

# Supporting Information

## Chemical Vapor Deposition of High Charge Carrier Mobility Benzothiadiazole-Based Conjugated Polymer Thin Films

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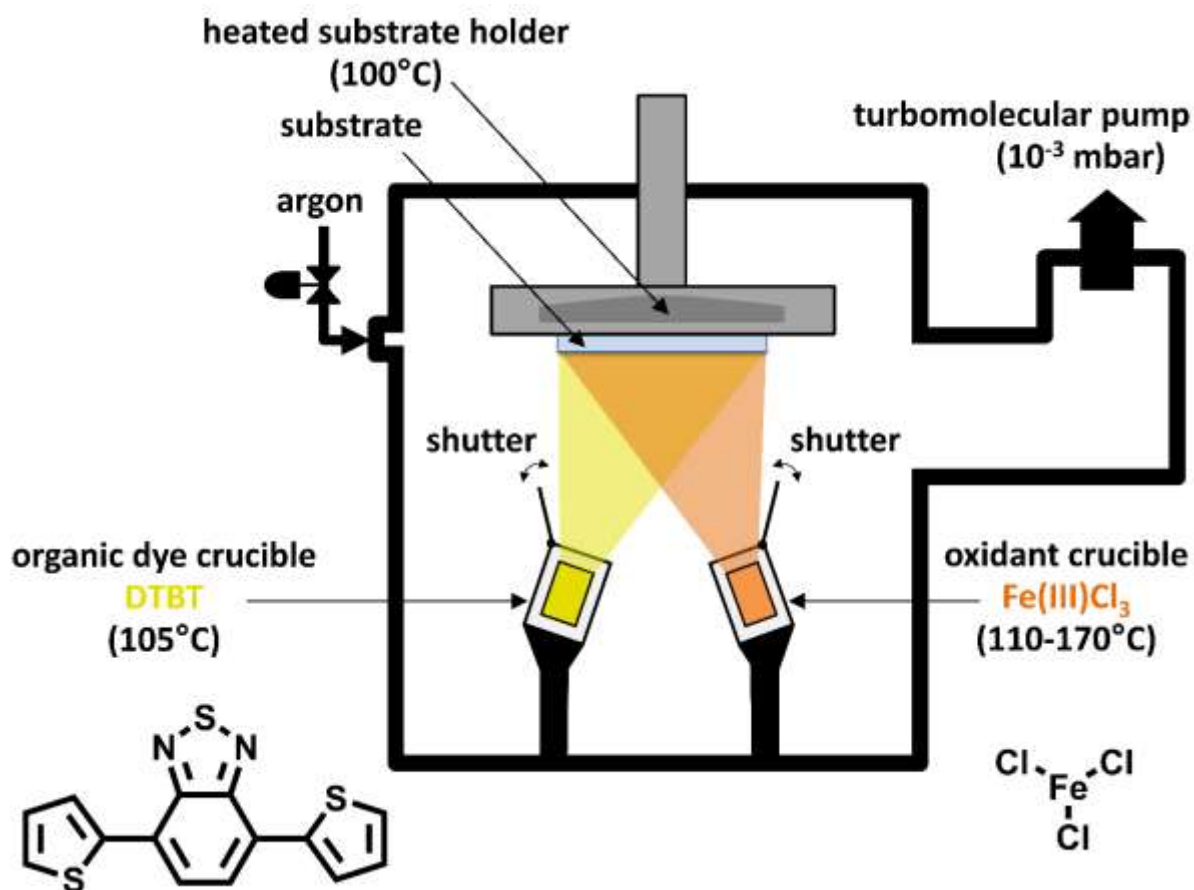
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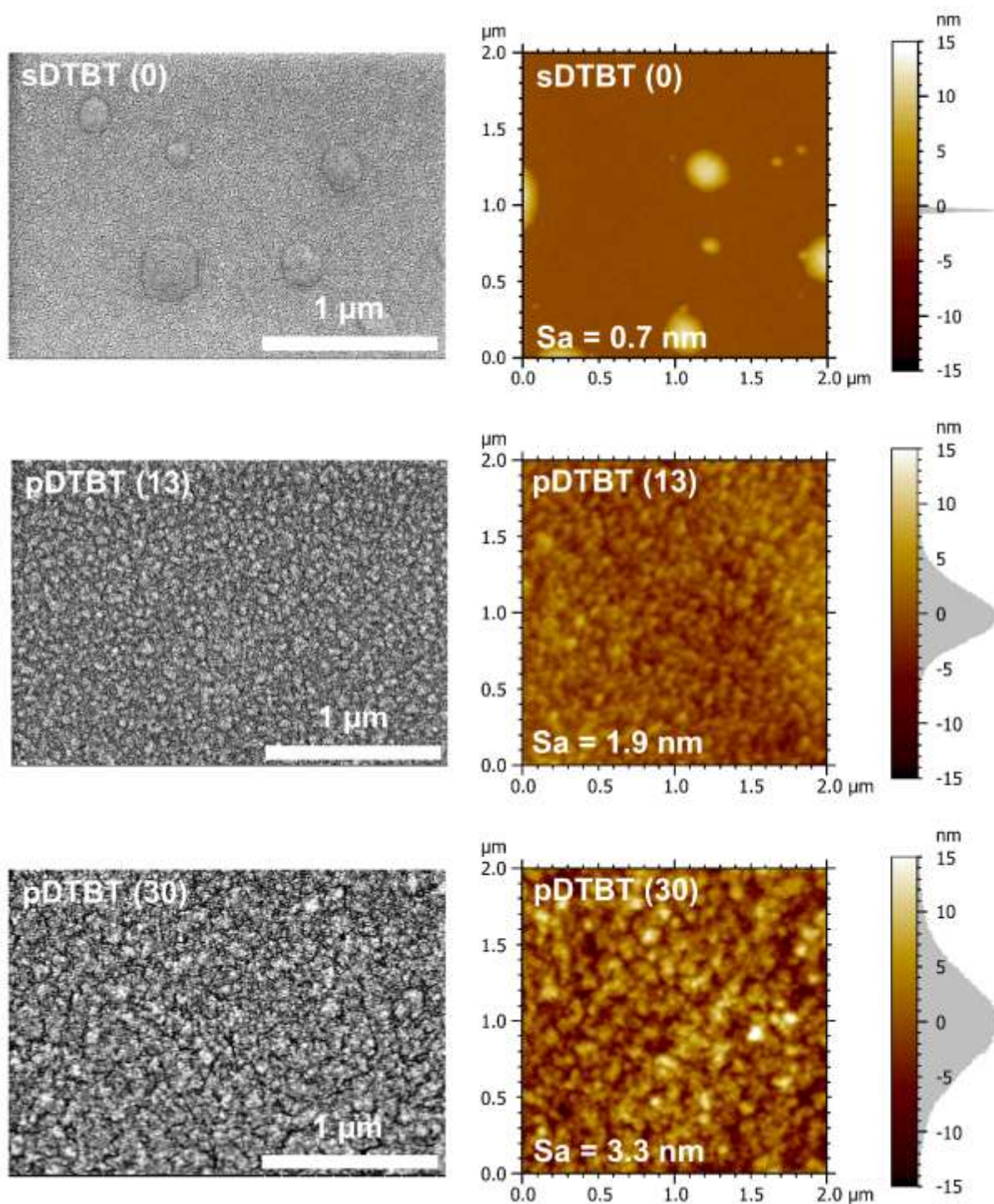
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**Table S1.** Deposition conditions and amounts of sublimed reactants for the preparation of the sublimed **sDTBT (0)** and oCVD **pDTBT** thin films prepared from the oCVD reaction of 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) and iron (III) chloride (FeCl<sub>3</sub>) for different oxidant (FeCl<sub>3</sub>) to monomer (DTBT) ratios (molar ratio provided in parentheses).

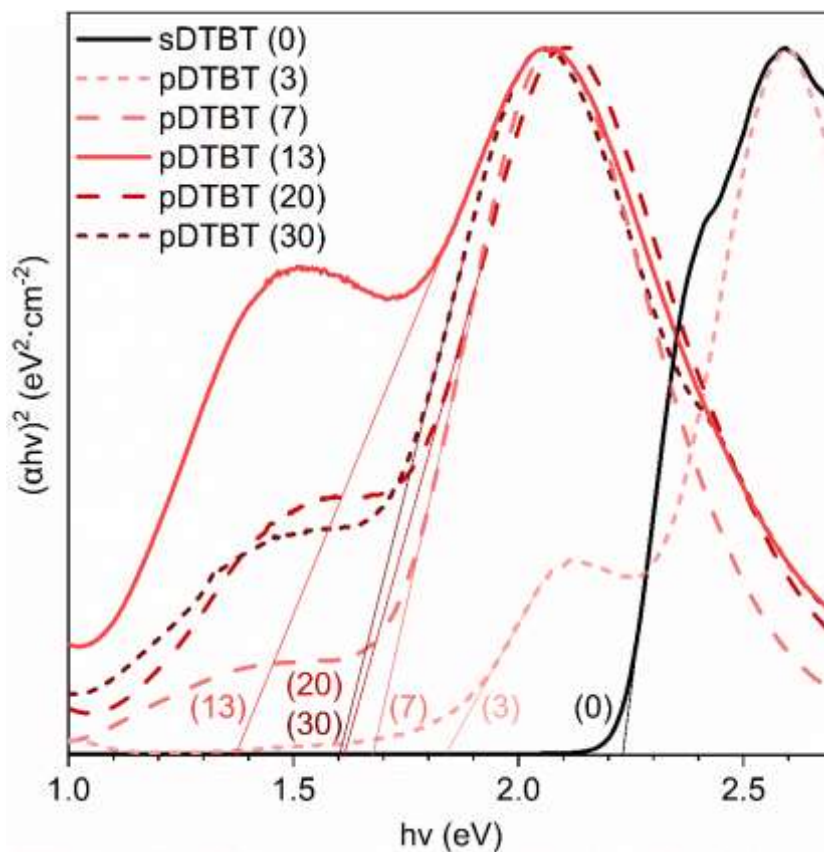
Sample name	sDTBT (0)	pDTBT (3)	pDTBT (7)	pDTBT (13)	pDTBT (20)	pDTBT (30)
Operating pressure	10 <sup>-3</sup> mbar					
Substrate temperature	100°C					
Monomer	4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT)					
Molecular formula	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> S <sub>3</sub>					
Molecular weight	299.98 g·mol <sup>-1</sup>					
Sublimation temperature	105°C					
Sublimed amount	8.8 ± 0.6 mg 29.3 ± 2.1 μmol					
Oxidant	N/A	Iron (III) chloride (FeCl <sub>3</sub> )				
Molecular formula		FeCl <sub>3</sub>				
Molecular weight		160.84 g·mol <sup>-1</sup>				
Sublimation temperature		110°C	130°C	140°C	150°C	170°C
Sublimed amount		13.5 mg 83.9 μmol	38.9 mg 241.9 μmol	55.1 mg 342.6 μmol	90.6 mg 563.3 μmol	136.0 mg 845.6 μmol
Oxidant to monomer molar ratio	0.0	2.9	7.0	12.5	20.1	30.2



**Scheme S1.** Schematic of the custom-built oCVD reactor used for the preparation of the sublimed **sDTBT (0)** and oCVD **pDTBT** thin films prepared from the oCVD reaction of 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) and iron (III) chloride (FeCl<sub>3</sub>) for different oxidant (FeCl<sub>3</sub>) to monomer (DTBT) ratios (molar ratio provided in parentheses). Two crucibles, placed at the bottom of the oCVD chamber and oriented upward towards the heated substrate holder (100°C), are used to sublime DTBT (105°C) and the oxidant (110°C-170°C).

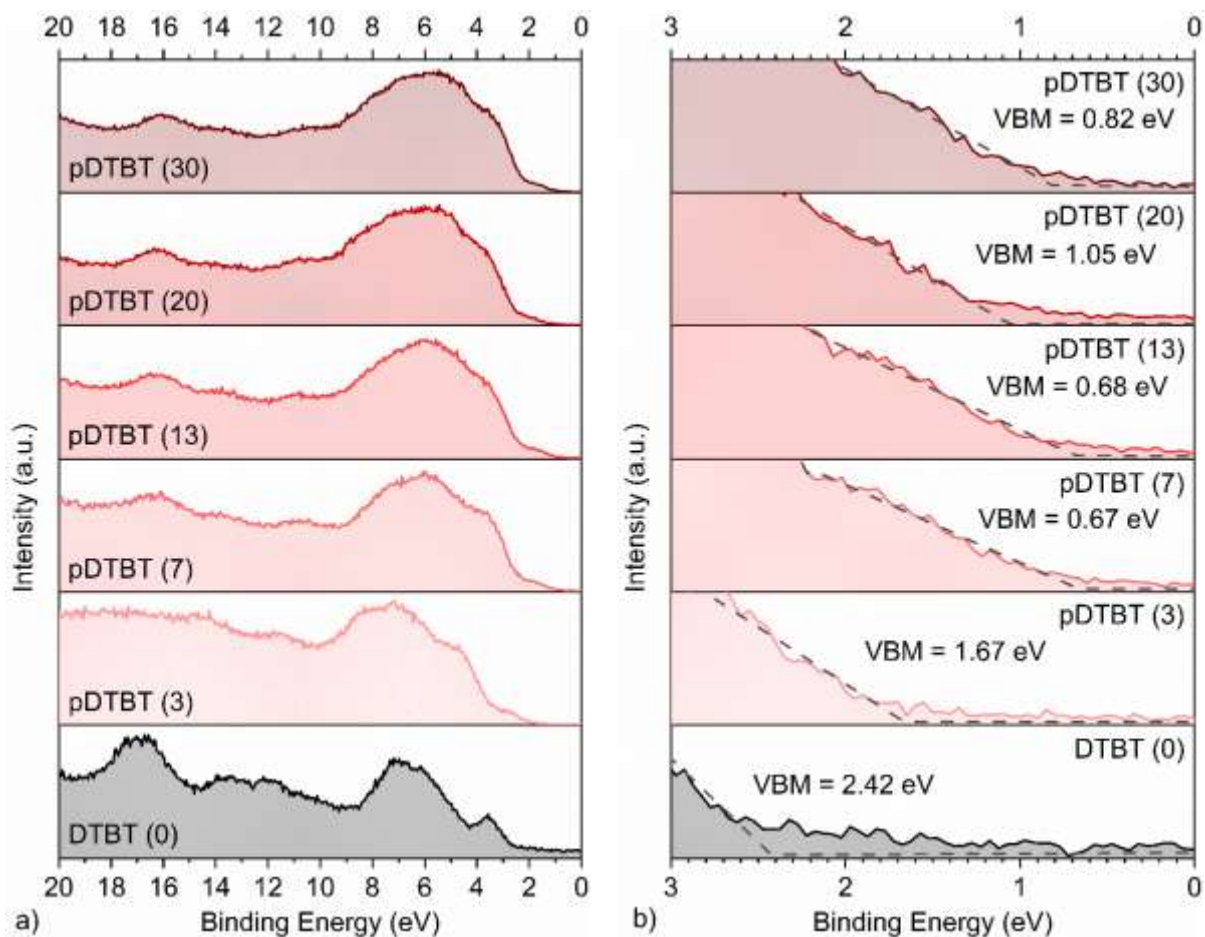


**Figure S1.** High magnification top view SEM images (left) and AFM topography images (right) of the sublimed **sDTBT (0)** and oCVD **pDTBT** thin films, *i.e.* **pDTBT (13)** and **pDTBT (30)**, prepared from different oxidant ( $\text{FeCl}_3$ ) to monomer (DTBT) ratios (molar ratio provided in parentheses). SEM and AFM analyses of the **pDTBT (13)** and **pDTBT (30)** reveal the formation of rather dense coatings with a rugged or granular surface. Upon increase of the oxidant to monomer ratio, the size of the main features observed at the surface increases. On the other hand, **sDTBT (0)** exhibits a smoother surface dotted with domes of 100-400 nm wide and 8-12 nm height possibly arising from the  $\pi$ - $\pi$  stacking of the non-polymerised DTBD units.



**Figure S2.** Tauc's plot as a function of  $(\alpha h\nu)^2$  on photon energy  $h\nu$  for the sublimed **sDTBT (0)** coating (black) and the oCVD **pDTBT** (red gradient) thin films prepared from DTBT and different oxidant ( $\text{FeCl}_3$ ) to monomer (DTBT) ratios (molar ratio provided in parentheses).





**Figure S3.** Valence band (VB) edge XPS spectra for the **DTBT (0)** monomer (black) and the oCVD **pDTBT** (red gradient) thin films prepared from DTBT and different oxidant ( $\text{FeCl}_3$ ) to monomer (DTBT) ratios (molar ratio provided in parentheses).

**Table S2.** Energy band gap, valence band maximum (VBM) and conduction band minimum (CBM) of the sublimed **sDTBT (0)** coating or **DTBT (0)** monomer and the oCVD **pDTBT** (red gradient) thin films pared from DTBT and different oxidant (FeCl<sub>3</sub>) to monomer (DTBT) ratios (molar ratio provided in parentheses). The energy band gap was evaluated from the Tauc plot (Figure S2), while the VBM values were obtained from the valence band XPS spectra (Figure S3). The VBM values were corrected with the work function of the XPS equipment (4.43 eV). The CBM values are calculated from the energy band gap and the VBM values.

Sample	Energy band gap (eV)	VBM from XPS (eV)	VBM vs. vacuum (eV)	CBM vs. vacuum (eV)
<b>sDTBT (0)</b>	2.23	-2.42	-6.85	-4.62
<b>pDTBT (3)</b>	1.83	-1.67	-6.10	-4.27
<b>pDTBT (7)</b>	1.68	-0.67	-5.10	-3.42
<b>pDTBT (13)</b>	1.38	-0.68	-5.11	-3.73
<b>pDTBT (20)</b>	1.62	-1.05	-5.48	-3.86
<b>pDTBT (30)</b>	1.60	-0.82	-5.25	-3.65