extraction were combined, dried over sodium sulfate, and concentrated in volume to around 10 ml (concentration beyond this initiated decomposition of the bromopyridine). 5-Trimethylstannyl-2,2'-bi(3,4-ethylenedioxythiophene) (**2**) (5.02 g, 11.3 mmol, 1.0 eq) was dissolved in dry THF (50 ml) under an argon atmosphere, and the bromopyridine solution was added. The reaction mixture was degassed for one hour via bubbling of argon and palladium tetrakis (1 g, 0.95 mmol, 0.1 eq) was added. After a final 30 minutes of bubbling argon the reaction was refluxed for forty-eight hours before being left to return to room temperature. The reaction mixture was decanted into sodium hydrogen carbonate solution and extracted with DCM and the organic phases were collected, dried over sodium sulfate, and evaporated to an orange-brown residue. Purification via column chromatography (83% ethyl acetate, 14% toluene, 3% triethylamine) yielded BEDOTPy (**3**) as a yellow powder (1.28 g, 30%). Melting Point: decomposes 184-186 °C; ¹H NMR (CDCl₃, δ_H 500 MHz): 4.33 (4H, m), 4.40 (4H, s), 6.35 (1H, s), 7.59 (2H, d, J = 1.57 Hz), 8.51 (2H, d, J = 1.58 Hz). IR (ATR) ν_{max}/cm⁻¹: 3358 (br), 2981, 2939, 2871, 2361, 2341, 1589, 1556, 1530, 1504; HRMS

calc. for $[M(C_{17}H_{13}NO_4S_2)+H]^+$ 360.0356, found 360.0368. CHN elemental analysis: found: C, 57.39; H, 3.59; N, 3.81%. Calc. for $C_{17}H_{13}NO_4S_2$: C, 56.81; H, 3.65; N, 3.90%

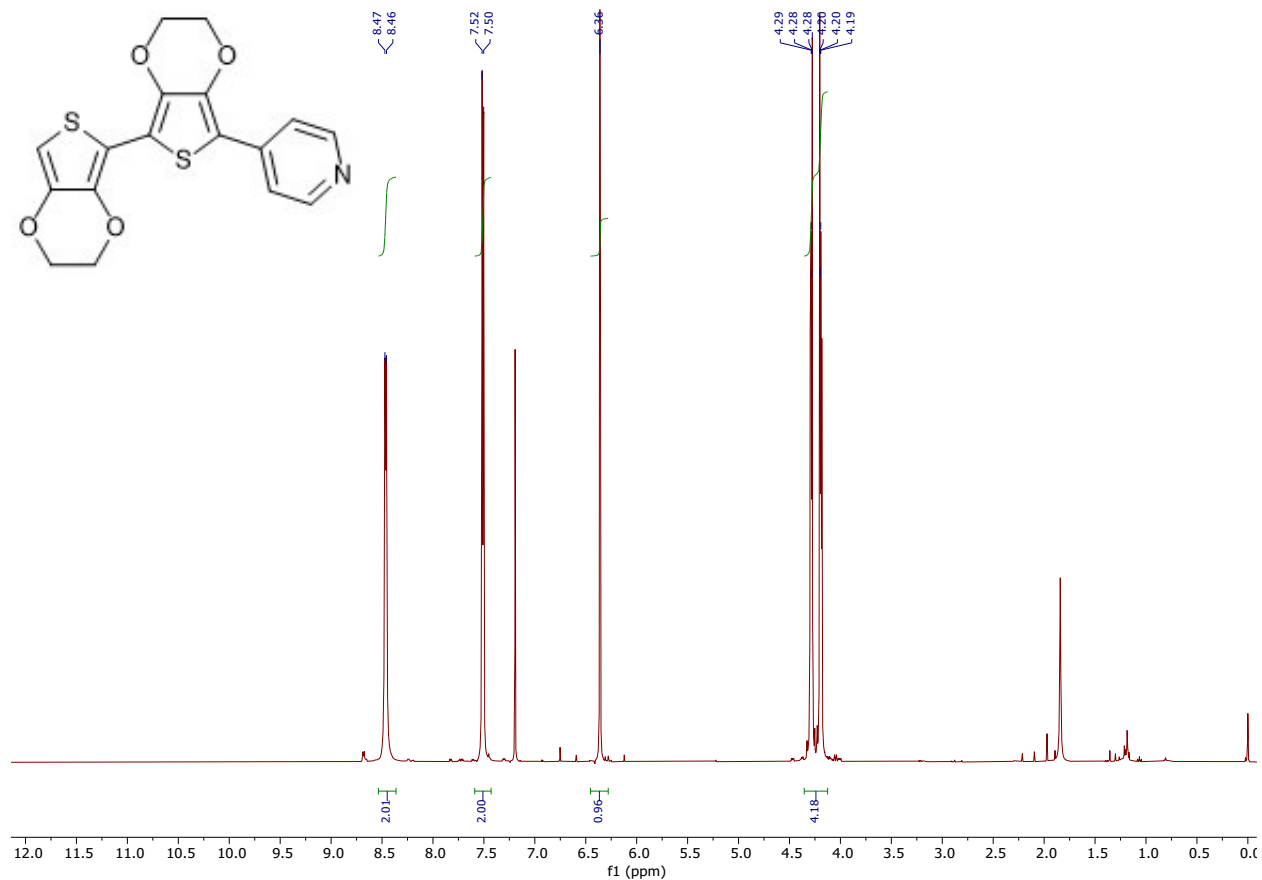
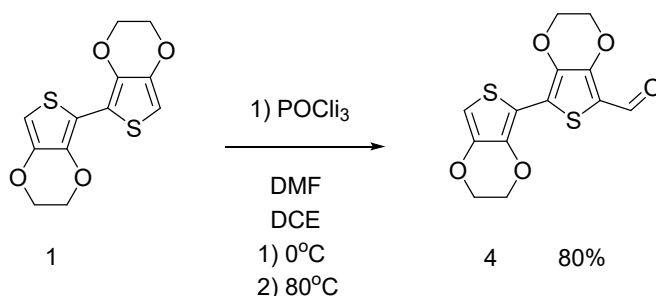


Fig. S1 ¹H NMR spectrum of BEDOTPy.

Synthesis of End-Capped BEDOTPy

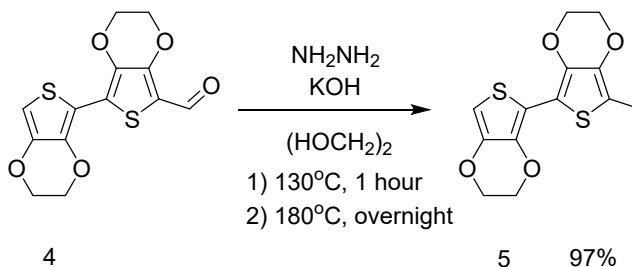
Synthesis of the methyl Me-BEDOTPy was achieved by first attaching an aldehyde to BEDOT (**4**), using phosphorus oxychloride and DMF via the Vilsmeier-Haack reaction. Then converting the aldehyde to a methyl group (**5**) using hydrazine with potassium hydroxide, via the Wolff-Kishner reduction method. 4-Iodopyridine was then used in a direct arylation, to yield the capped monomer unit (**6**).

2,2'-Bi(3,4-ethylenedioxythiophene)-5-carbaldehyde (**4**)



2,2'-Bi(3,4-ethylenedioxythiophene)-5-carbaldehyde (**4**) was prepared following a modified literature procedure.¹ To a solution of (**1**) (1.0 g, 3.54 mmol) and anhydrous dimethylformamide (DMF) (0.29 mL, 3.71 mmol) in anhydrous 1,2-dichloroethane (freshly distilled) (45 mL) was added phosphorus oxychloride (POCl₃) (freshly distilled) (0.35 mL, 3.71 mmol) dropwise at 0 °C under an ar atmosphere, and the mixture was refluxed for 18 h at 80 °C. After being cooled to room temperature, the mixture was poured into an aqueous solution of sodium acetate (1 M, 150 mL) and then stirred for 2 h. The organic phase was separated by decantation and the aqueous phase was extracted with DCM. The combined organic phases were dried over magnesium sulfate (MgSO₄) and evaporated in vacuum. A purification by filtration through a basic alumina gave a yellow solid (**4**) (1.3 g, 80% yield).

5-Methyl-2,2'-bi(3,4-ethylenedioxythiophene) (**5**)



To avoid any possible contamination from non-functionalised (**1**), we have conveniently prepared Me-BEDOT (**5**) by a Wolff-Kishner reduction of BEDOTCHO following the procedure of the reduction of isovanillin.⁸ To 2,2'-bi(3,4-ethylenedioxythiophene)-5-carbaldehyde (**4**) (0.5 g, 1.61 mmol) in ethylene glycol (45 mL) were added potassium hydroxide (KOH) (0.9 g, 16.11 mmol) and hydrazine hydrate (0.25 mL, 8.06 mmol). The reaction mixture was heated at 130 °C for 1 h, then at 180 °C for overnight. The solution was cooled to room temperature, then poured into water. The organic layer was extracted with diethyl ether. The organic extract was dried over MgSO₄ and evaporated to give (**5**) (465 mg, 97%) as a brown solid that was purified using a silica column DCM-Hexane 1:2, providing an off-white solid with mp 164-166 °C. HRMS calc. for [M(C₁₃H₁₂O₄S₂)+H]⁺ 297.0250, found 297.0252. ¹H NMR (CDCl₃, δH, 400 MHz),

6.23 (1H, s), 4.35-4.16 (8H, m), 2.25 (3H, s). ^{13}C NMR (CDCl_3 , δC , 100 MHz), 141.39, 137.54, 137.16, 136.54, 110.71, 110.22, 105.51, 97.01, 65.17, 65.11, 64.76, 64.70, 10.86.

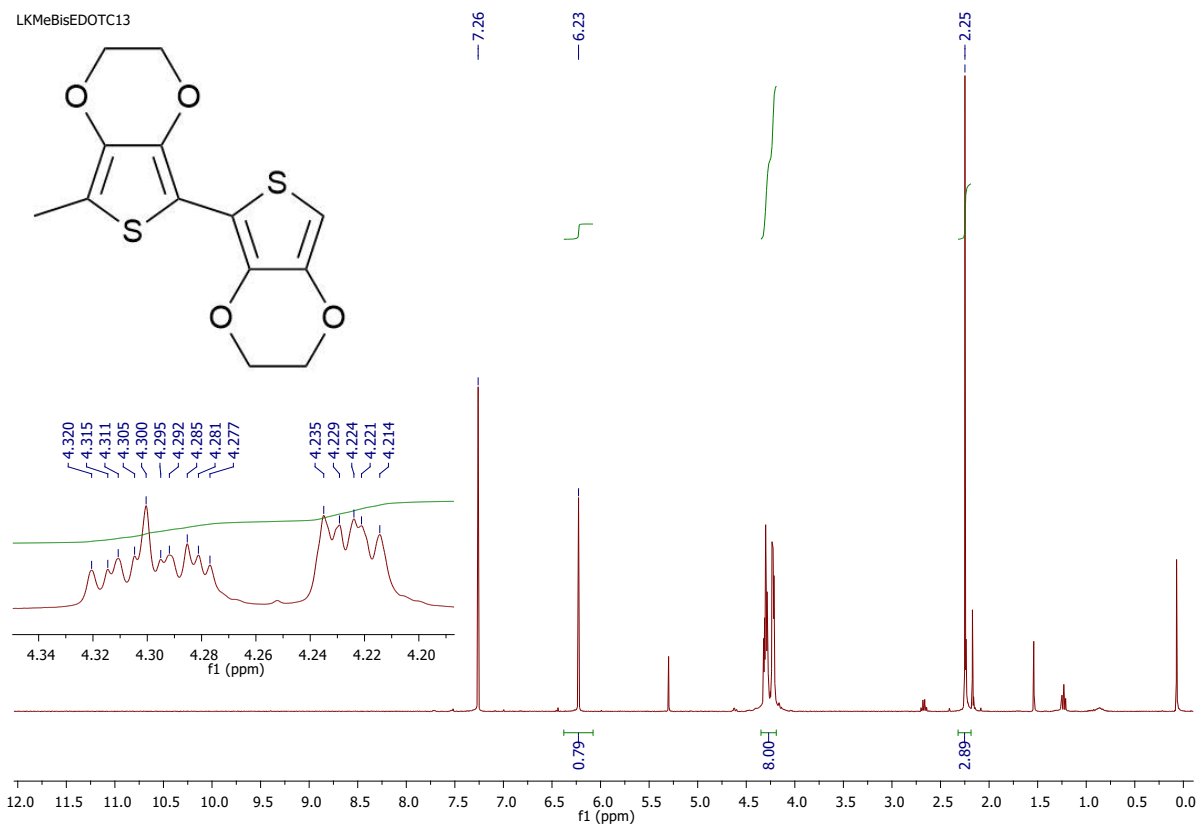


Fig. S2 ^1H NMR spectrum of Me-BEDOT.

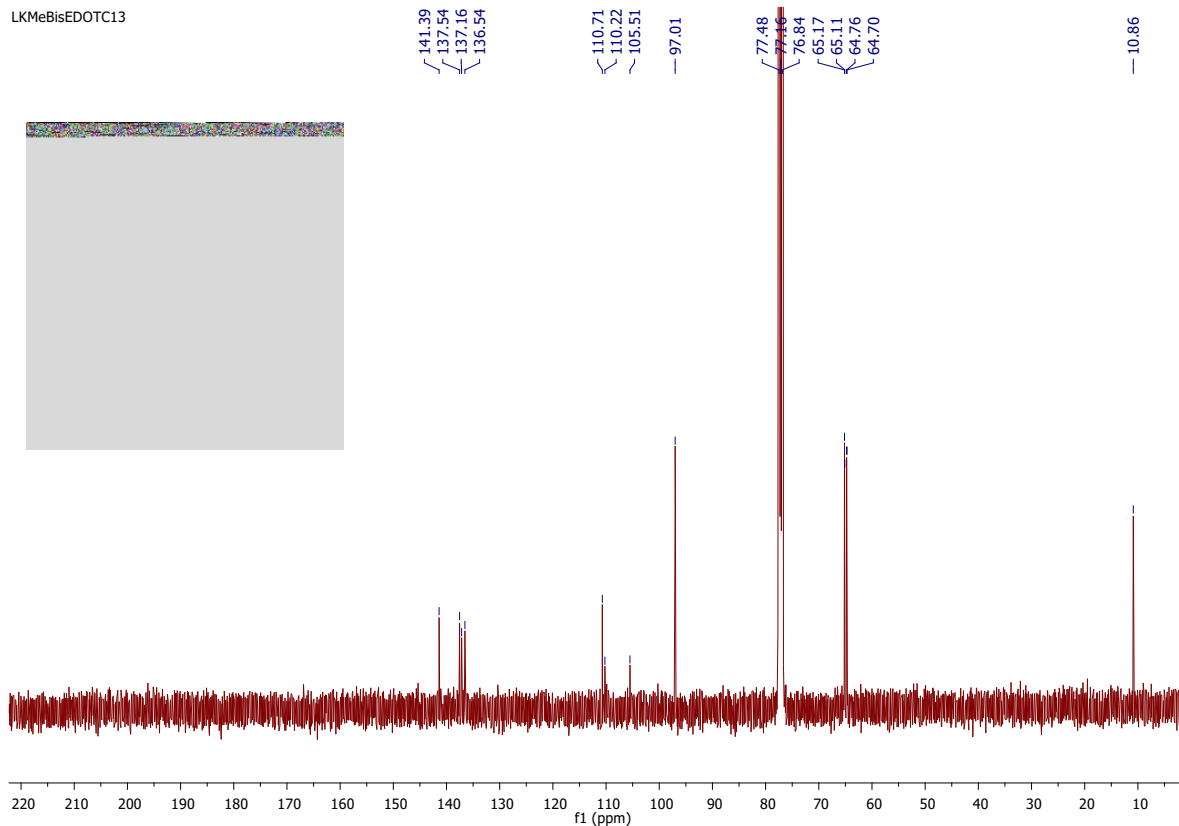
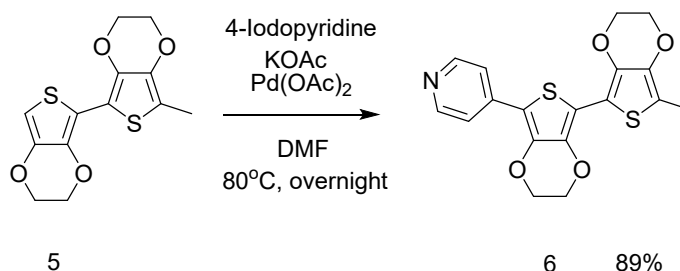


Fig. S3 ^{13}C NMR spectrum of Me-BEDOT.

4-[5-Methyl-2,2'-bi(3,4-ethylenedioxythiophene)-5'-yl]pyridine (Me-BEDOTPy, 6)



4-[5-Methyl-2,2'-bi(3,4-ethylenedioxythiophene)-5'-yl]pyridine was obtained by procedure similar to that described in the literature.⁹ To a solution of 5-Methyl-2,2'-bi(3,4-ethylenedioxythiophene) (**5**) (100 mg, 0.34 mmol) in DMF (10 mL), 4-iodopyridine (30 mg, 0.34 mmol), potassium acetate (43 mg, 1.09 mmol) and palladium acetate (3.3 mg, 0.04 mmol) were added successively. The mixture was stirred at 80 °C overnight.⁹ After cooling to room temperature, the reaction mixture was poured into water. The brown residue was filtered and washed with water. The product was purified by graduated chromatography on basic alumina (eluent: CH₂Cl₂, CH₂Cl₂-Ethyl Acetate, Ethyl Acetate). Evaporation of solvents gave 45 mg, 89% yield with mp 196-198°C. HRMS calc for [M(C₁₈H₁₅NO₄S₂)+H]⁺ 374.0515, found 374.0523. ¹H NMR

(CDCl₃, δH, 400 MHz), 8.49 (2H, br), 7.58 (2H, d, ³J = 6 Hz), 4.43-4.32 (6H, m), 4.29-4.22 (2H, m), 2.27 (3H, s). ¹³C NMR (CDCl₃, δC, 100 MHz), 149.90, 141.03, 140.75, 138.09, 137.69, 136.69, 119.42, 112.48, 111.88, 110.90, 105.19, 65.35, 65.10, 64.83, 64.68, 10.99.

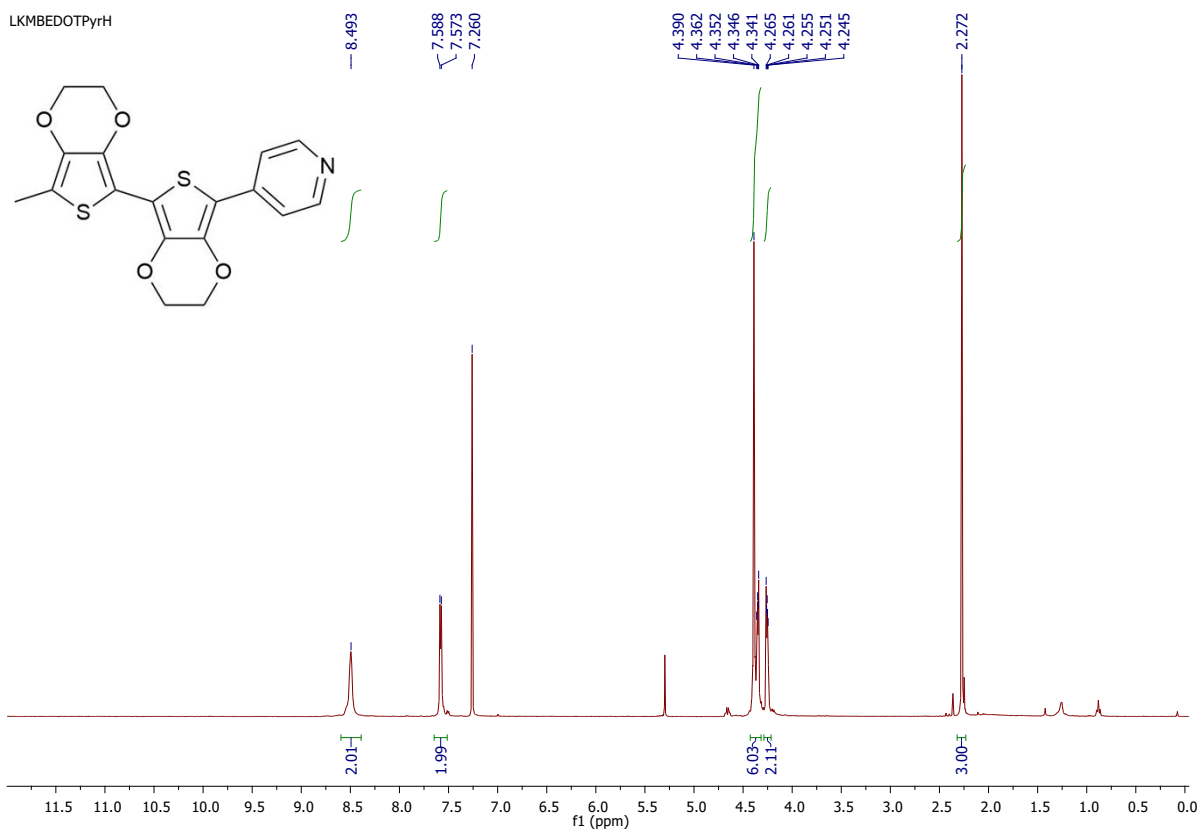


Fig. S4 ¹H NMR spectrum of Me-BEDOTPy.

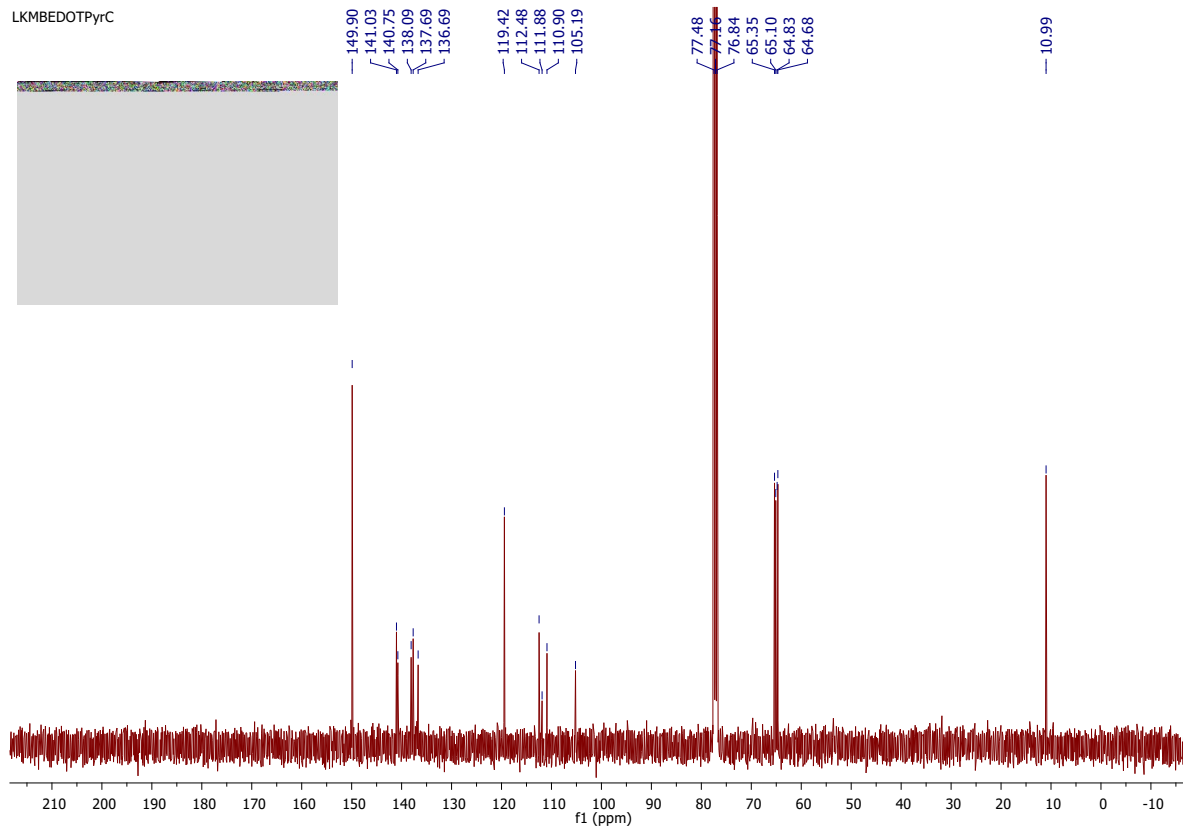
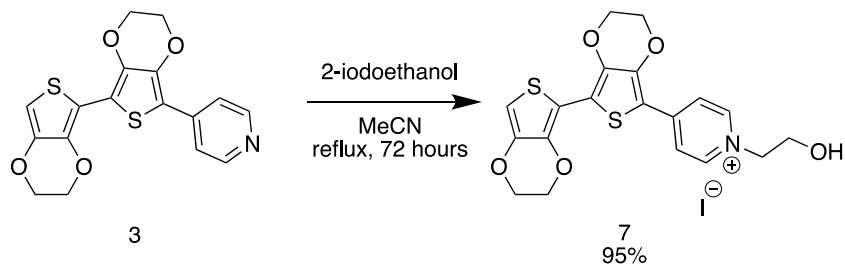


Fig. S5 ^{13}C NMR spectrum of Me-BEDOTPy.

BEDOTPy-EtOH-I, **7**



BEDOTPy (0.1 g, 0.278 mmol) was added to a flask which was evacuated and flushed with Ar ($\times 3$). Anhydrous acetonitrile (30 mL) and 2-iodoethanol (0.5 mL) were added and the reaction mixture was stirred at reflux for 72 hours. The reaction mixture was then concentrated and cooled to room temperature. Ice-cold diethyl ether (100 mL) was added causing precipitation. The solid was washed further with diethyl ether (250 mL) and dried in a vacuum desiccator, giving the desired product as a dark red solid. Yield = 140 mg (95%); m.p. 215-216 $^{\circ}\text{C}$ (dec); δ_{H} (DMSO- d_6 , 400.13 MHz) 8.67 (2H, d, $J = 8.0$ Hz), 8.11 (2H, d, $J = 8.0$ Hz), 6.88 (1H, s), 5.23-5.20 (1H, m), 4.60-4.58 (2H, m), 4.52-4.43 (6H, m), 4.31-4.29 (2H, m), 3.84-3.80 (2H, m); δ_{C} (DMSO- d_6 , 100.61 MHz) 146.6, 145.8, 144.1, 141.2, 139.8, 137.4, 120.1, 107.6, 107.3, 102.3, 65.8, 65.6, 64.7, 64.3, 61.5, 60.1; IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3300 (br), 2945, 2867, 2367, 1630,

1559, 1508; m/z (MALDI-TOF) 404.08; HRMS: found [M-I] +, 404.0609; $C_{19}H_{18}INO_5S_2$ requires [M-I] +, 404.0621

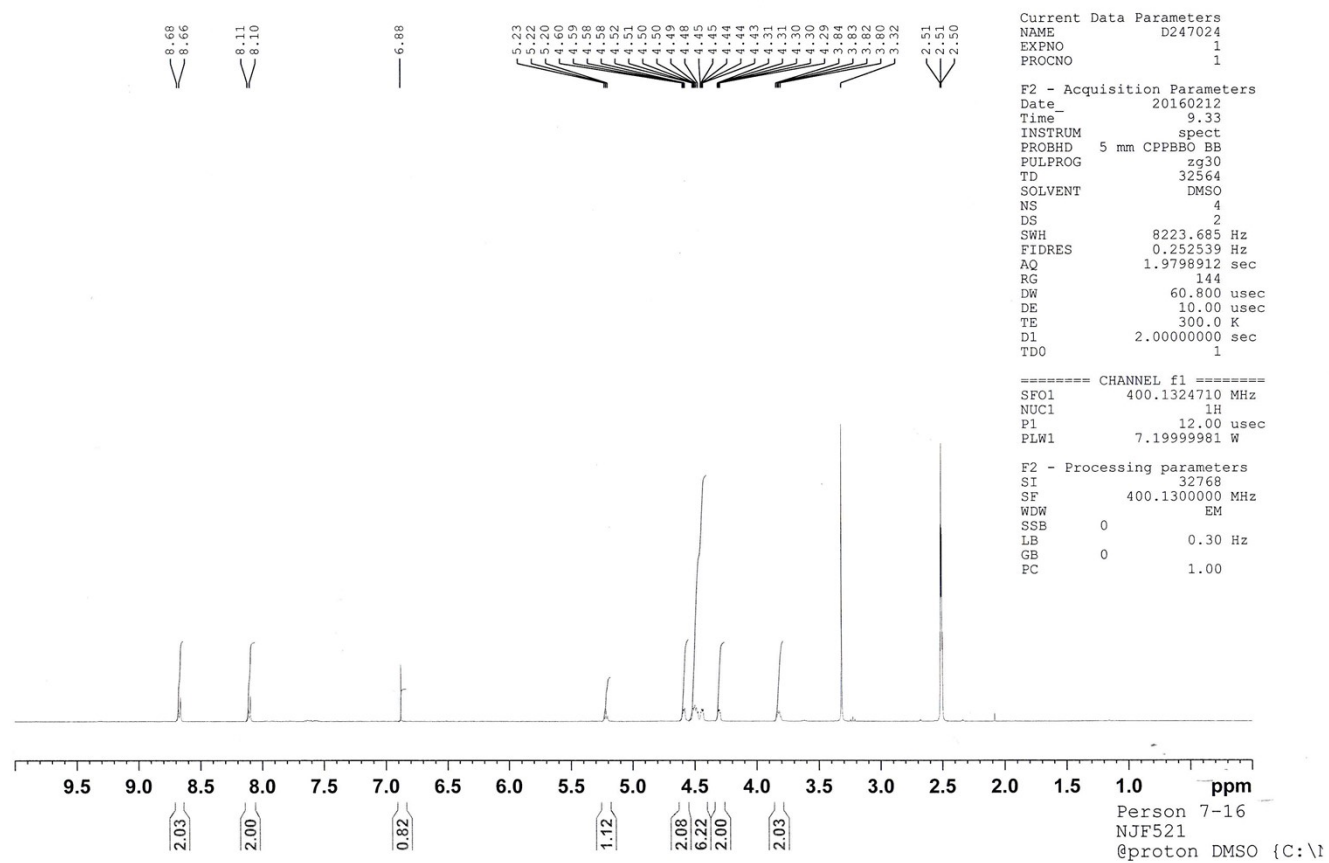


Fig. S6. 1H NMR spectrum of BEDOTPy-EtOH-I

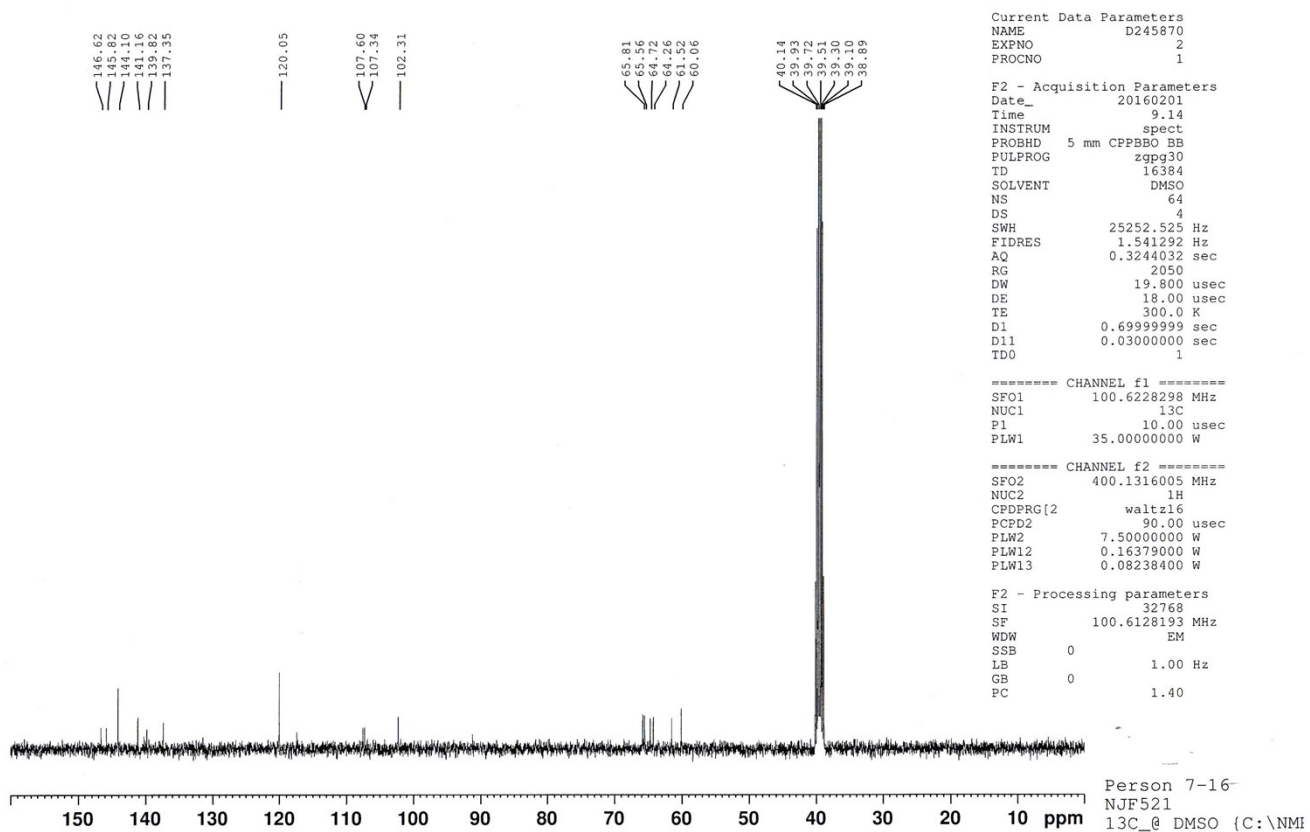


Fig. S7. ^{13}C NMR spectrum of BEDOTPy-EtOH-I

Electrochemical Study of Me-BEDOTPy

The electrodimersation was performed twice: i) over the first oxidation peak only (between -2.8 V and 0.47 V for 100 cycles) (**Fig. S8**). The resulted CV waves were stable with a slight increase in current by increasing the number of cycles without generating any new peaks and therefore no film was observed on the bottom of the working electrode. ii) Electrodimersation was also tested over the whole oxidation potential window (-0.28 V to 1.3 V for 60 cycles) (**Fig. S9**). For the first 20 cycles the intensity of the first peak at 0.47 V decreased dramatically. However, the intensity of the second oxidation peak was increased by increasing the number of cycles but not in a stable way as they showed higher potential shifting. For the last 20 cycles (**Fig. S9(a)**), the second oxidation peak current also started to disappear. Additionally, the position of the peak was shifted to a higher potential by increasing the number of cycles reaching 1.3 V at the final scan. Overall, the decrease in the current of the first peak upon cycling and the lack of the emergence of a peak at lower potentials indicate that not only is there no extension in conjugation, but the most electron rich component of the molecule, the bi-EDOT unit, is being degraded. It is expected that the methyl group blocks coupling through the thiophene units between cation radical intermediates, and that is proven here, but the results also strongly indicate that there is no coupling and extension of conjugation through the pyridine rings.

After multi-cycling, an unstable light orange film was deposited on the bottom of the electrode. Cyclic voltammetry was applied in monomer free solution (**Fig. S9(b)**) showing a very low intensity oxidation peak at 1.1 V. When the film stability was tested (**Fig. S9(c)**), the oxidation peak disappeared despite the film being still stuck on the electrode surface. This film oxidation peak could be attributed to a charge transfer and ionic species forming an unstable film. The scan rate analysis show instability for the film oxidation peak by changing the scan rate from 0.01 V s^{-1} to 0.15 V s^{-1} (**Fig. S9(d)**). The anodic current showed a non linear increase whilst increasing the scan rate, **Fig. S9(e)** with a correlation coefficient $r^2=0.89$.

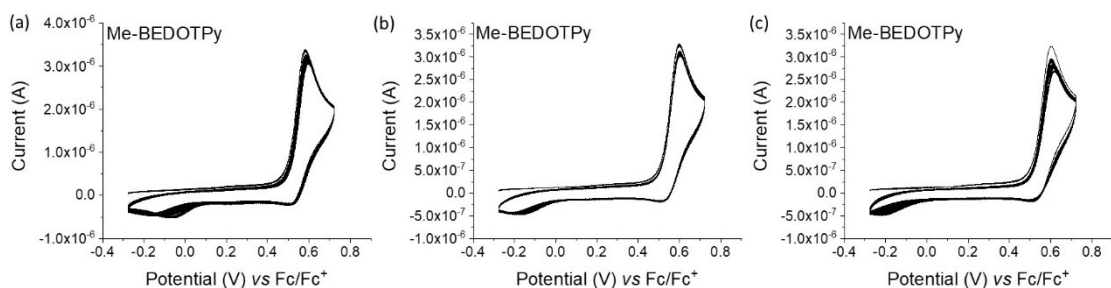


Fig. S8 Multi scan cyclic voltammetry over the first oxidation peak of the Me-BEDOTPy monomer showing (a) the first 40 scans followed by (b) 20 scans and then (c) another 40 scans. Conditions: Pt disc as working electrode, Pt wire as a counter electrode and Ag wire as a reference electrode in ca. 0.1 mM of the compound and DCM with TBAPF₆ (0.1 M) as electrolyte at a scan rate of 0.1 V/s.

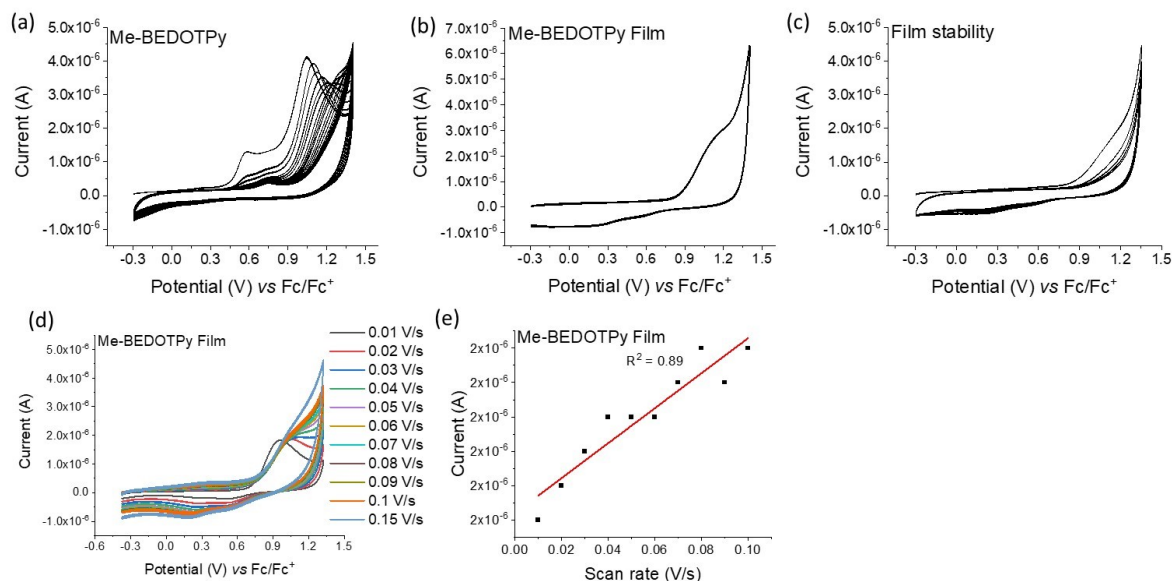


Fig. S9 Cyclic voltammograms of Me-BEDOTPy show (a) repetitive cycling (41-80 cycles) over the oxidation range of Me-BEDOTPy; (b) deposited film scan in monomer free solution; (c) repetitive cycles for the film (10 scans); (d and e) scan rate measurements for the deposited film. Conditions: Pt disk as working electrodes, Pt wire as a counter electrode and Ag wire as a reference electrode in ca. 0.1 mM of the compound in DCM with TBAPF₆ (0.1 M) as electrolyte at a scan rate of 0.1 V/s.

Electrochemical study of BEDOTPy-EtOH-I

BEDOTPy-EtOH-I monomer exhibited two reversible peroxidation peaks (shoulders) at 0.54 V and 0.68 V and a quasi-reversible main peak at 0.84 V (**Fig. S10(a)**), all referenced to half wave potential of Fc/Fc⁺. The onset potential of the monomer oxidation is 0.34 V. The monomer was electrodimersed by applying multi cycle scan (**Fig. S10(b) and (c)**) which resulted in film deposition on the working electrode surface.

The electrodeposited film of (BisEDOTPy-EtOH-I)₂ exhibited three reversible oxidation peaks referenced to half wave potential of Fc/Fc⁺ at -0.07 V, 0.39 V, 0.90 V respectively (**Fig. S10(d)**). The reduction process for the film was similar to the reduction of the BisEDOTPy film as it was bleached when applying a negative potential. Also, the scan rate experiment for the electrodeposited film of (BisEDOTPy-EtOH-I)₂ on Pt working electrode was performed. The anodic peak current showed linear increase (**Fig. S10(e) and (f)**) with a correlation coefficient ($r^2=0.999$) confirming that charge transport through the film is not diffusion limited.

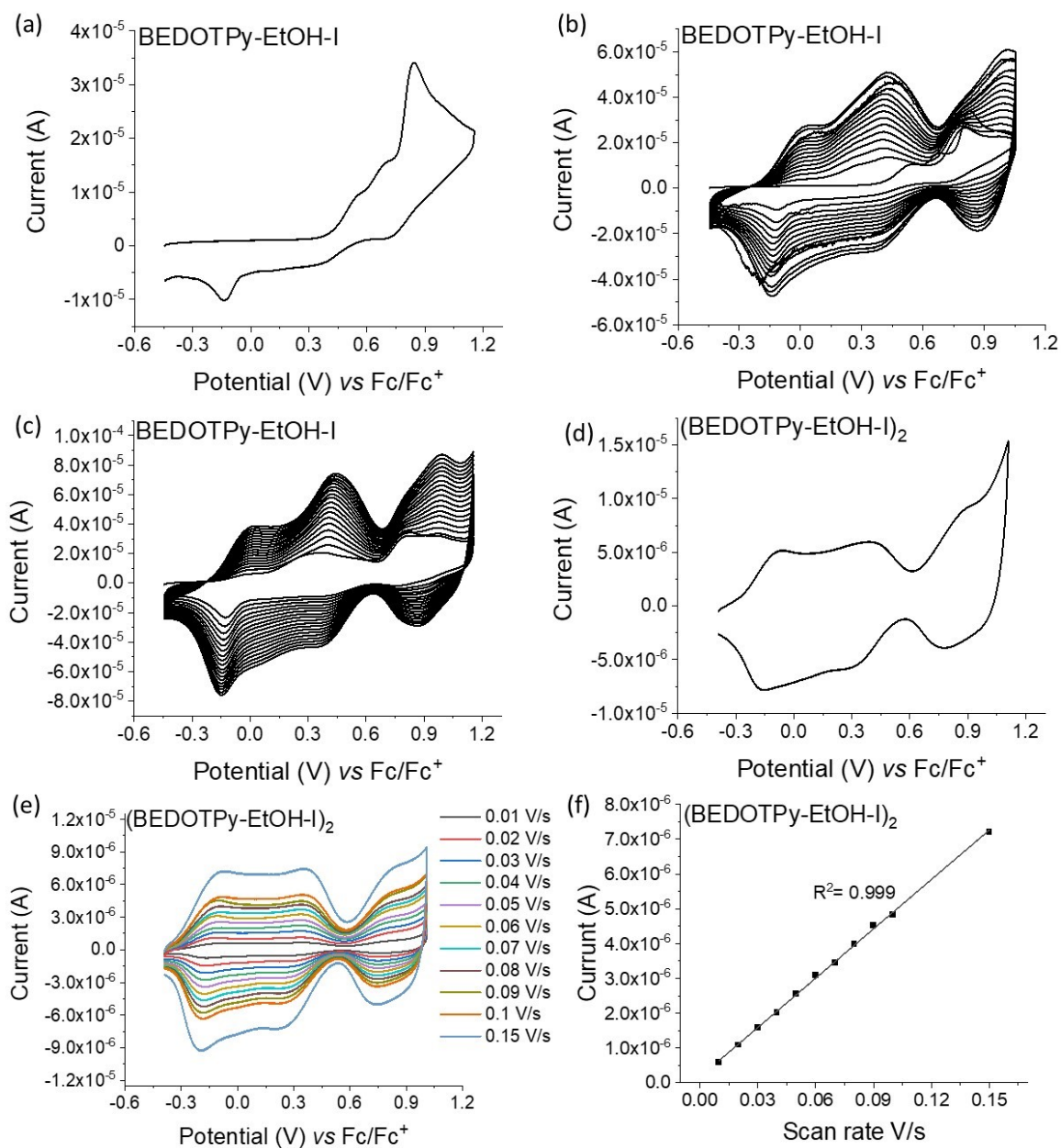


Fig. S10 Cyclic voltammograms referenced to ferrocene redox couple for (a) oxidation of the BisEDOTPy-EtOH-I; (b and c) film growth on the electrode surface (0-30 cycles) and (31-70 cycles) respectively by repetitive cycling over the oxidation potential; (d) oxidation of (BisEDOTPy-EtOH-I)₂ in monomer-free solution; (e and f) scan rate measurements for the coupled product show increasing current upon increasing the scan rate. Conditions: Pt/ITO as the working electrode, Pt wire as the counter electrode and Ag wire as the reference electrode in *ca.* 0.1 mM of the compound in dichloromethane (DCM) with TBAPF₆ (0.1 M) as the supporting electrolyte at a scan rate 0.1 V/s for a-d.

Both the monomer BEDOTPy-EtOH-I (0.03 mM solution state in DCM) and (BEDOTPy-EtOH-I)₂ (thin film deposited on an ITO glass electrode) have been characterised by UV-Vis spectroscopy. As can be seen in **Fig. S11**, BEDOTPy-EtOH-I displays maximum absorption peaks at 491 nm. The large red shifted wavelength compared to BEDOTPy is due to the stronger electron deficient nature of the pyridinium unit compared to that of pyridine. The dimer (BEDOTPy-EtOH-I)₂ exhibited a maximum absorption at 554 nm due to extension in the conjugated unit.

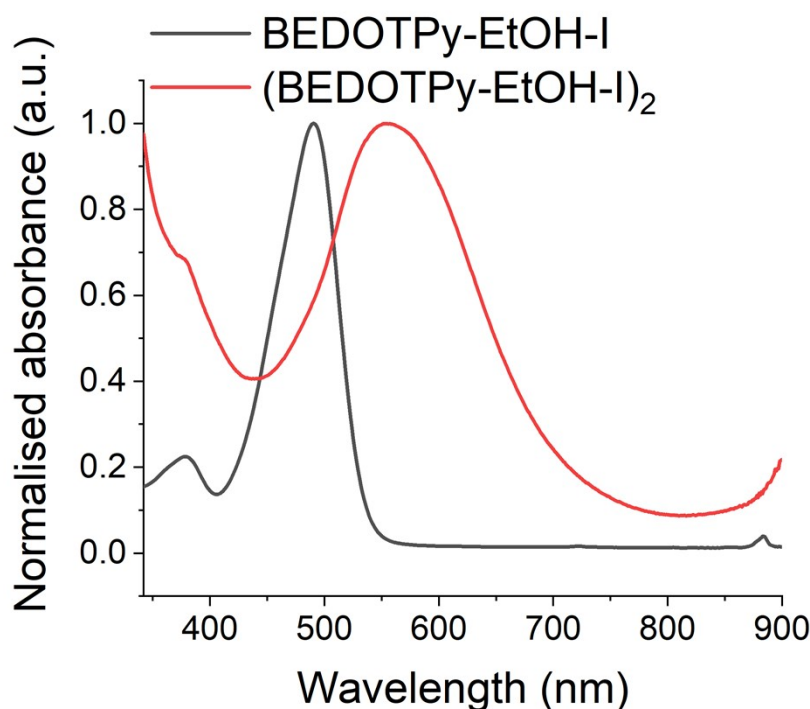


Fig. S11 UV-Vis absorption spectra show BisEDOTPy-EtOH-I (0.03 mM solution state in DCM) has its λ_{\max} at 491 nm and its corresponding dimer (BisEDOTPy-EtOH-I)₂ (solid state) λ_{\max} at 554 nm.

Bulk electrolysis and product analysis

To investigate the properties of the electrogenerated product, oxidative bulk electrolysis was performed in a monomer solution. BEDOTPy (40 mg) was dissolved in DCM (96 ml) containing TBAPF₆ as an electrolyte (3.8 g). A constant potential of 1.1 V, which covered the oxidation peak of BEDOTPy, was applied for 24 hours. The current did not decrease to zero and stayed constant at 10 A throughout the run, also at the end of the run the total charge was 1.9×10^5 C. The system was found to follow a non-Faradaic (capacitive) response as the material was taking more charge and putting lots of electrons into the system during the experiment compared to the typical Faraday response which would require 0.01 A, 21.5 C and 35.8 min. At the end of the run, some precipitate of the dication and its counter ions 2(PF₆⁻) was observed with a net weight of 78.2 mg and % yield of 69.8%. The (BEDOTPy)₂ product was de-doped chemically using hydrazine monohydrate and then purified by column chromatography. Then it was analysed by ¹H NMR (Fig. S12), electrospray (Fig. S13), and MALDI-TOF mass spectrometry (Fig. S14). The mass of the resulted product was 717.09 Da for [M(C₃₄H₂₄N₂O₈S₄)+H]⁺ which confirms the formation of the dimer and supports the ¹H NMR results. These results confirm that the formed product is a dimer.

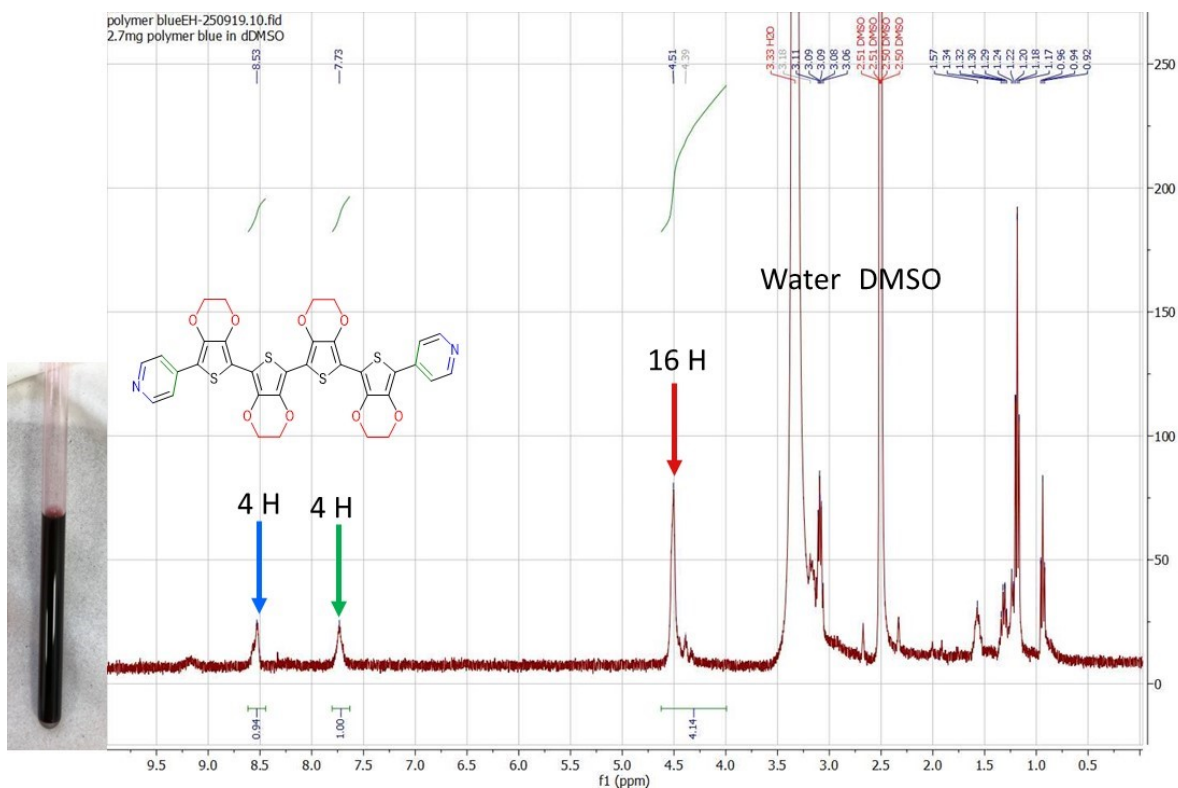


Fig. S12 ¹H NMR for electrochemically synthesised (BEDOTPy)₂ in DMSO-D₆.

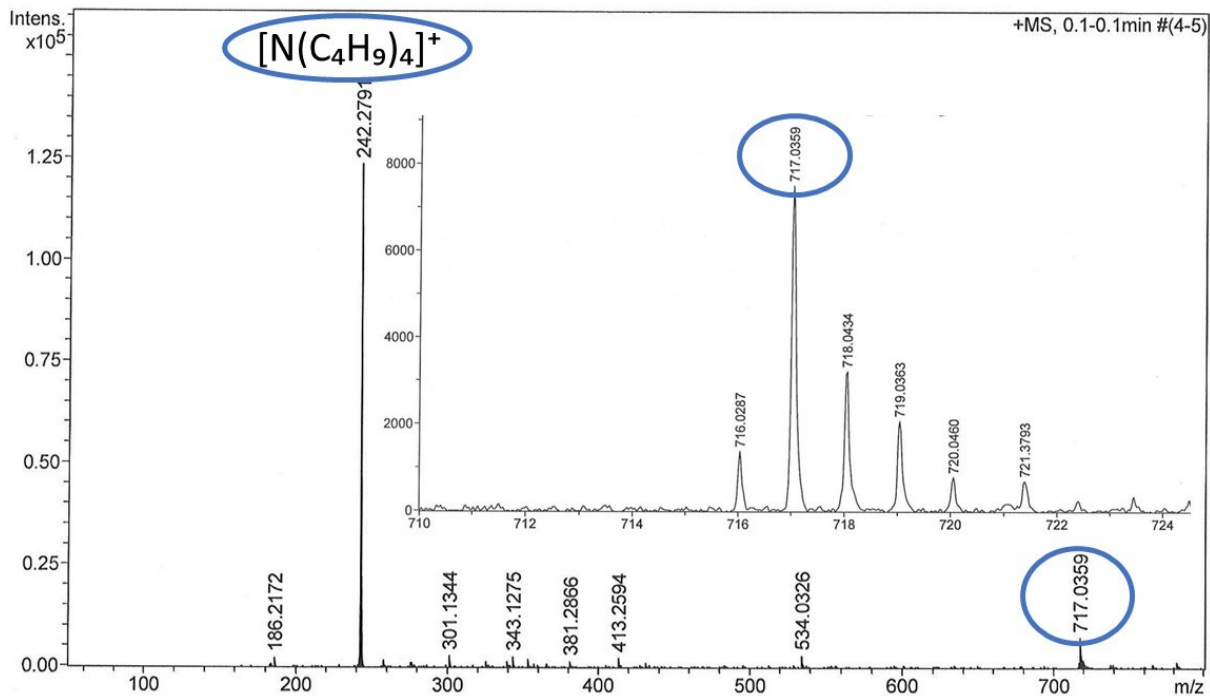


Fig. S13 Mass spectrometry for electrochemical synthesised (BEDOTPy)₂ shows MW of a dimer (717 Da).

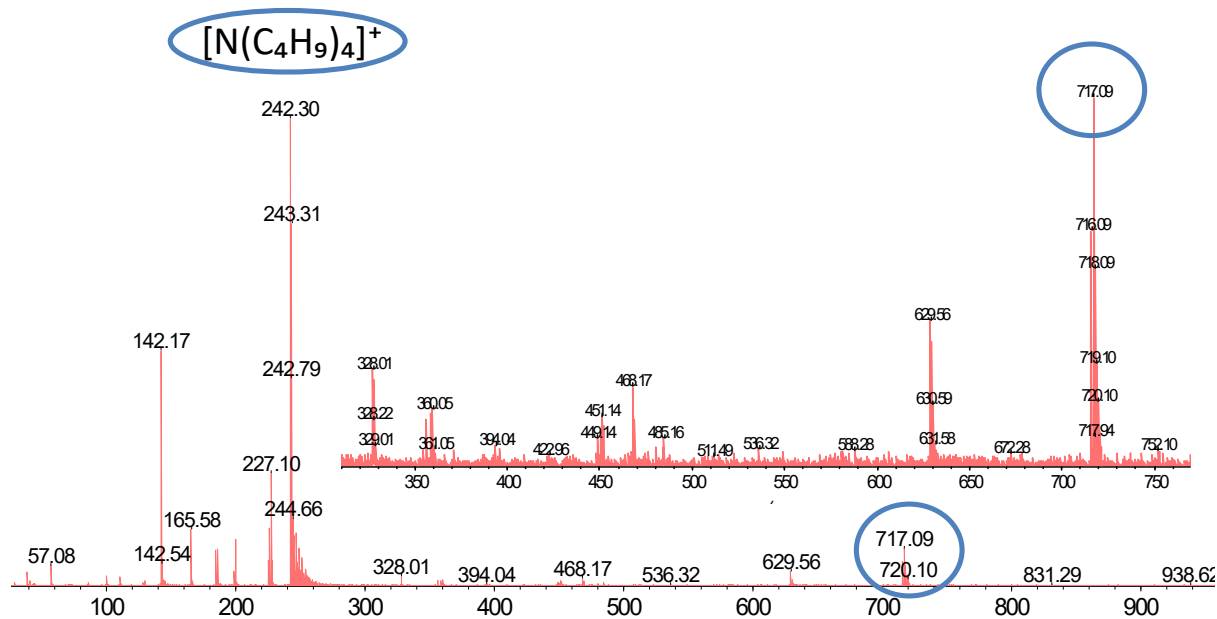


Fig. S14 MALDI spectra for the electro-synthesized product of (BEDOTPy)₂ show no molecular weight higher than 1000 g/mol.

Chemical Doping and De-doping for BEDOTPy

In order to further confirm the electrogenerated product (BEDOTPy)₂ characteristics, chemical doping and de-doping were also performed for the monomer. BEDOTPy was doped chemically using nitrosonium hexafluoro antimonate (NOSbF₆). The monomer solution (1 equivalent, 50 mg in 8 ml anhydrous acetonitrile) was mixed under Argon atmosphere with NOSbF₆ (2.5 equivalent, 90 mg in 8 ml anhydrous acetonitrile) and left under ar for 48 hours. The doped solution λ_{max} has a bathochromic shift at 482 nm compared to the monomer this is due to increasing the length of the conjugation as discussed previously. Then the doped mixture was washed with excess DCM resulting in a blue precipitate which is corresponding to the dication radical formation. Then it was filtered, and the precipitate was collected (net weight = 30 mg). Filtered product solubility was checked using different solvents (DCM, chloroform, ethanol, methanol and water). The product was soluble only in acetonitrile. The product was then de-doped by hydrazine monohydrate causing a red precipitate soluble only in DMSO. The de-doped product has an absorption spectrum (λ_{max} at 482 nm) similar to the electrodeposited film spectrum (**Fig. S15**). The difference in λ_{max} absorption between both products is due to their physical state (solution state and solid state) which allow for intramolecular interaction in the solid state. Also, the de-doped product was analysed by ¹H NMR spectroscopy (**Fig. S16**) and mass spectrometry (**Fig. S17**) to prove that the obtained product is a dimer (BEDOTPy)₂.

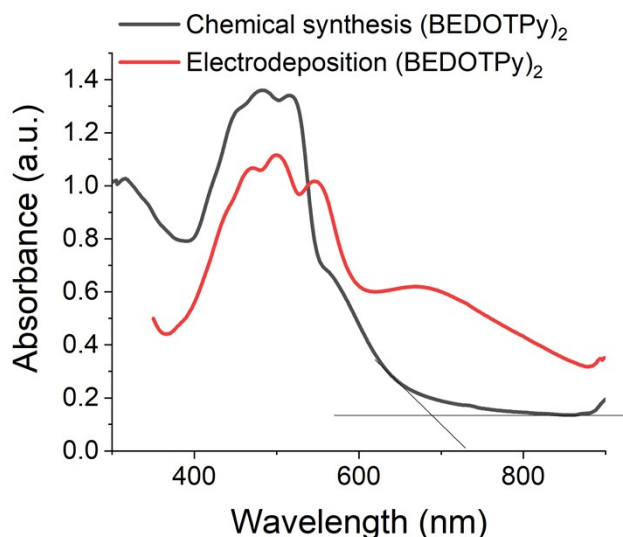


Fig. S15 Absorption spectra for the chemically synthesised (BEDOTPy)₂ (de-doped in solution state) and the electrodeposited (BEDOTPy)₂ in the solid state.

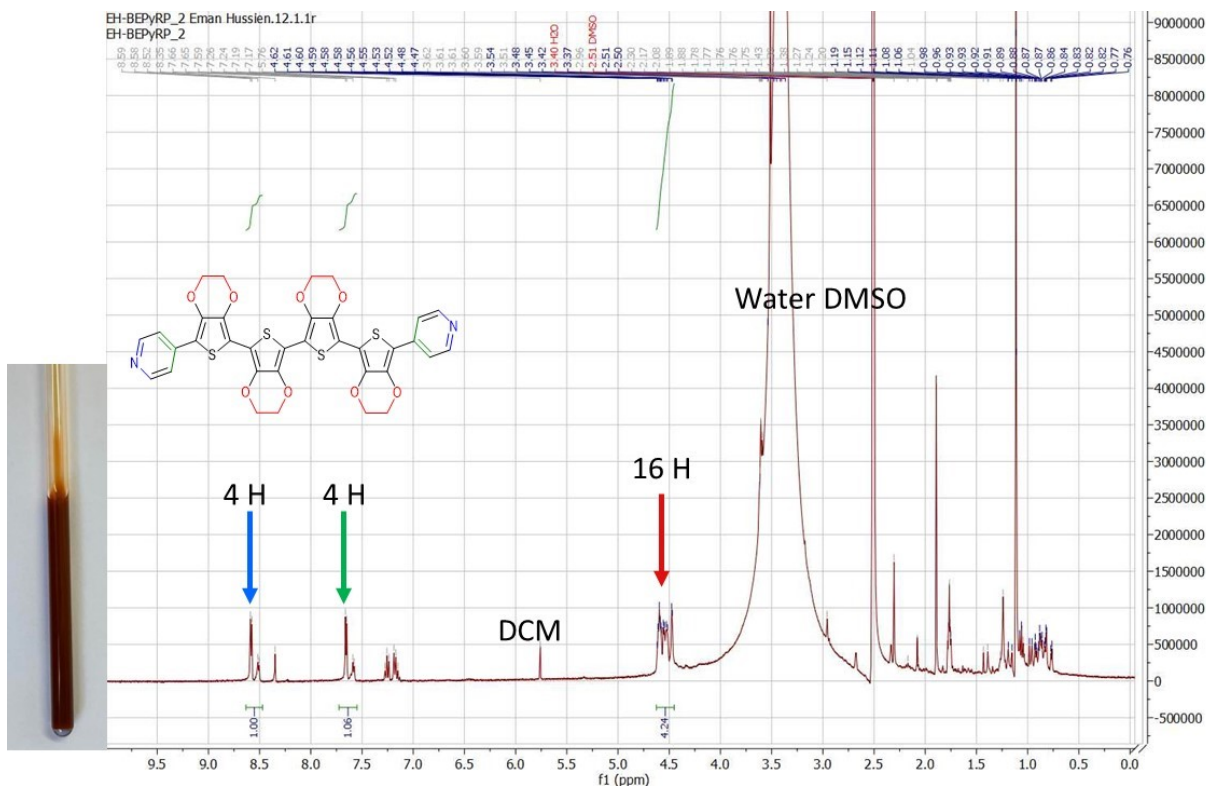
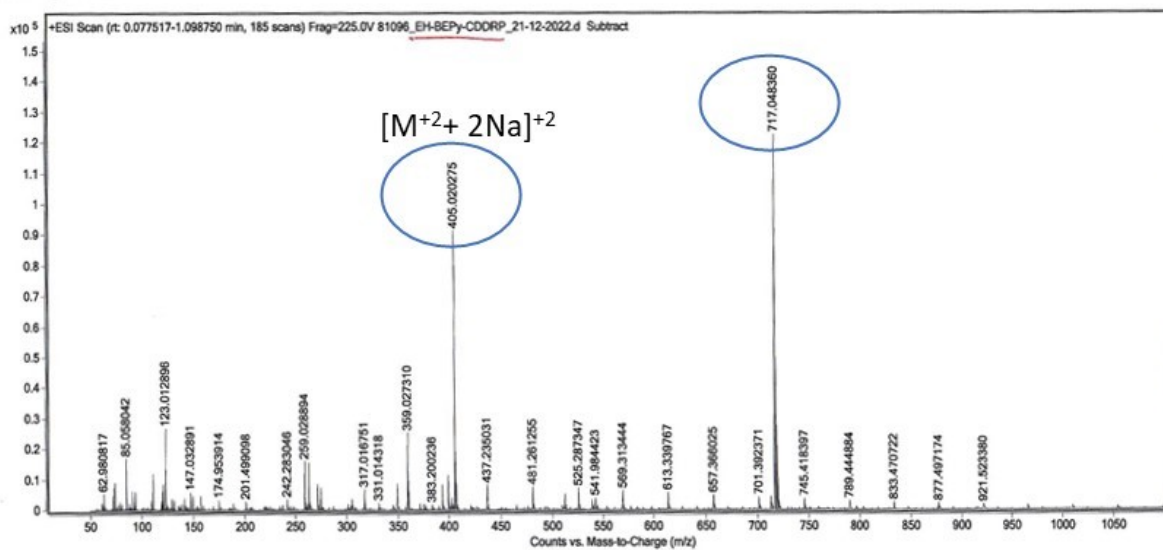


Fig. S16 ^1H NMR for a chemically de-doped $(\text{BEDOTPy})_2$ in DMSO-D_6 .

Full spectrum



Fig

. S17 Mass spectrometry for a chemically synthesised $(\text{BEDOTPy})_2$ shows MW of a dimer (717 Da).

Thermal Analysis of (BEDOTPy)₂

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been performed for the electrogenerated (BEDOTPy)₂ to study any physical changes due to changing the temperature. TGA (Fig. S18) shows the thermal decomposition temperatures (Td) at 5% weight loss for (BEDOTPy)₂ at 340 °C. DSC (Fig. S19) shows an endothermic peak at 109 °C exhibited in the first heating cycle, the same peak shifted to temperature 108.1 °C in the second heating cycle. No glass transition temperature was identified. In the cooling cycle, an exothermic peak appeared at 94.5 °C. This level of thermal stability is sufficient for optoelectronic device applications.¹⁰

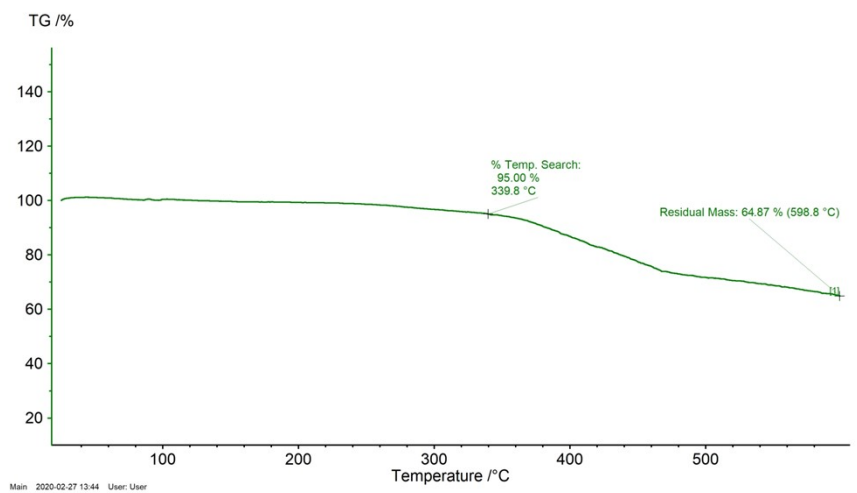


Fig. S18 TGA for the electrogenerated (BEDOTPy)₂ shows the onset of degradation temperature at around 340 °C.

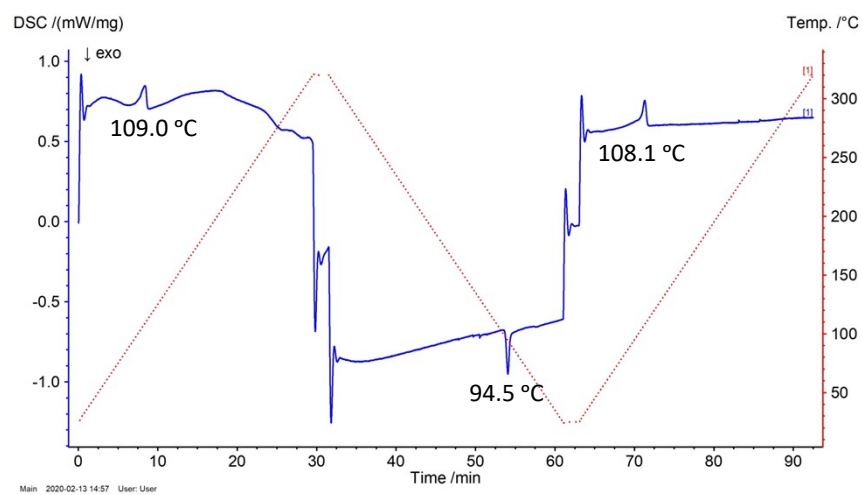


Fig. S19 DSC plot for the electrogenerated (BEDOTPy)₂ shows the effect of increasing temperature (from RT to 300 °C) on the polymer in step one, cooling down in step two (to RT) then increasing the temperature again up to 300 °C in step three.

BEDOTPy conductivity

Conductivity measurements were carried out using a 2-probe method on fabricated resistors. Films of oxidised BEDOTPy or BEDOTPy-EtOH-I were deposited by spin-coating or drop-casting (see below) onto glass substrates (15 × 15 mm, 1 mm thickness), followed by the deposition of aluminium electrodes (70 nm) by thermal evaporation (~10⁻⁵ mbar). Silver paint (RS components) was applied to the ends of the electrodes to improve contact. A Keithley 4200 semiconductor characterisation system was used to measure current-voltage characteristics. All measurements were carried out at room temperature, in a nitrogen-filled glovebox. The resistance is measured by applying a voltage sweep from -100 V to +100 V between electrode pairs, separated by a distance of 0.1 cm and recording the current. According to Ohm's law ($R = V/I$) the resistance is determined by calculating the inverse gradient of the IV graph (Current vs Voltage).

The resistance is used to calculate resistivity using the following equation:

$$\rho = R \frac{A}{l}$$

Where ρ = resistivity, R = resistance, A = cross-sectional area and l = length. In the case of the devices described above the cross-sectional area can be defined as the thickness of the film multiplied by the width of the electrode (0.1 cm) and the length is the distance separating the electrodes (0.15 cm). Finally, the conductivity is calculated as the inverse of resistivity, shown in the equation below:

$$\sigma = \frac{1}{\rho}$$

Where σ = conductivity.

Film thickness was determined by scoring films and measuring the height profile using an atomic force microscope (AFM) (Veeco, Dimension 3100). The same AFM was used for topography studies.

Spin-coated films

Glass substrates (15 × 15 mm) were cleaned by immersing in deionised H₂O, acetone and iso-propanol with ultrasonication, with the substrates immersed in each solvent for 5 minutes. They were then dried over a stream of compressed air before being treated with UV/plasma for 10 minutes.

To a suspension of BEDOTPy-EtOH-I (4.5 mg, 8.47 μ mol) in anhydrous acetonitrile (500 μ L) was added a solution of nitrosonium hexafluorophosphate (3.7 mg, 21.2 μ mol) in anhydrous acetonitrile (500 μ L)

before the solution was stirred at 40°C for 1 hour. The solution was then deposited at a spin speed of 2000 rpm.

Drop-cast films

Glass substrates were cleaned as described for the spin-coating procedure, except without UV/plasma cleaning. To a suspension of BEDOTPy or BEDOTPy-EtOH-I (0.8 mg) in anhydrous acetonitrile (100 µL) was added a solution of nitrosonium hexafluoroantimonate or nitrosonium hexafluorophosphate (5.56 µmol) in anhydrous acetonitrile (100 µL). The oxidant solution was added to the suspension, followed by the addition of anhydrous DMSO (800 µL).

Glass substrates were immersed in deionised H₂O and subject to ultrasonication for 5 minutes. The process was repeated for washing in acetone and isopropanol before the substrates were dried under a stream of compressed air. The doped dimer solution was dropped onto the glass substrate using a pipette, in ambient conditions, to completely cover the surface, before the solution was allowed to dry at room temperature, forming a dark blue film.

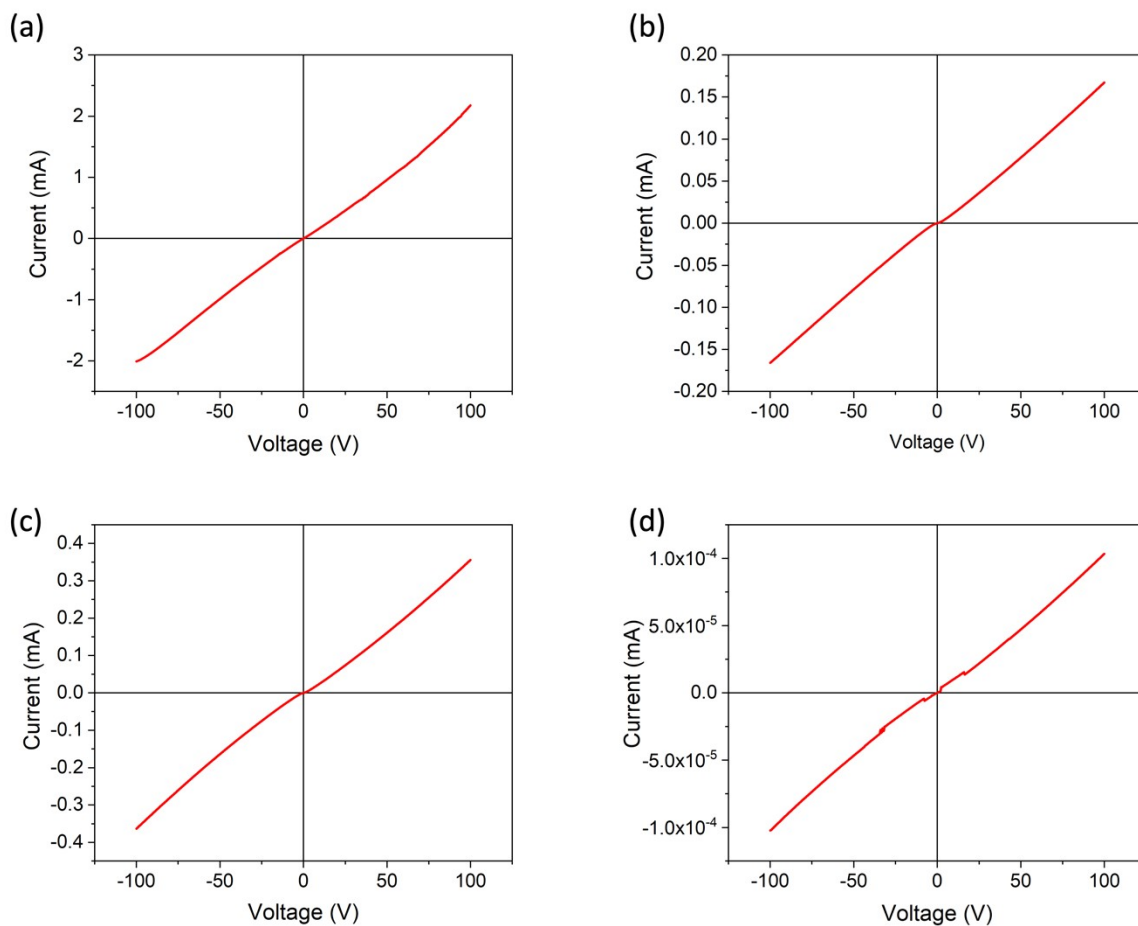


Fig. S20. Current-voltage plots for resistors created by depositing the following solutions on to glass substrates (a) BEDOTPy (0.8 mg)/NOSbF₆ (2.5 eq), 1:4 MeCN/DMSO, drop-cast; (b) BEDOTPy-EtOH-I (0.8 mg)/NOSbF₆ (2.5 eq), 1:4 MeCN/DMSO, drop-cast; (c) BEDOT-EtOH-I (0.8 mg)/NOPF₆ (2.5 eq), 1:4 MeCN/DMSO, drop-cast and (d) BEDOT-EtOH-I (4.5 mg)/NOPF₆ (2.5 eq), MeCN, spin-coated.

Water droplet contact angle measurements

Water droplet contact angle measurements were carried out using an Ossila Contact Angle Goniometer at room temperature.

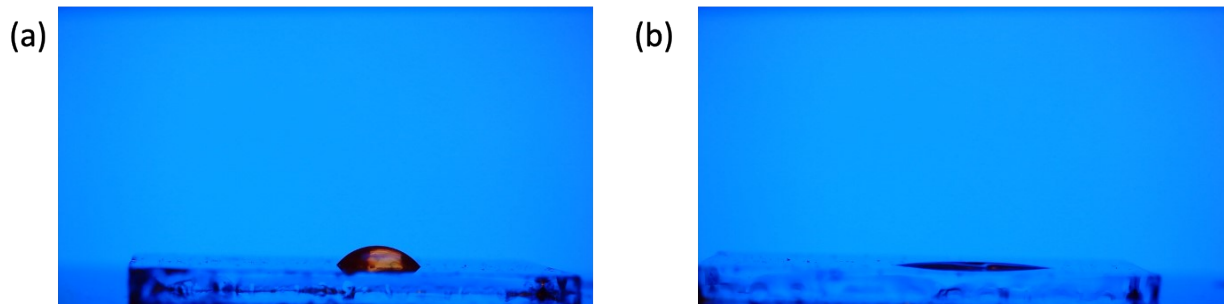


Fig. S21. Water droplet contact angle measurements of (a) (BEDOTPy-EtOH-I)₂ doped with NOPF₆ (average angle = 51.8 ± 3.8°) and (b) PEDOT:PSS (average angle = 17.2 ± 1.6°).

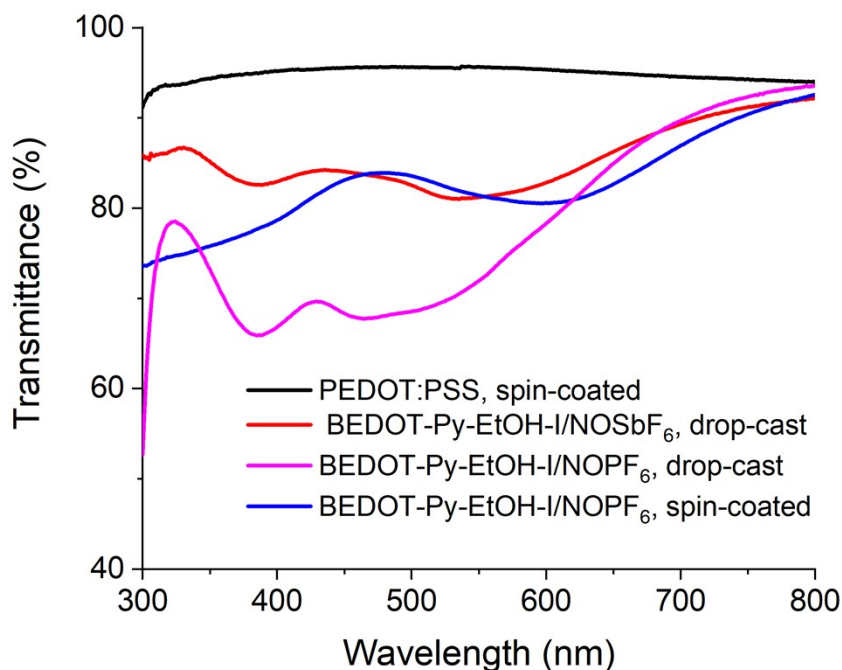


Fig S22. Transmittance spectra of PEDOT:PSS and doped (BEDOT-Py-EtOH-I)₂ films, deposited by spin-coated or drop-casting with NOSbF₆ or NOPF₆ dopants.

OLED fabrication and testing

ITO-coated glass substrates (KINTEC, 7Ω/sq, 15 × 15 × 1.1 mm) were washed by ultrasonication in deionised H₂O, acetone and isopropanol, with the substrates immersed in each solvent for 5 minutes. The substrates were then dried over a stream of compressed air and treated with UV/plasma (Diener, Zepto plasma cleaner) for 10 minutes. The hole transport layer was then deposited by following the spin-coating

procedure above for BEDOTPy-EtOH-I or spin-coating PEDOT:PSS (P VP Al 4083, Ossila) at 3000 rpm. The emissive layer solution (Super Yellow, 5 mg ml⁻¹ in toluene) was deposited by spin-coating at 1400 rpm. The cathodes (15 × 35 mm), Ca (40 nm)/Al (60 nm), were deposited by thermal evaporation at a pressure ~5 × 10⁻⁶ mbar. A Keithley Semiconductor Characterisation (SCS) 4200 was used to bias the device for OLED measurements and luminance was measured using an Irradian L203 luminance photometer. For lifetime measurements, the devices were held at 2 mA with luminance measured every minute for approximately 14 hours.

Table S1. Summary of OLED performance. Voltages for maximum luminance and current efficiencies are shown in parenthesis

Hole transport layer solution	Turn on voltage at 1 cd m ⁻² [V]	Maximum luminance (cd m ⁻²)	Maximum current efficiency (cd A ⁻¹)
BEDOTPy-EtOH-I 4.5 mg ml ⁻¹ /NOPF ₆ (2.5 eq)	2.88	21718 (9.36 V)	2.24 (4.68 V)
PEDOT:PSS	2.64	36611 (8.04 V)	4.30 (4.08 V)

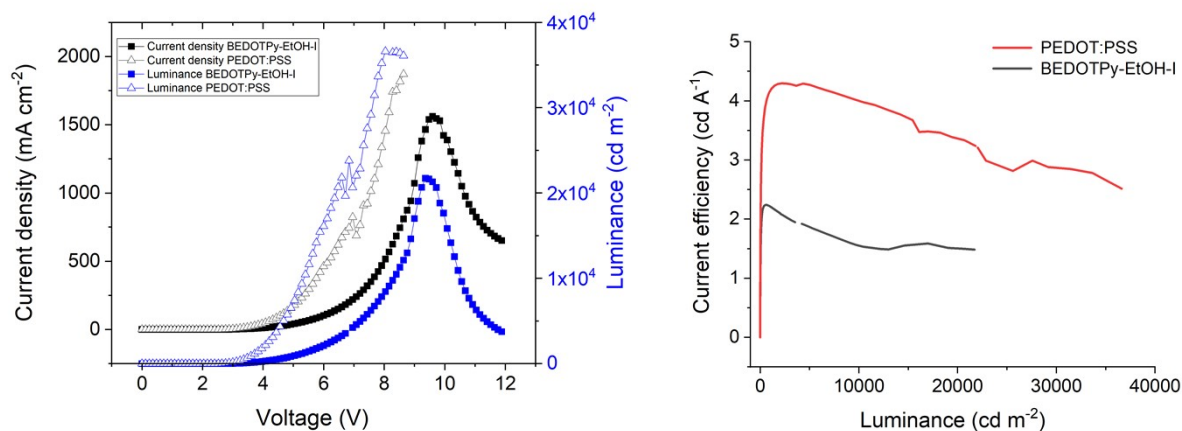


Fig. S23. (a) Current density and luminance vs voltage plots for devices and (b) current efficiency vs luminance plots for OLEDs containing PEDOT:PSS and dimerised, doped BEDOTPy-EtOH-I/NOPF₆.

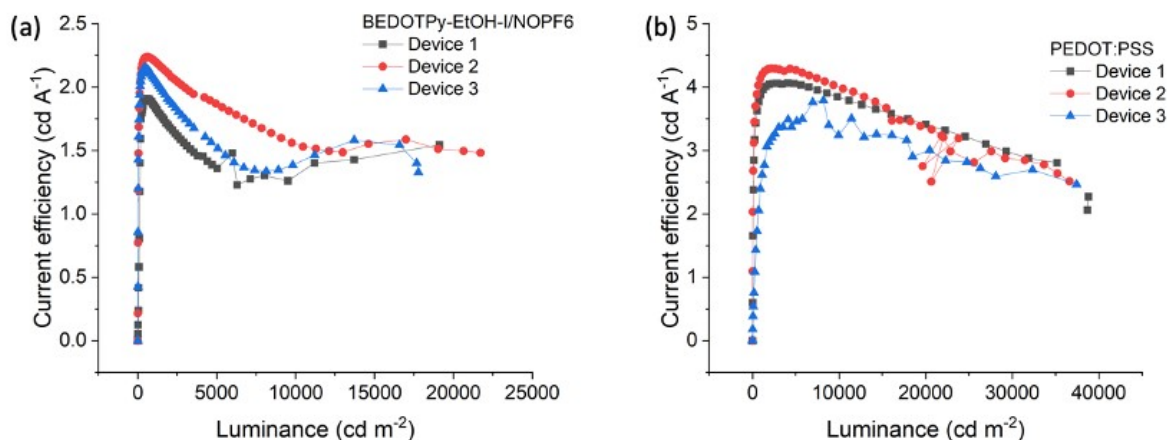


Fig. S24. Current efficiency vs luminance plots for OLEDs of repeat OLEDs containing (a) dimerised, doped BEDOTPy-EtOH-I/NOPF₆ and (b) PEDOT:PSS hole transport layers

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