

## Electronic Supplementary Information

# Functionalization of Boron-Doped Diamond with a Push-Pull Chromophore via Sonogashira and CuAAC Chemistry

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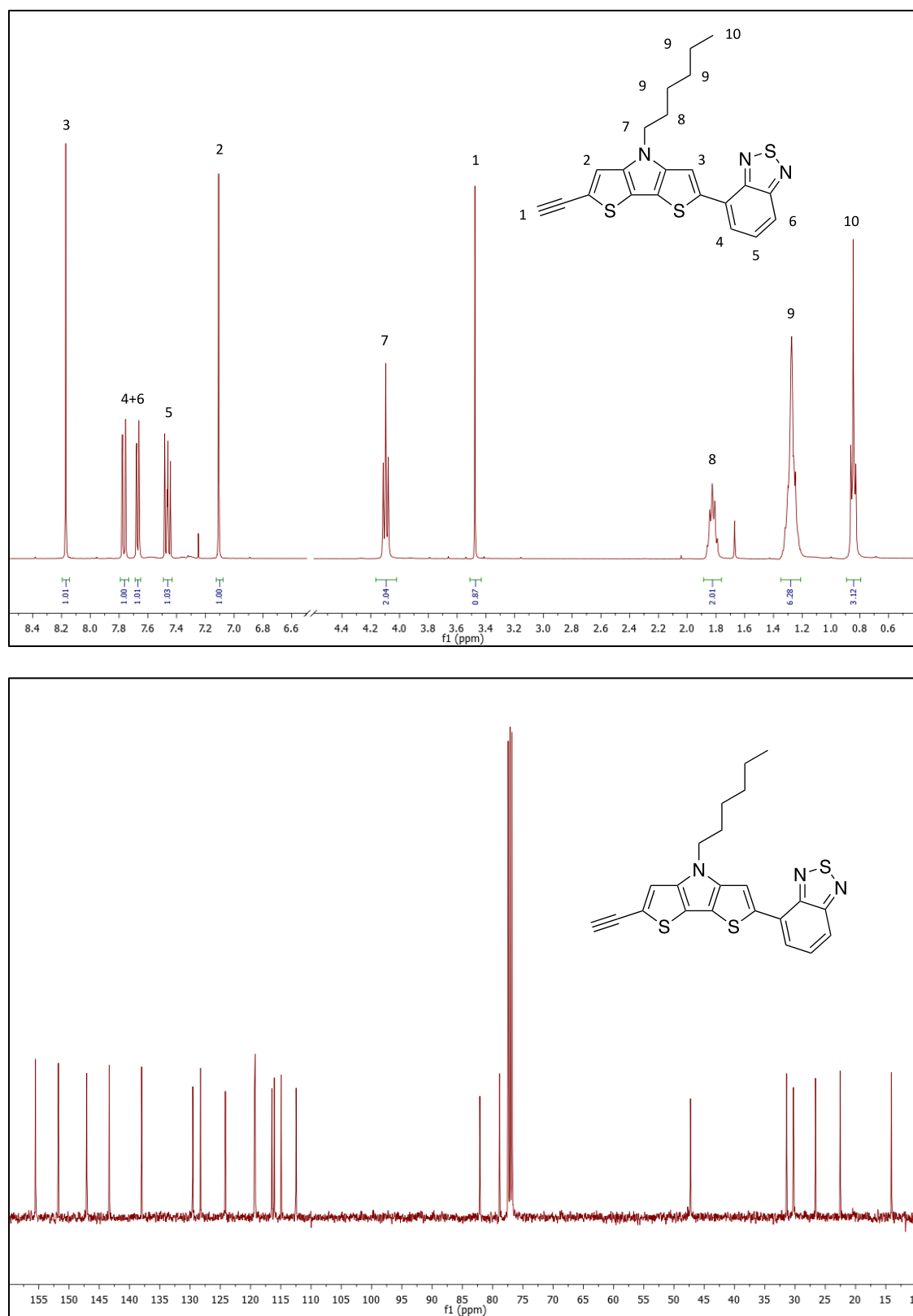
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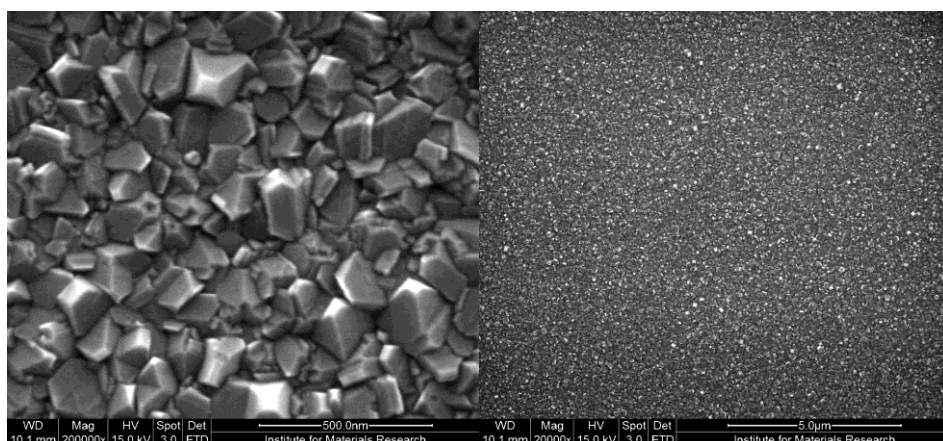
# 1. NMR Spectra



**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2-(benzo[2,1,3]thiadiazol-4-yl)-6-ethynyl-4-hexyl-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (**9**) in  $\text{CDCl}_3$  (400/100 MHz).

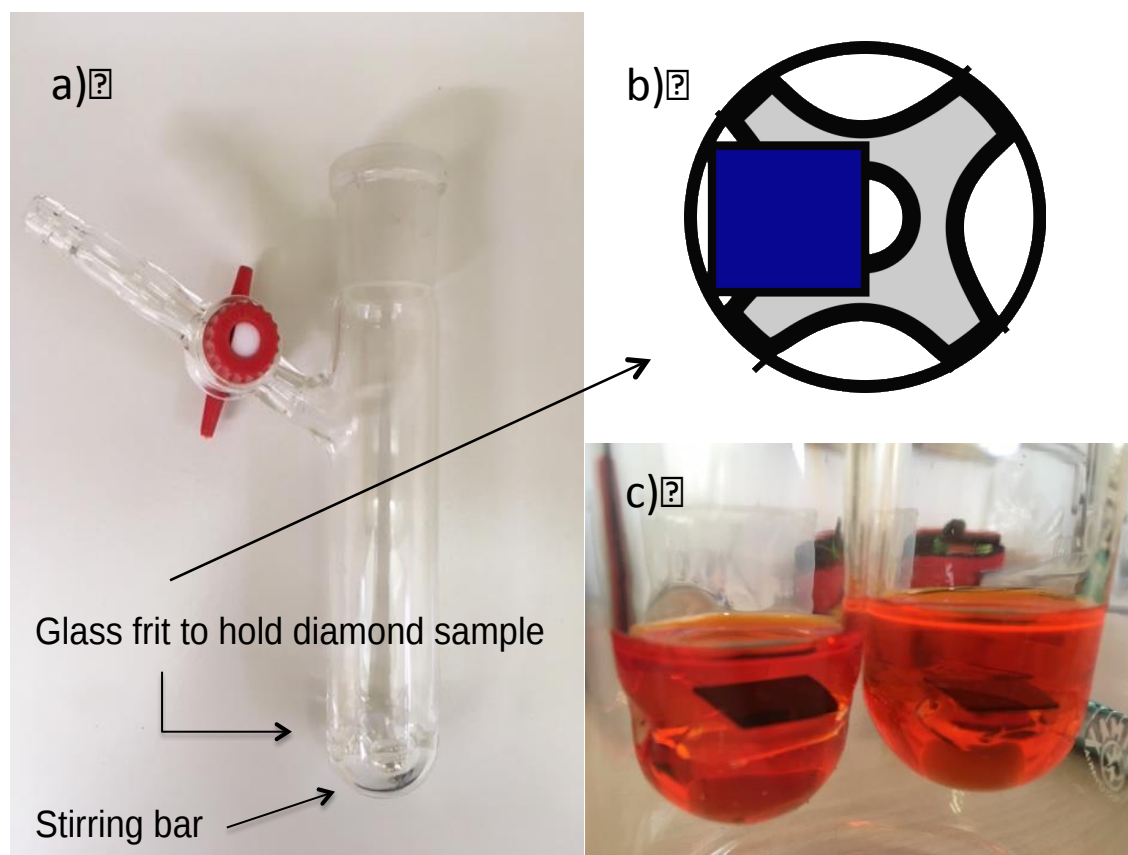
## 2. Diamond Growth

B:NCD depositions were performed at 30 Torr with an applied forward microwave power of 3500 W in a 2.45 GHz ASTeX 6500 series reactor. A total flow rate of 500 sccm, a 1% CH<sub>4</sub> in H<sub>2</sub> concentration and a trimethylborane/CH<sub>4</sub> ratio of 20000 ppm (2%) were kept constant. Thicknesses were determined *in situ* from the interference fringes in the reflection spectrum of a 473 nm laser. The depositions were stopped once the desired thickness of 150 nm was reached, with a growth rate of approximately 2.3 nm/min. Sample morphologies of the films were investigated using an FEI Quanta 200F field emission gun scanning electron microscope (FEG-SEM). All of the samples showed similar growth morphologies to the representative SEM images shown below (Figure S2).



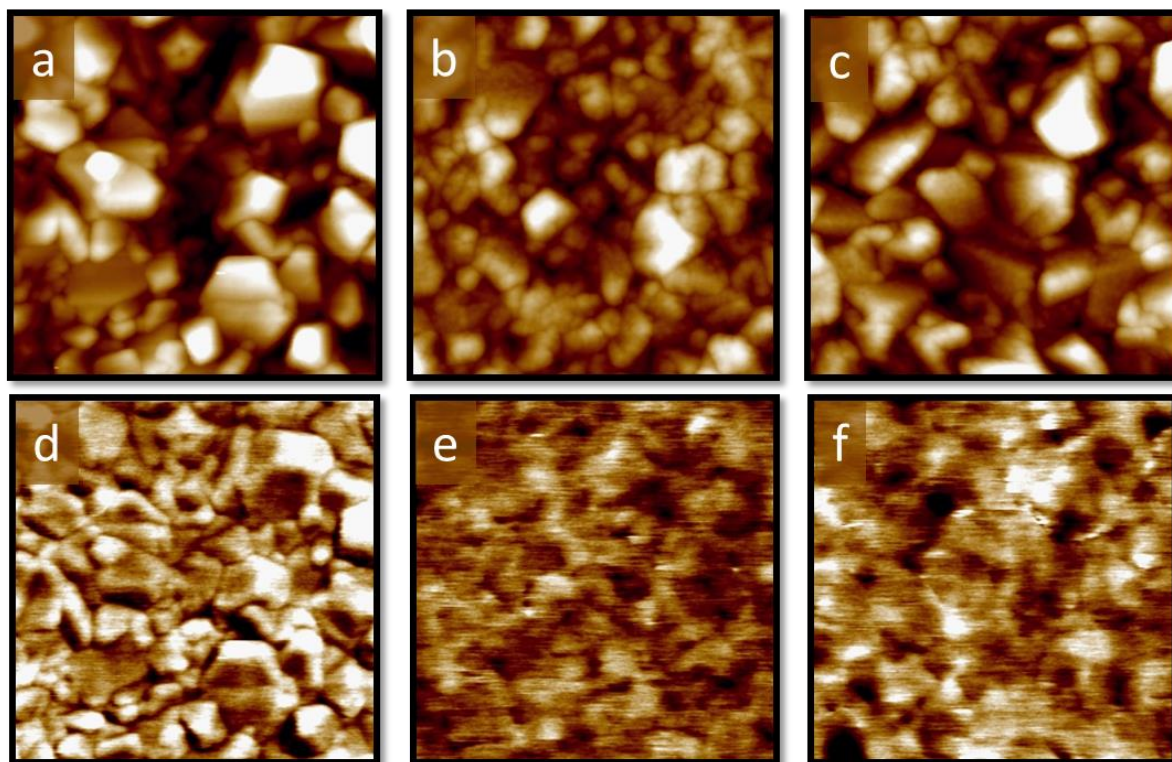
**Figure S2.** Field emission gun scanning electron microscope (FEG-SEM) images of freshly grown H-terminated B:NCD thin films.

### 3. Schlenk Vials for Diamond Surface Functionalization



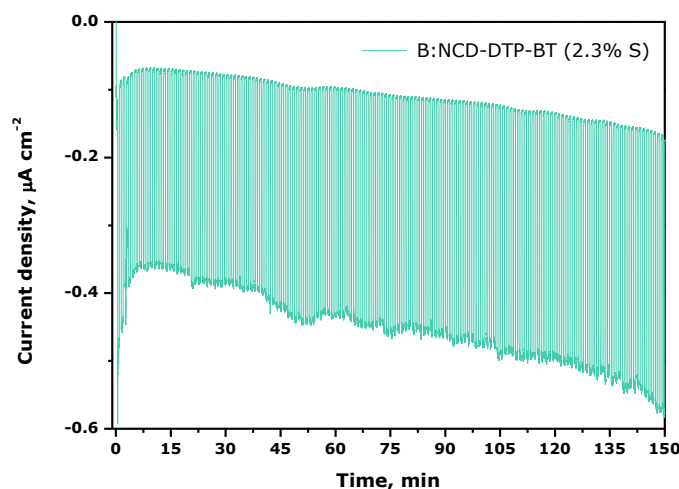
**Figure S3.** a) Tailor-made Schlenk vial equipped with a porous glass frit. The holes in the frit are large enough for a stirring bar to pass through, but the diamond samples remain on top. This allows stirring during the reaction without damaging the substrates. b) Schematic representation of the glass frit (gray) with a diamond sample on top (blue). c) Surface functionalization of a B:NCD sample with the push-pull chromophore.

#### 4. AFM Measurements

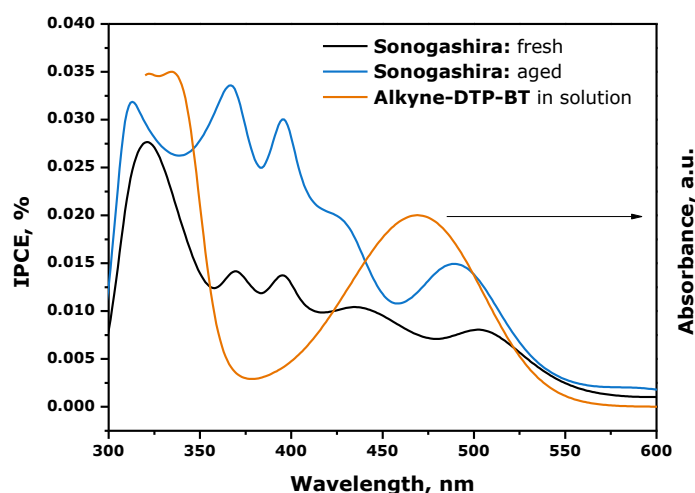


**Figure S4.** AFM topographies of a) a bare B:NCD thin film substrate terminated by hydrogen, b) a B:NCD film with the chromophore grafted via CuAAC chemistry, and c) a B:NCD film with the chromophore grafted via Sonogashira cross-coupling. The RMS roughness of the surface is 13, 10, and 13 nm, respectively. Below the AFM topographies, the corresponding KPFM potential images are depicted (d-f). RMS values of the potential images are 4.8, 3.2, and 4.2 mV, respectively.

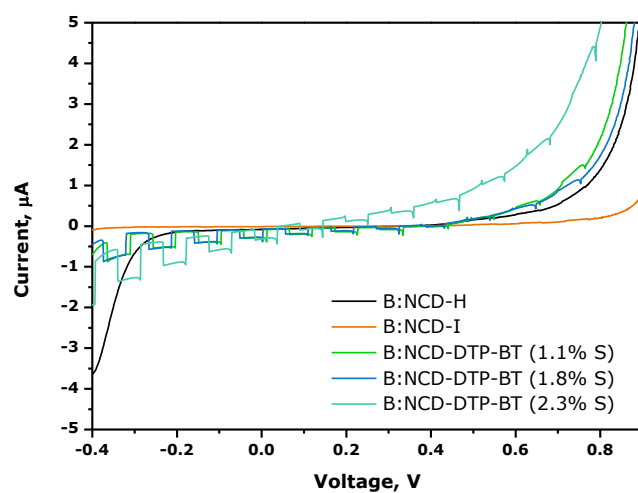
## 5. Photoelectrochemical Measurements



**Figure S5.** Photocurrent densities ( $\mu\text{A cm}^{-2}$ ) of a B:NCD-DTP-BT functionalized diamond electrode in a 5 mM methyl viologen solution (in 0.1 M  $\text{Na}_2\text{SO}_4$ ) under white light illumination ( $90 \text{ mW cm}^{-2}$ ; simulated AM 1.5G solar spectrum, 30 s 1:1 dark/light interval) at a bias of  $-0.3 \text{ V}$ . Surface functionalization was performed via Sonogashira cross-coupling. After an initial photocurrent of *ca.*  $500 \text{ nA cm}^{-2}$ , a steep decrease is observed. However, after illuminating for approximately 15 minutes, the photocurrents starts increasing again.



**Figure S6.** Incident photon-to-current efficiencies (IPCEs) for fresh (black curve) and aged (150 min, blue curve) B:NCD-DTP-BT samples functionalized via Sonogashira cross-coupling. The orange curve represents the UV-VIS absorption spectrum of the alkyne-DTP-BT chromophore.



**Figure S7.** Chopped light polarization curve for H-terminated (B:NCD-H), iodophenyl functionalized (B:NCD-I) and DTP-BT functionalized (B:NCD-DTP-BT) diamond electrodes in a 5 mM methyl viologen solution (in 0.1 M Na<sub>2</sub>SO<sub>4</sub>) under white light illumination (90 mW cm<sup>-2</sup>; simulated AM 1.5G solar spectrum) while changing the applied bias from +0.9 to -0.4 V.