Supplementary Electronic Information

Directional Charge Carriers Transport in Oriented Benzodithiophene Covalent Organic Framework Thin Films

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Section 1. X-ray diffraction of thin BDT-COF film

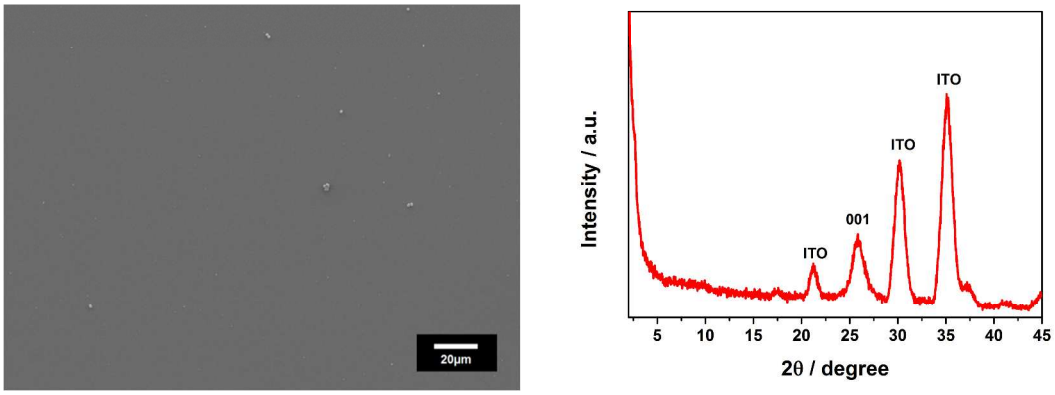

Figure S1.Left) Top view SEM image of BDT-COF thin film grown on ITO. right) XRD pattern of BDT-COF thin film on ITO. The strong and sharp reflection at 26.1° 2θ is related to the stacked 2D COF layers, all other reflections are attributed to the ITO film.

Section 2. UV-vis and Tauc plots

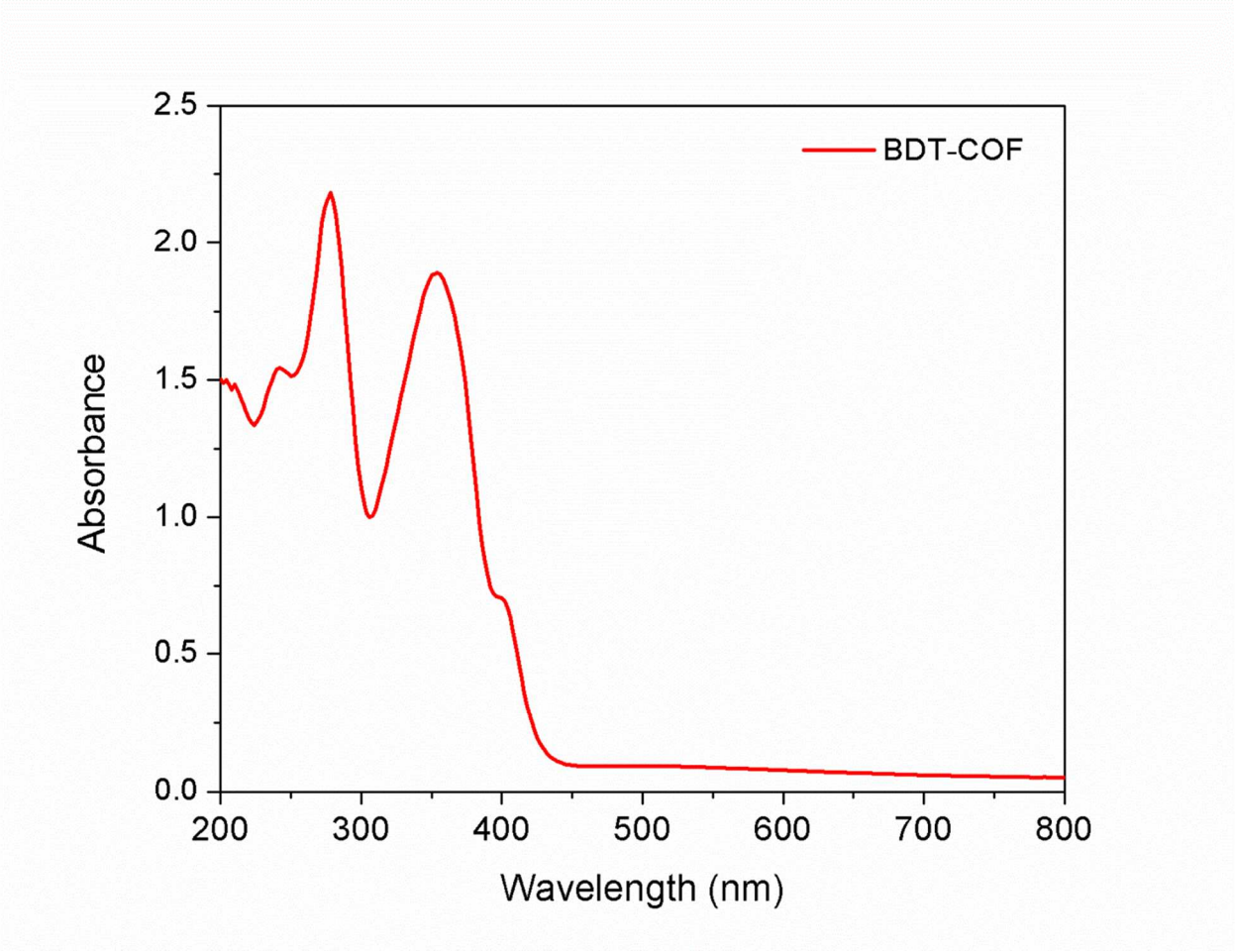

Figure S2. UV-Vis spectra of BDT-COF on a quartz substrate.

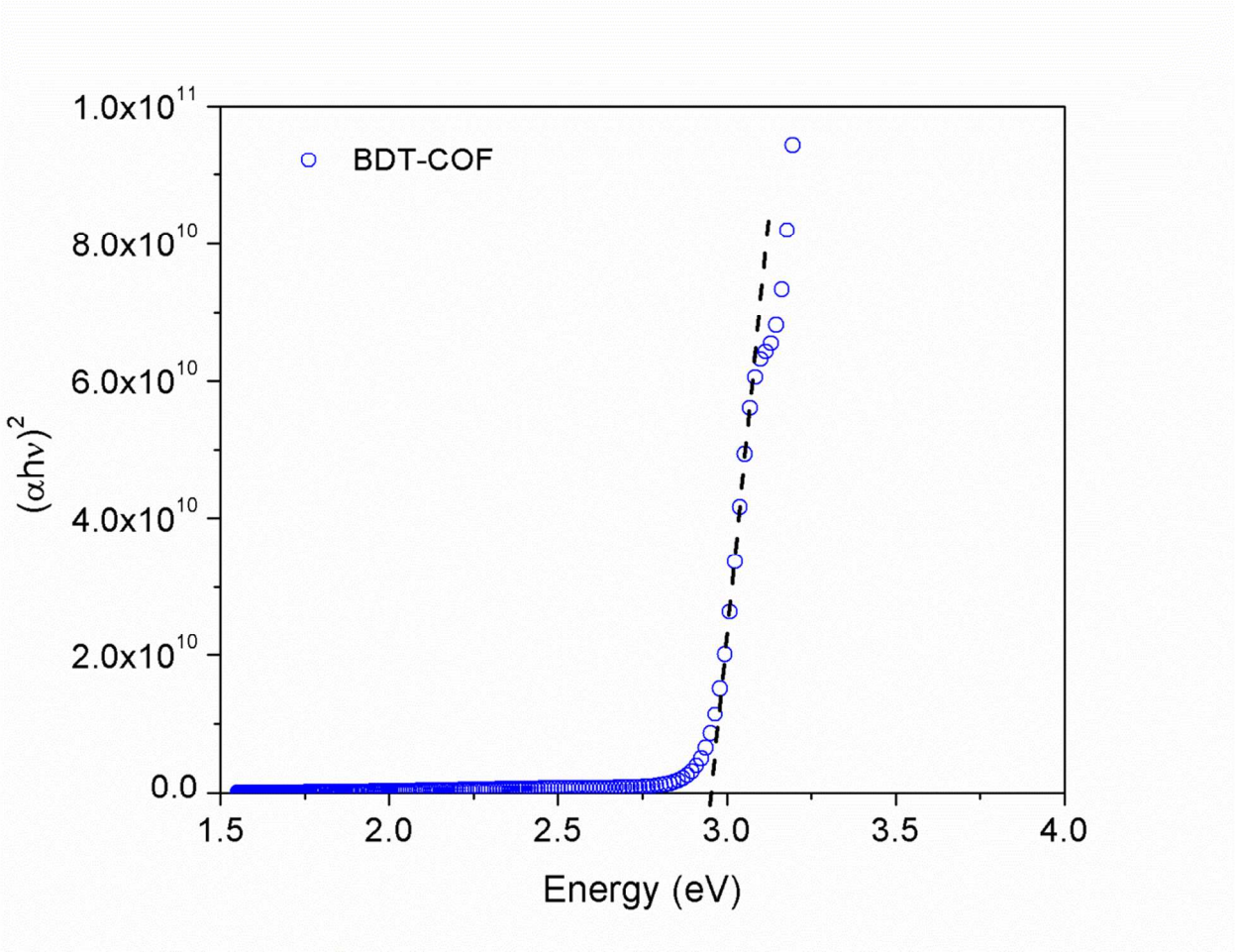

Figure S3.Tauc plot of BDT-COF grown on a quartz substrate.

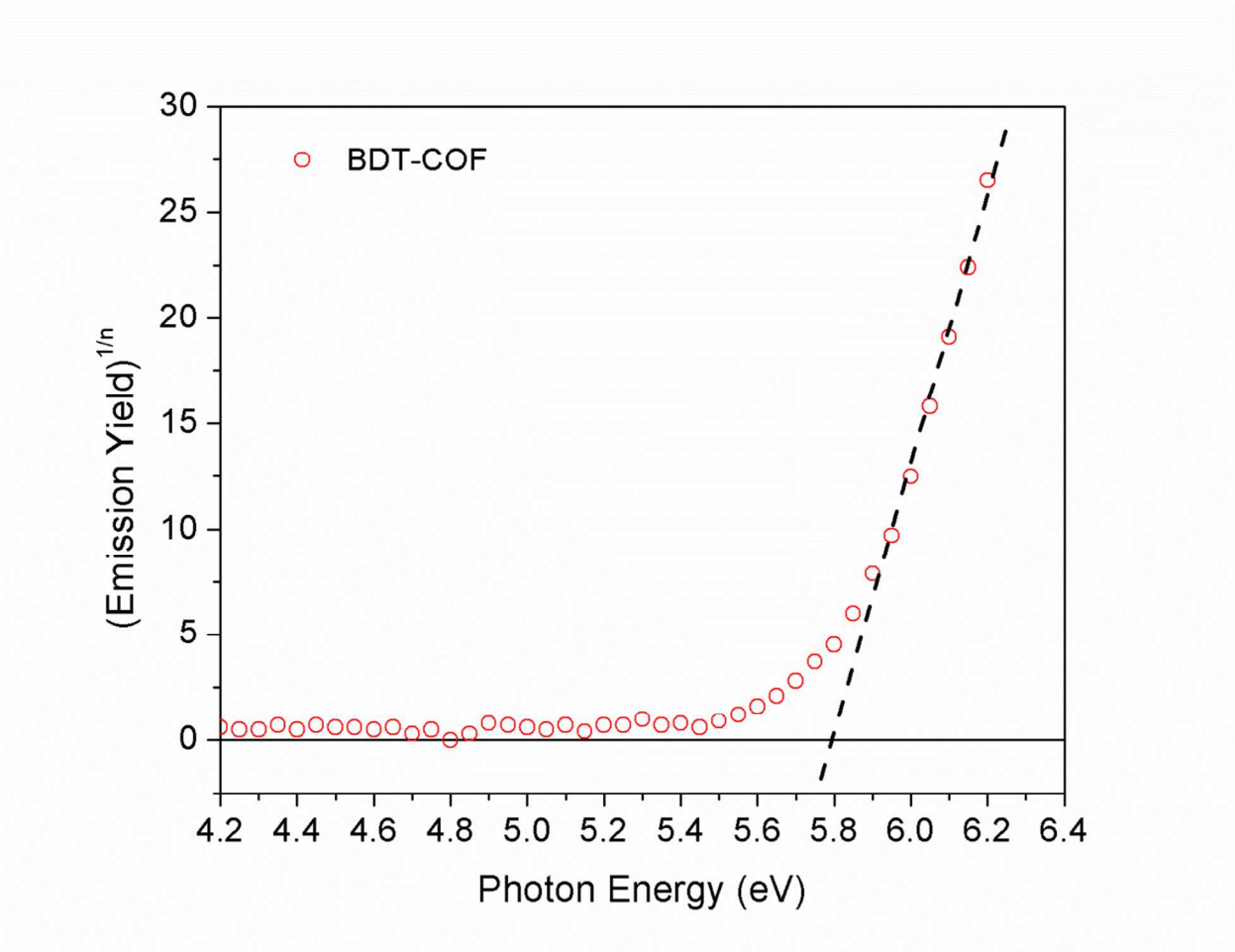

Figure S4. PESA spectra of BDT-COF grown on a quartz substrate.

Section 3. Cross-section SEM of HODs

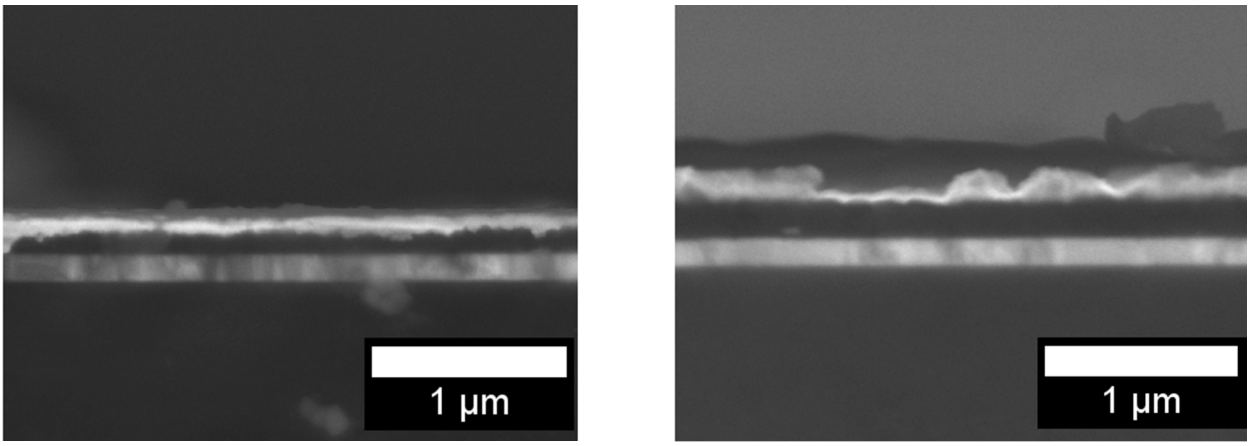

Figure S5. Cross section SEMs of HODs with different thickness: left) 120 nm, right) 150 nm (Evident layers layout of the HODs: ITO/COF/gold)

Section 4: Mobility data

Table S1. Calculated hole mobility for 80-100 nm thick sample in the dark

Device	**μ_h ($cm^2 V^{-1} s^{-1}$)**
1	$5.3 \cdot 10^{-7}$
2	$4.4 \cdot 10^{-7}$
3	$1.2 \cdot 10^{-7}$
4	$1.3 \cdot 10^{-7}$
Average	$3 \cdot 10^{-7}$

Table S2. Calculated hole mobility for 120-150 nm thick sample in the dark

Device	**μ_h ($cm^2 V^{-1} s^{-1}$)**
1	$1.0 \cdot 10^{-8}$
2	$1.2 \cdot 10^{-8}$
Average	$1 \cdot 10^{-8}$

Table S3. Calculated hole mobility for 190-210 nm thick sample in the dark

Device	**μ_h ($cm^2 V^{-1} s^{-1}$)**
1	$5.9 \cdot 10^{-9}$
2	$4.7 \cdot 10^{-9}$
3	$5.1 \cdot 10^{-9}$
Average	$5 \cdot 10^{-9}$

Table S4. Calculated hole mobility for 190-210 nm thick sample in the light

Device	**μ_h ($cm^2 V^{-1} s^{-1}$)**
1	$5.8 \cdot 10^{-8}$
2	$1.5 \cdot 10^{-8}$
3	$1.7 \cdot 10^{-8}$
Average	$3 \cdot 10^{-8}$

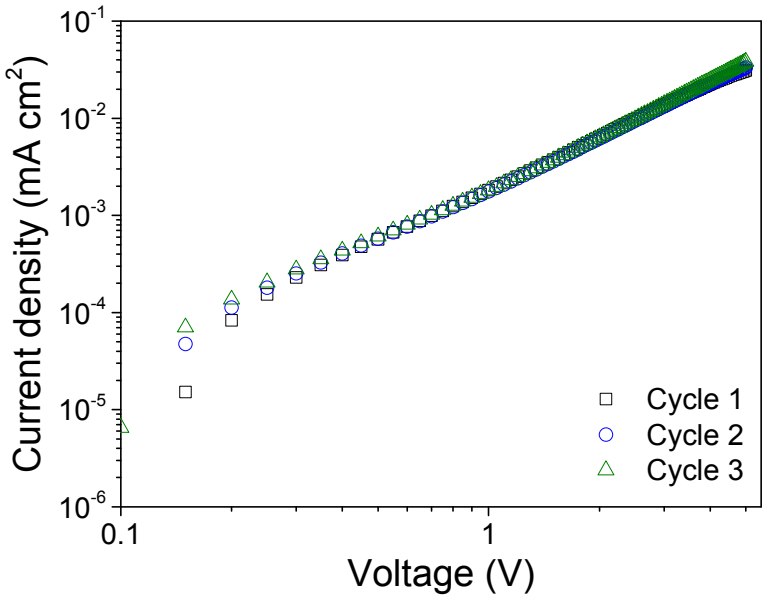

Figure S6. Current density as a function of voltage (*J*-*V*) of a single hole-only device containing BDT-COF layers measured three consecutive times under ambient conditions.

Section 5. In-plane Conductivity

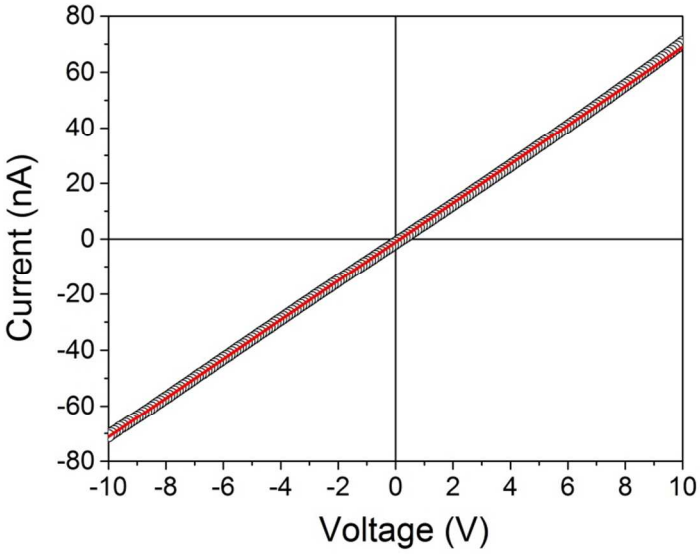

Figure S7. Photocurrent obtained for oriented BDT-COF films on interdigitated Au electrodes as a function of applied voltage. The red line shows a linear fit through the data points.

Section 6. MD simulations

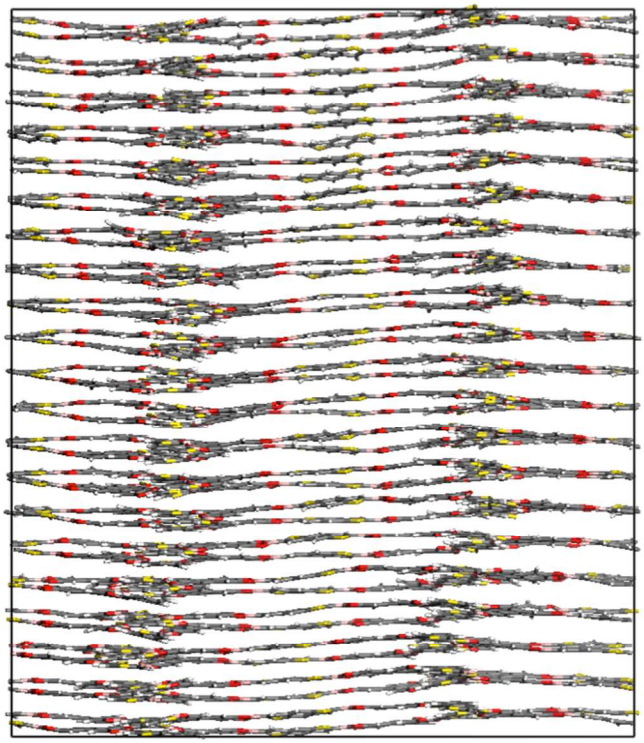

Figure S8. Side view of equilibrated BDT-COF unit cell after a 1 ns MD run, showing the slight waving of individual layers.