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Supporting Information

Facile polymerization method for poly(3,4-ethylenedioxythiophene) and related polymers using iodine vapour

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Note added after first publication

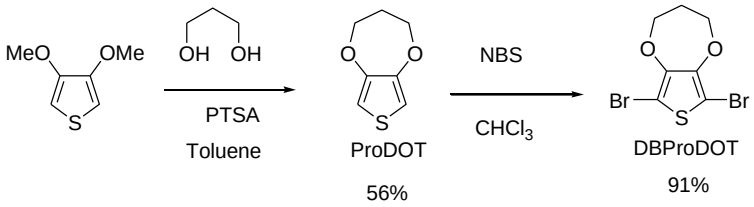
This supporting information replaces the version published on 18th September 2019, which contained errors in Fig. S1(a).

Table of content

1. Synthesis of monomers

Monomers 2,5-dichloro-3,4-ethylenedioxythiophene (DCEDOT)[1], 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)[1], 2,5-diiodo-3,4-ethylenedioxythiophene (DIEDOT)[1], 2,5-dibromo-3,4-propylenedioxythiophene (DBProDOT)[2], DBEDOT-C_6[3], and DBEDOT-C_8[3] were prepared by previously reported method.

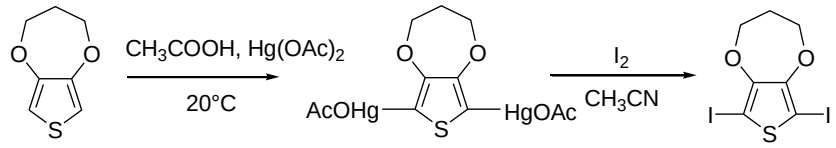
Synthesis of 2,5-dibromo-3,4-propylenedioxythiophene (DBProDOT; M3)



Synthesis of ProDOT. To a well stirred solution of 3,4-dimethoxythiophene (1.0 g, 6.9 mmol) in dry toluene (50 mL) was added 4 equivalents of propane-1,3-diol and followed by *p*-toluenesulphonic acid (PTSA) (80 mg). The resulting reaction mixture was allowed to stir for 48 hours at 100 °C with under N_2 atmosphere. The resulting mixture was diluted with 100 mL H_2O and extracted with ether (3× 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4. After that, solvent was evaporated and purified by the column chromatography to produce ProDOT in 56% yield (600 mg). UV-vis (hexane) λ_{max} at 250 nm, ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.51 (s, 2H), 4.06 (t, J=5.4 Hz, 4H), 2.18 (t, J=5.4 Hz, 2H), ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.8, 106.5, 71.3 and 33.9.

Synthesis of DBProDOT (M3). To a well stirred solution of ProDOT (300 mg, 1.92 mmol) in 20 mL dry $CHCl_3$ at 0 °C, was added 2 equivalents of *n*-bromosuccinimide (NBS) in small portions. The resulting reaction mixture was allowed to stir for 1.0 hour at room temperature. The reaction mixture was diluted with 30 mL H_2O and extracted with chloroform (3× 25 mL) and dried over Na_2SO_4. The solvent was evaporated under reduce pressure and purification was carried out by column chromatography. The compound DBProDOT was obtained in 91% yield (550 mg) as a white solid. UV-vis (hexane) λ_{max} at 253 nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (t, J=5.0 Hz, 4H), 2.28-2.22 (m, 2H).

Synthesis of 2,5-diiodo-3,4-propylenedioxythiophene (DIProDOT; M4)



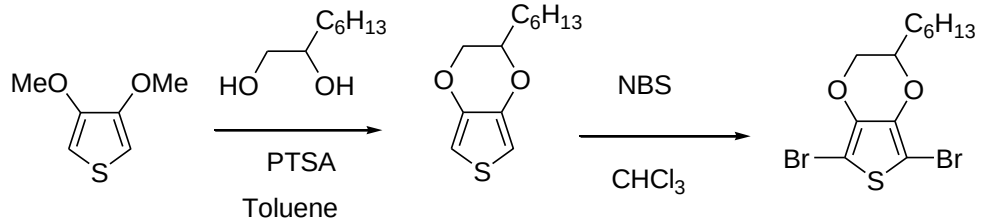
ProDOT **1** **DIProDOT**

75% 48%

Synthesis of 2,5-diacetoxymercuri-ProDOT (1). To a well stirred solution of ProDOT (1.0 g, 6.4 mmol) in acetic acid (60 mL) at 20 °C, was added drop-wise a solution of mercury (II) acetate [$Hg(OAc)_2$] (4.085 g, 12.8 mmol) in acetic acid (100 mL) over 2 hours. The resulting reaction mixture was allowed to stir for 12 hours. A white precipitate was appeared and resulting precipitate was filtered and washed with methanol followed by diethyl ether. The filtered product was dried under vacuum to give **1** as a white solid (3.25 g, 75%). Without further characterization, the compound was used for next step.

Synthesis of DIProDOT (M4). To the stirred solution of **1** (3.25 g, 4.7 mmol) in acetonitrile (250 mL), was added drop-wise a solution of iodine (2.43 g, 9.6 mmol) in acetonitrile (200 mL). A yellow-orange colored solution was obtained. After concentration of the resulting solution, saturated solution of potassium iodide was added. The combined resulting mixture was diluted with 100 mL H_2O, extracted with chloroform (3×50 mL) and finally dried over Na_2SO_4. The organic solvent was evaporated and purification was carried out by column chromatography. The compound DIProDOT was obtained in 48% yield (90 mg) as a light brown colored solid. UV-vis (hexane) λ_{max} at 328 nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (t, J=5.0 Hz, 4H), 2.20-2.16 (m, 2H).

Synthesis of hexyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT-C_6; M5)



EDOT-C_6 DBEDOT-C_6

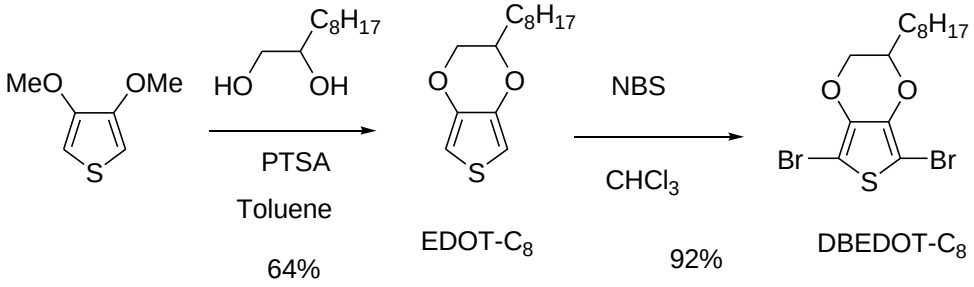
68% 89%

Synthesis of EDOT-C_6. To a well stirred solution of 3,4-dimethoxythiophene (420 mg, 2.92 mmol) in dry toluene (20 mL) was added 4 equivalents of 1,2-octanediol and followed by *p*-toluenesulphonic acid (PTSA) (50 mg). The resulting reaction mixture was allowed to stir for 30 hours at 100 °C with under N_2 atmosphere. The resulting mixture was diluted with 100 mL H_2O and extracted with ether (3× 50 mL). The combined organic extracts were washed with brine, dried over

Na_2SO_4. After that, solvent was evaporated under reduce pressure and purified by the column chromatography. The pale yellow oily liquid EDOT-C_6 was obtained in 68% yield (448 mg). UV-vis (hexane) λ_{max} at 257 nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.32 (s, 2H), 4.19-4.10 (m, 2H), 3.89 (dd, J=11.5 and 8.0 Hz, 1H), 1.72-1.50 (m, 4H), 1.40-1.21 (m, 6H), 0.91 (t, J = 7.0 Hz, 3H).

Synthesis of DBEDOT-C_6 (M5). To a well stirred solution of EDOT-C_6 (300 mg, 1.32 mmol) in 20 mL dry $CHCl_3$ at 0 °C, was added 2 equivalents (470 mg, 2.64 mmol) of *n*-bromosuccinimide (NBS) in small portions. The resulting reaction mixture was allowed to stir for 1.0 hour at room temperature. The resulting mixture was then diluted with 30 mL H_2O and extracted with chloroform (3× 25 mL) and dried over Na_2SO_4. After that, solvent was evaporated and purification was carried out by column chromatography. The compound DBEDOT-C_6 was obtained in 89% yield (454 mg) as a pale yellow oily liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (dd, J=3.0 and 11.5 Hz, 1H), 4.14-4.04 (m, 1H), 3.85 (dd, J=11.5 and 3.0 Hz, 1H), 1.72-1.62 (m, 2H), 1.56-1.17 (m, 8H), 0.83 (t, J = 7.0 Hz, 3H).

Synthesis of octyl-2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT-C_8; M6)



Synthesis of EDOT-C_8. To a well stirred solution of 3,4-dimethoxythiophene (400 mg, 2.77 mmol) in dry toluene (20 mL) was added 4 equivalents of 1,2-decanediol and followed by *p*-toluenesulphonic acid (PTSA) (50 mg). The resulting reaction mixture was allowed to stir for 30 hours at 100 °C with under N_2 atmosphere. The resulting mixture was diluted with 100 mL H_2O and extracted with ether (3× 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4. After that, solvent was evaporated and purified by the column chromatography. The pale yellow oily liquid EDOT-C_8 was obtained in 64% yield (450 mg) and was characterized by UV-vis-NIR absorption and NMR spectroscopy. UV-vis (hexane) λ_{max} at 256 nm; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (s, 2H), 4.16-4.08 (m, 2H), 3.86 (dd, J=11.5 and 8.0 Hz, 1H), 1.71-1.50 (m, 4H), 1.40-1.20 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H).

Synthesis of DBEDOT-C_8 (M6). To a well stirred solution of EDOT-C_8 (300 mg, 1.18 mmol) in 20 mL dry $CHCl_3$ at 0 °C, was added 2 equivalents of *n*-bromosuccinimide (NBS) (420 mg, 2.36 mmol) in small portions. The resulting reaction mixture was allowed to stir for around 1.0 hour at room

temperature. The resulting solution was then diluted with 30 mL H_2O and extracted with chloroform (3× 25 mL) and dried over Na_2SO_4. After that, solvent was evaporated and purification was carried out by column chromatography. The compound DBEDOT-C_8 was obtained in 92% yield (448 mg) as a yellow oily liquid. The compound was characterized by NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ, 4.23 (dd, J=2.0 and 11.5 Hz, 1H), 4.17-4.12 (m, 1H), 3.92 (dd, J=11.5 and 7.0 Hz, 1H), 1.72-1.50 (m, 4H), 1.46-1.23 (m, 10H), 0.91 (t, J = 7.0 Hz, 3H).

2. General procedure for dedoping of polymers.

To a stirred mixture of as prepared polymer (100 mg) in deoxygenated $CHCl_3$ (10 mL) at room temperature was added hydrazine hydrate (50 mg in 2 mL acetonitrile). (Solvents $CHCl_3$, MeOH and hexane were purged with dry N_2 for 30 minutes for deoxygenation). The resulting mixture was stirred overnight at room temperature. $CHCl_3$ was removed under reduced pressure and the resulting residue was collected in to a Whatman extraction thimble under N_2 atmosphere. The resulting dedoped black residue was purified by repeated Soxhlet extraction with deoxygenated MeOH (6 cycles) and hexane (6 cycles). For insoluble polymers (*br*-PEDOT, *i*-PEDOT, *br*-PProDOT and *i*-PProDOT), after Soxhlet extraction, the resulting polymer was dried under reduced pressure and the polymers were kept under N_2 atmosphere. For soluble polymers (PEDOT-C_6 and PEDOT-C_8), after Soxhlet extraction, the resulting polymer in Whatman extraction thimble was further Soxhlet extraction with deoxygenated $CHCl_3$. After few cycles the soluble portion of the polymer in $CHCl_3$ was collected in to round bottom flask and finally $CHCl_3$ was removed under reduced pressure yielded deep black blue polymers.

Further doping of the dedoped polymers

About 50 mg of elemental iodine was placed in the bottom of a vial (10 mL). Then a well-ground powder of dedoped polymer (100 mg) in a Whatman paper was hung in the vial (10 mL). The iodine vapour was slowly diffused to polymer at room temperature and continued for 6 hours for further doping.

3. Preparation of polymer films for UV-vis measurement.

For insoluble polymers (*br*-PEDOT, *i*-PEDOT, *br*-PProDOT and *i*-PProDOT). Neutral polymer (dedoped) was crushed into very fine powder. The fine powder (10 mg) was put into deoxygenated $CHCl_3$ (2 mL) and make a suspension mixture under N_2 atmosphere. The resulting suspension

mixture was drop-cast on the glass slide and spread over the slide and dried under N_2 atmosphere. This slide was used for UV-vis measurements.

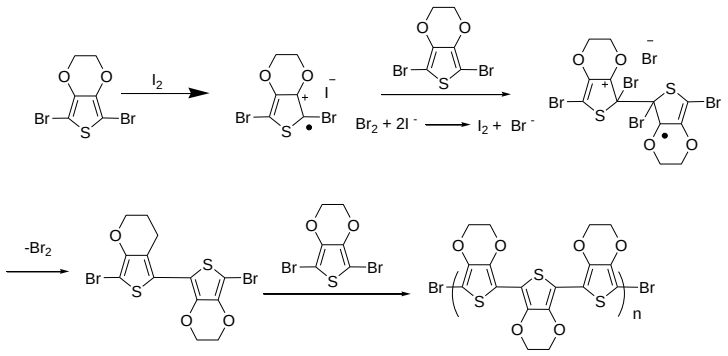
For soluble polymers (PEDOT-C_6 and PEDOT-C_8). Neutral polymer (dedoped) (10 mg) was dissolved into deoxygenated $CHCl_3$ (2 mL) and make a solution under N_2 atmosphere. The resulting solution was drop-casted on the glass slide and spread over the slide and dried under N_2 atmosphere. This slide was used for UV-vis measurements.

4. Sample preparation procedure for GPC

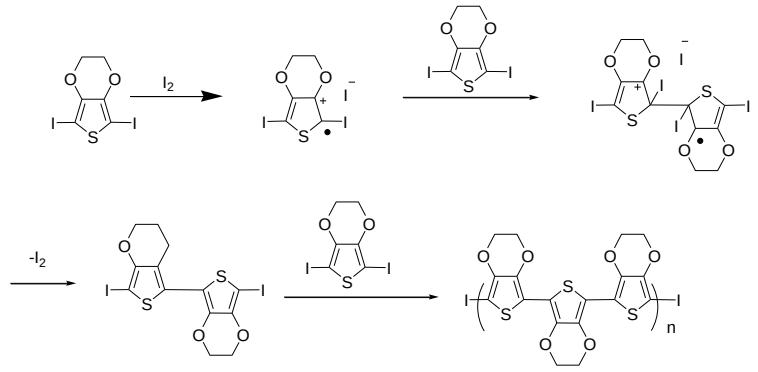
The polymer was dissolved initially in $CHCl_3$ (2 mg/mL), and allowed to solubilize for 3 hours period at 50 °C. Then at room temperature the solution was filtered through a Millipore 0.5 µm filter. Injections of ~200 µL were performed and retention times were calibrated against narrow molecular weight polystyrene standards.

5. Proposed mechanism of the polymerization

The polymerization occurs by an oxidation of DBEDOT promoted by I_2 to produce radical cation. The radical cation reacts with another monomer unit to form radical cation dimer followed by the release of bromine (Scheme 1) or iodine (Scheme 2). During the polymerization process, bromine and iodine generated in bromo and iodo derivative respectively act as dopant for the resulting polymers. It is significant to mention that Br_2 is a strong oxidizing agent so oxidizes I^- to I_2 and itself reduces to Br^-. Following the same procedure leads to the formation of polymers.[4]

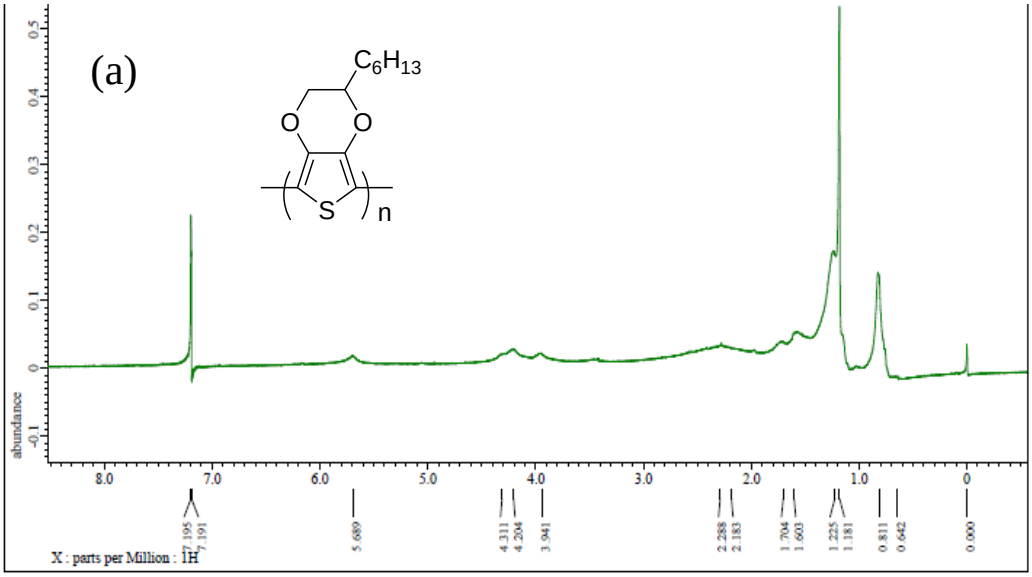


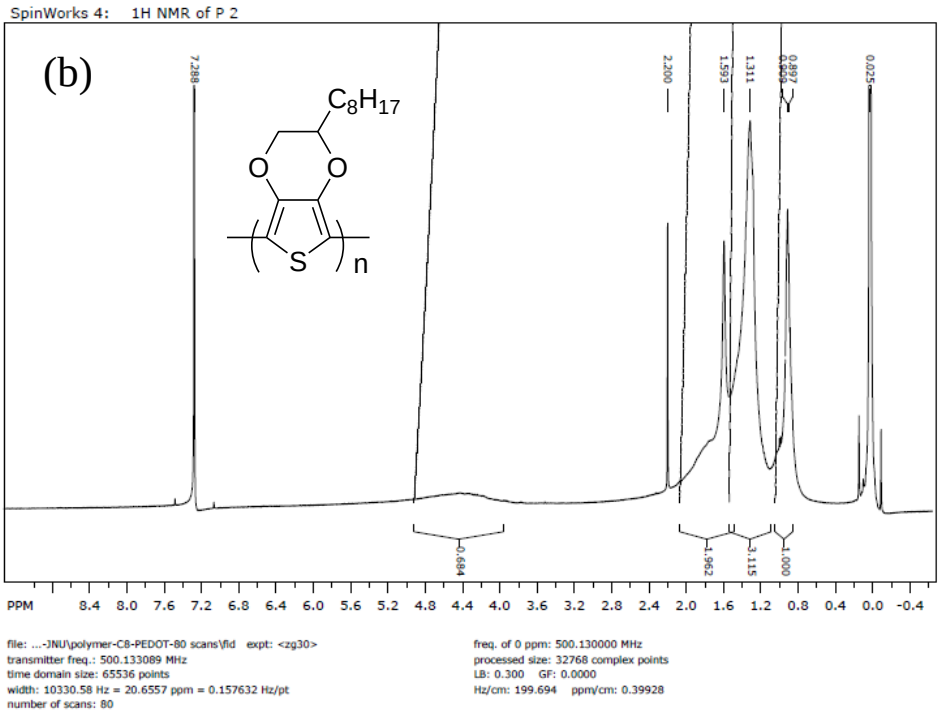
Scheme S1. Proposed mechanism for the iodine vapour polymerization of *br*-PEDOT



Scheme S2. Proposed mechanism for the iodine vapour polymerization of *i*-PEDOT.

6. NMR, GPC, UV-vis, FT-IR and CV data





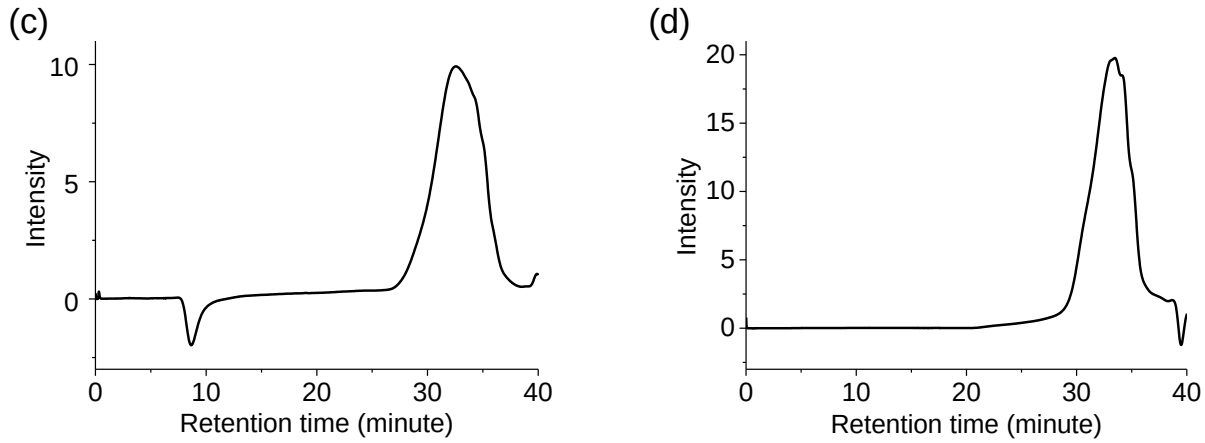


Fig. S1. ^{1}H NMR of neutral (a) PEDOT-C_6 in $CDCl_3$, (b) PEDOT-C_8 in $CDCl_3$ and GPC curve of (c) PEDOT-C_6 and (d) PEDOT-C_8 in $CHCl_3$. GPC measurements were performed in $CHCl_3$ at 40 °C and molecular weight of polymer is calculated from the retention time using polystyrene standard reference kit.

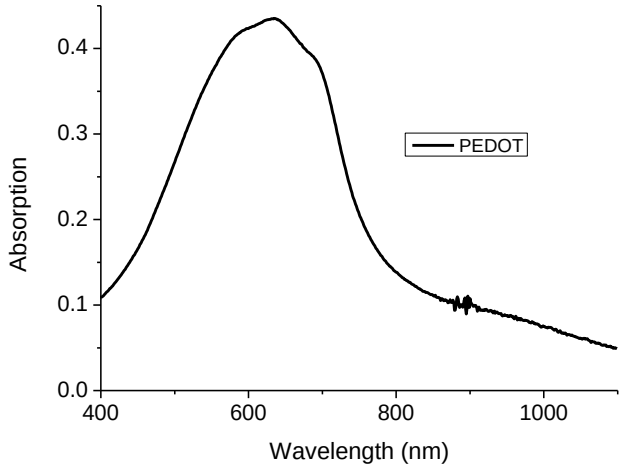


Fig. S2. UV-vis spectrum of electrochemically polymerized PEDOT on ITO coated glass in monomer free 0.1 M $TBAPF_6$ in acetonitrile at applied potential of -0.8 V (neutral state or undoped). Polymer film on ITO was prepared by electropolymerization of EDOT monomer at 0.1 M $TBAPF_6$ in acetonitrile at scan rate 50 mV/s between -1.0 V to 1.6 V.

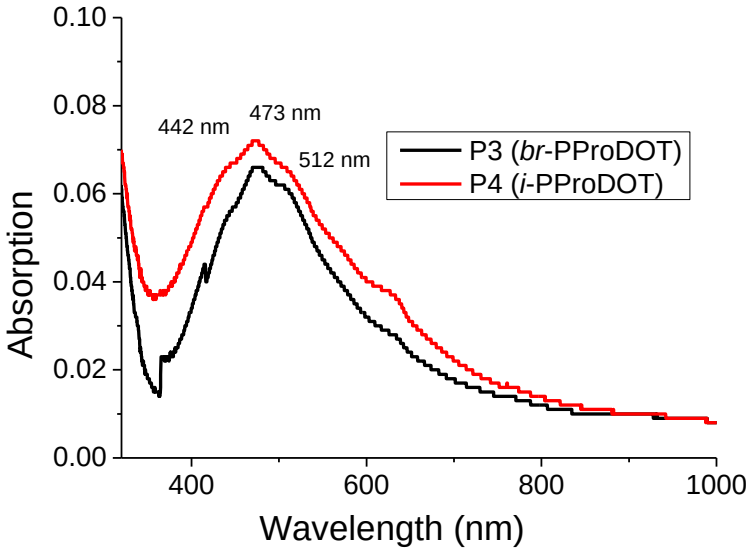


Fig. S3. UV-vis spectra of PProDOT polymers films on glass slide prepared by iodine vapour polymerization.

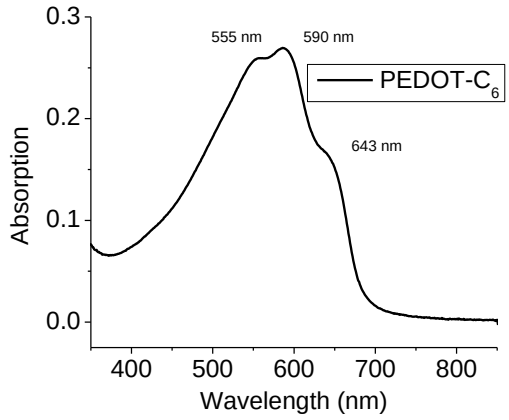


Fig. S4. UV-vis spectrum of PEDOT-C_6 polymer in $CHCl_3$ prepared by iodine vapour polymerization.

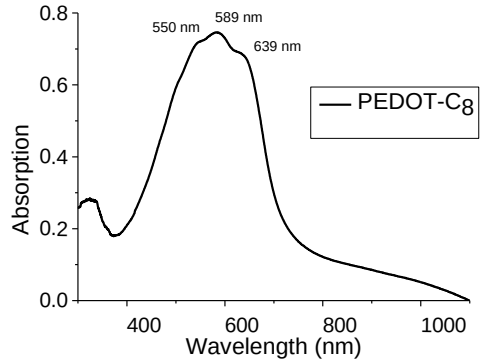


Fig. S5. UV-vis-NIR spectrum of PEDOT-C_8 polymer film prepared by iodine vapour polymerization.

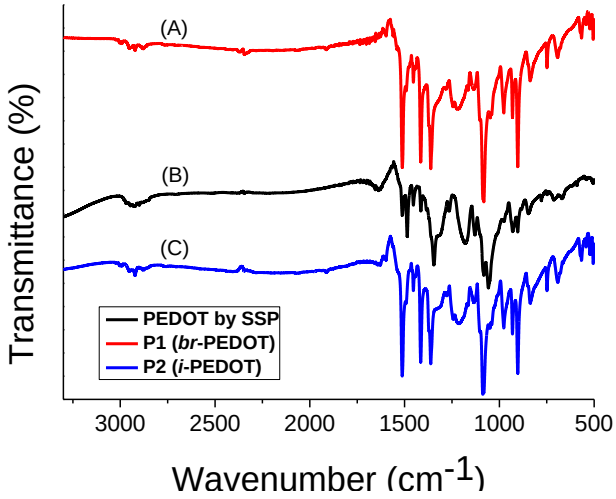


Fig. S6. FT-IR spectra of the (A) PEDOT by SSP, (B) *br*-PEDOT and (C) *i*-PEDOT in KBr pellet.

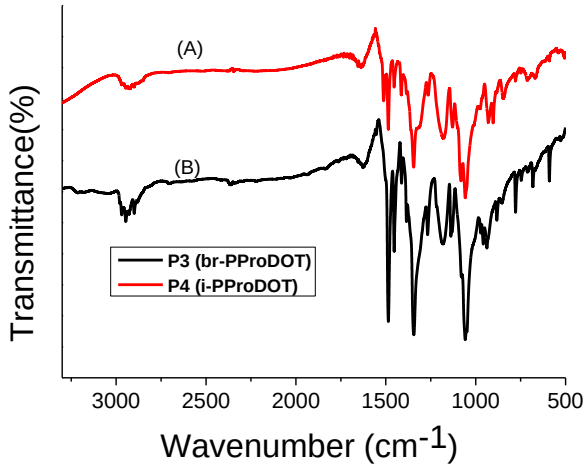


Fig. S7. FT-IR spectra of the (A) *br*-PProDOT and (B) *i*-PProDOT in KBr pellet.

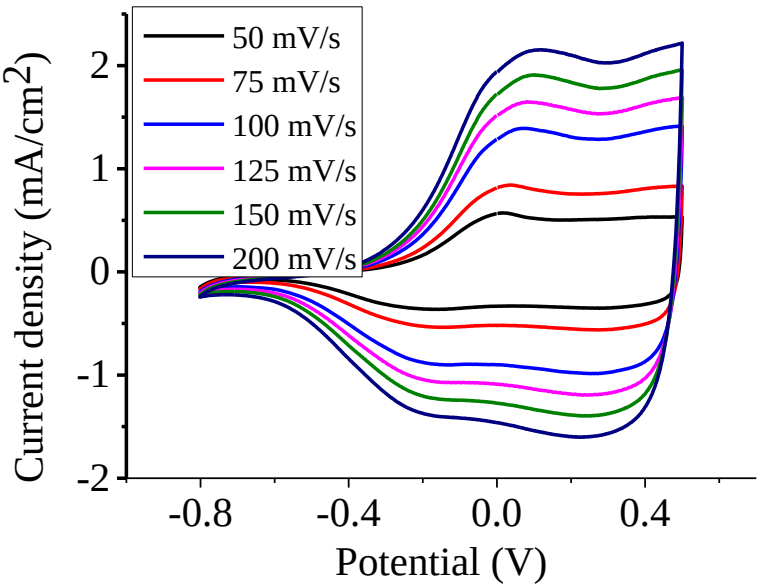


Fig. S8. CV of PEDOT synthesized by SSP on glassy carbon electrode with Ag/Ag^{+} as the reference electrode in 0.1 M $TBAPF_6$ in acetonitrile at different scan rates.

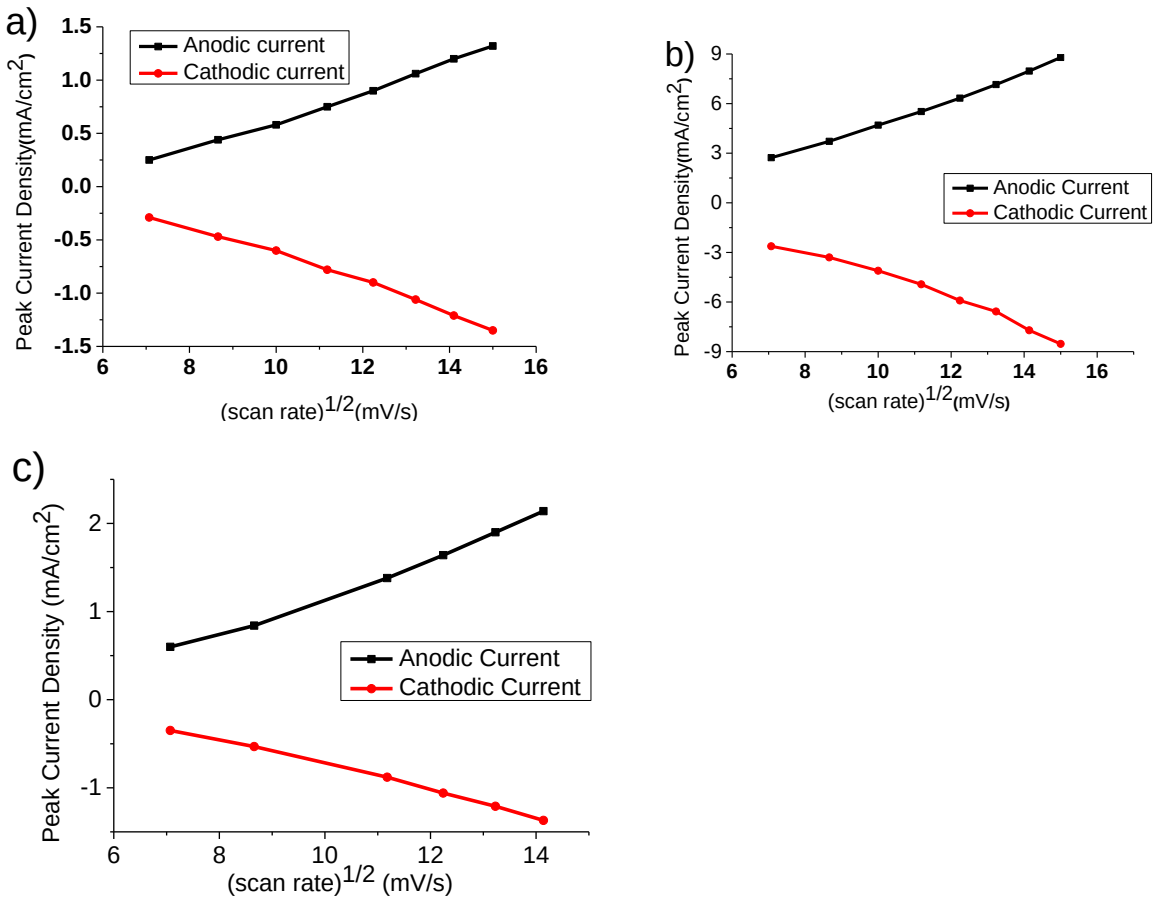


Fig. S9. Plot of redox peak currents vs SQRT of scan rates derived from CV data of a) *br*-PEDOT at 50-225 mV/s scan rates; b) *i*-PEDOT at 50-225 mV/s scan rates and c) PEDOT synthesized by SSP at 50-200 mV/s scan rates on a glassy carbon electrode in 0.1 M $TBAPF_6$ in acetonitrile.

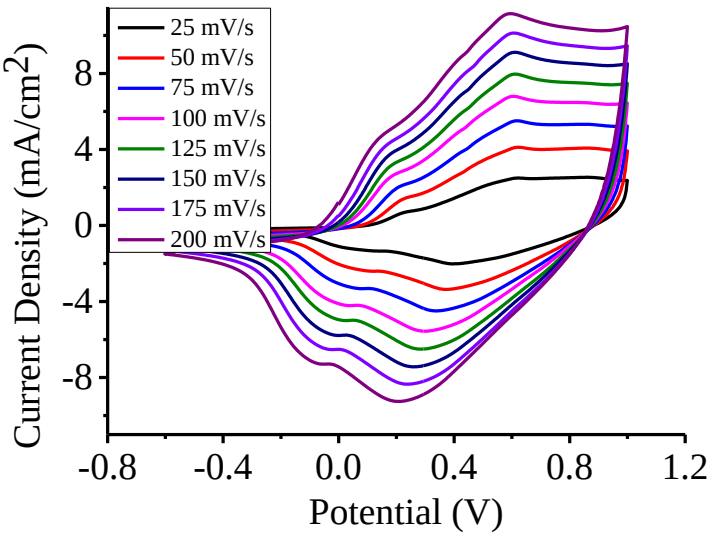


Fig. S10. CV of *br*-PPrODOT synthesized by iodine vapour polymerization on glassy carbon electrode with Ag/Ag^+ as the reference electrode in 0.1 M $TBAPF_6$ in acetonitrile at different scan rates.

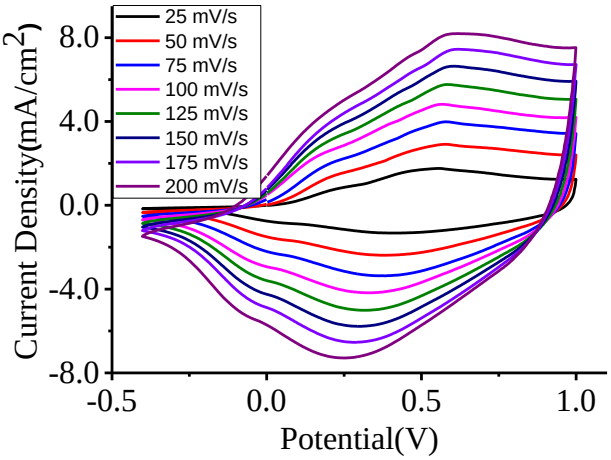


Fig. S11. CV of *i*-PPrODOT synthesized by iodine vapour polymerization on glassy carbon electrode with Ag/Ag^+ as the reference electrode in 0.1 M $TBAPF_6$ in acetonitrile at different scan rates.

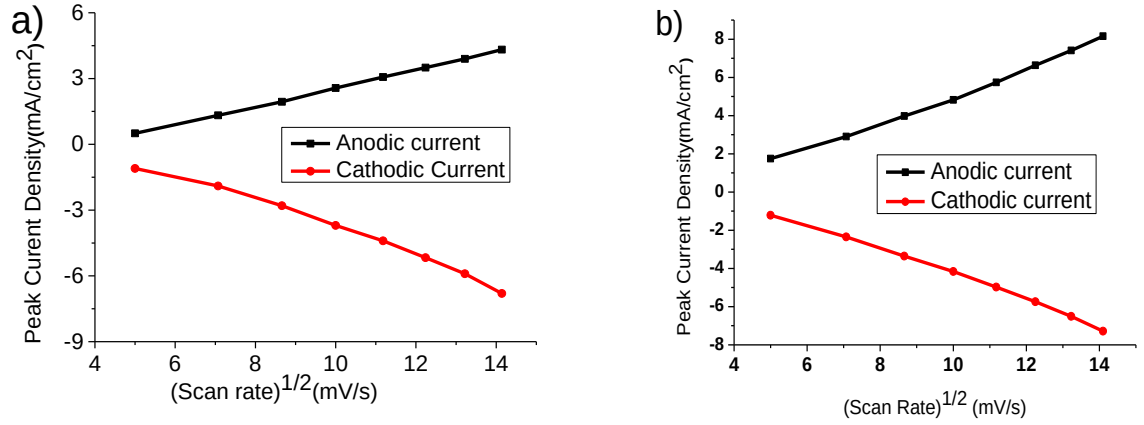


Fig. S12. Plot of redox peak currents vs SQRT of scan rates derived from CV data of (a) *br*-PPrODOT at 25-200 mV/s scan rates and (b) *i*-PPrODOT at 25-200 mV/s scan rates on a glassy carbon electrode in 0.1 M $TBAPF_6$ in acetonitrile.

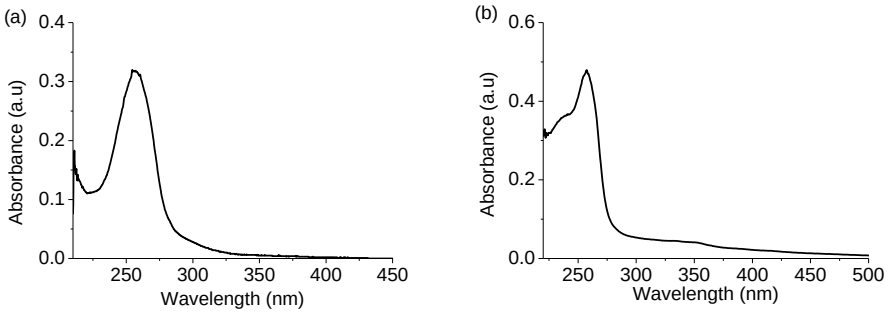


Fig. S13.UV-vis absorption spectra of (a) EDOT-C_6 and (b) EDOT-C_8 in hexane.

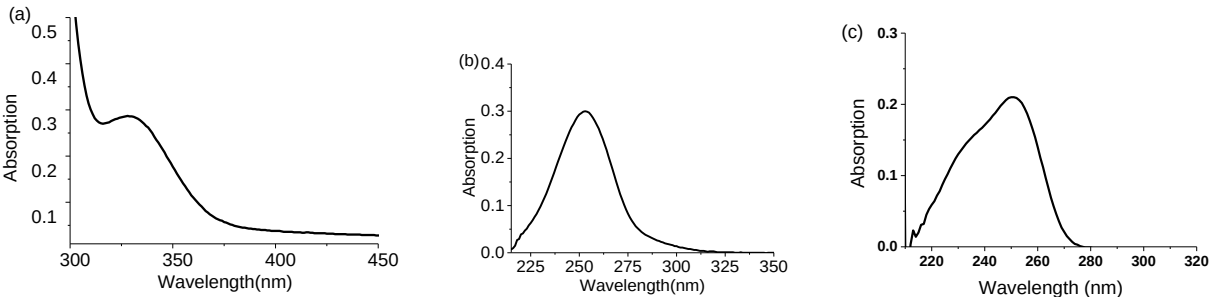


Fig. S14. UV-vis absorption spectra of (a) DIProDOT, (b) DBrProDOT, and (c) ProDOT in hexane.

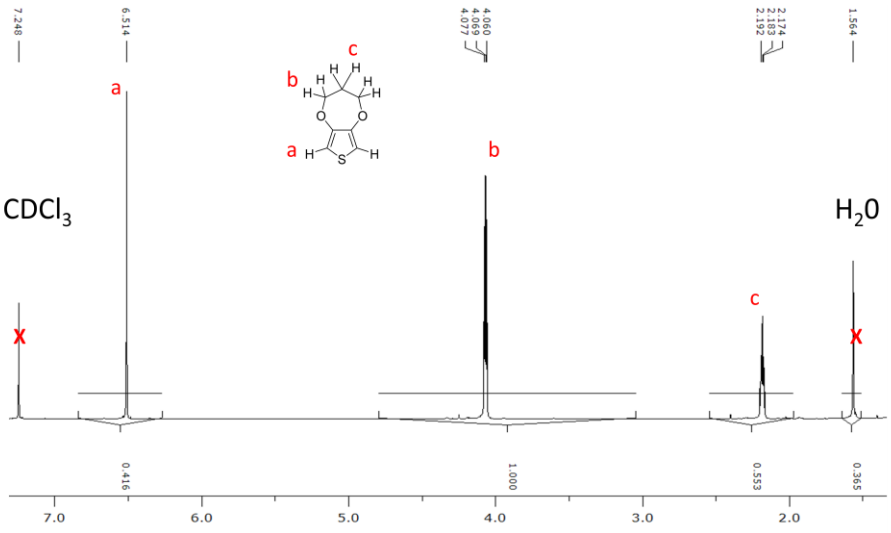


Fig. S15. ^{1}H NMR spectrum of ProDOT at 600 MHz in $CDCl_3$.

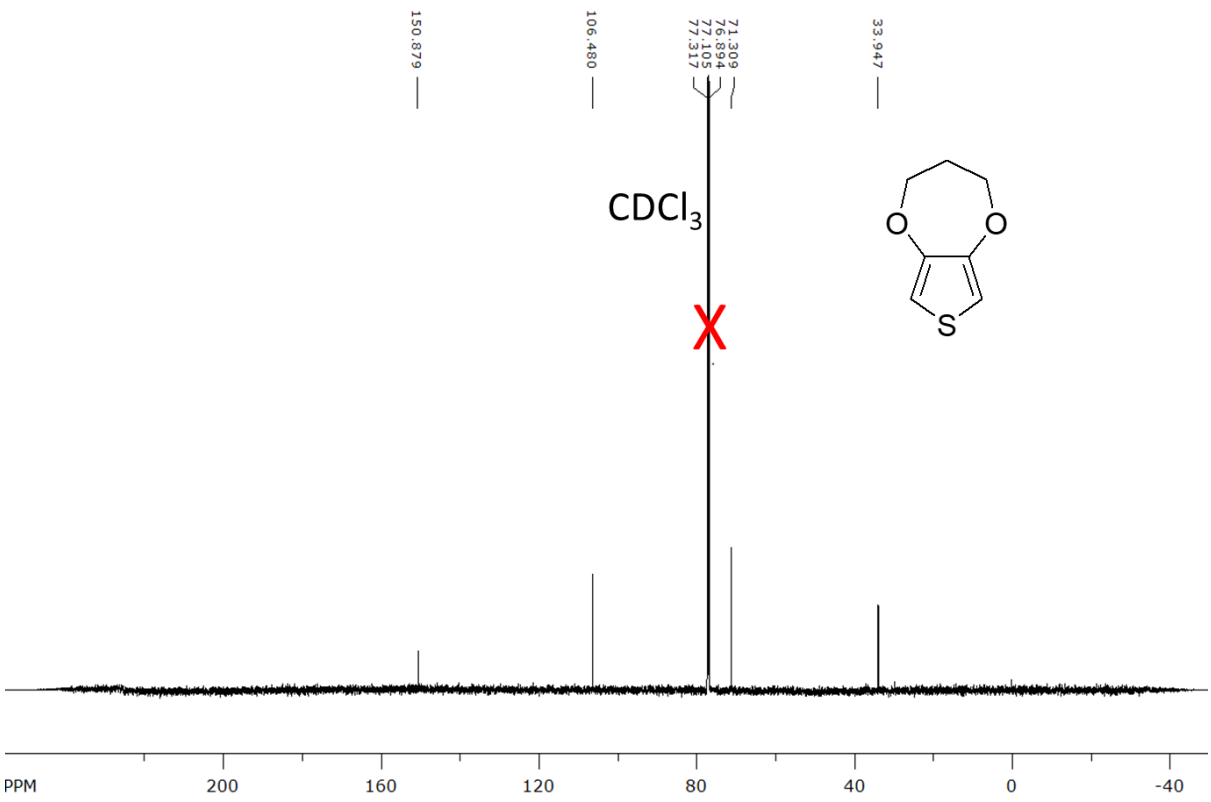


Fig. S16. ^{13}C NMR spectrum of ProDOT at 150 MHz in $CDCl_3$.

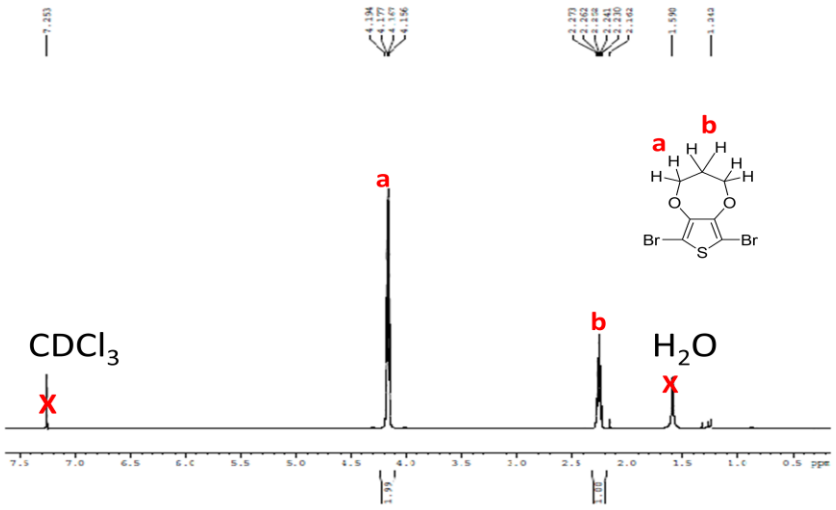


Fig. S17. ^{1}H NMR spectrum of DBProDOT at 500 MHz in $CDCl_3$.

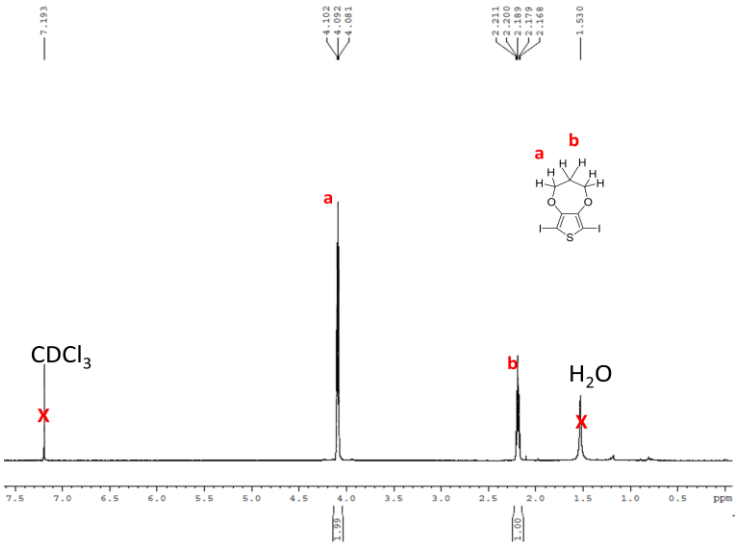


Fig. S18. ^{1}H NMR spectrum of DIProDOT at 500 MHz in $CDCl_3$.

References

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