

Supporting Information section

Insights into the Chemistry of Vapor Phase Infiltration for Imaging Non-Fullerene Acceptors

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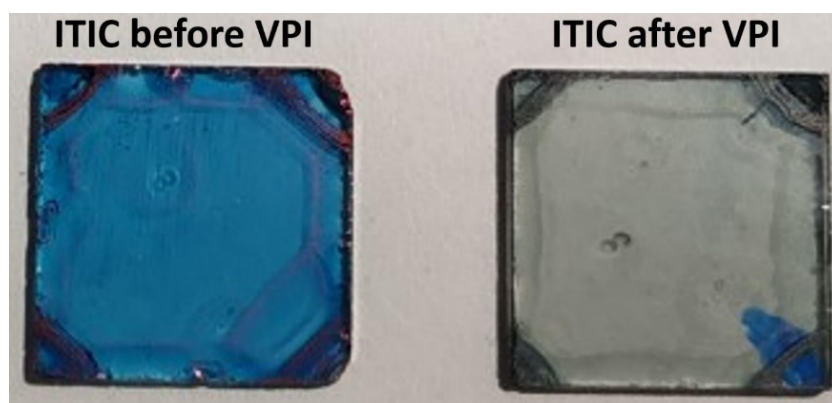


Figure S1- Optical images of ITIC films on a quartz substrate, before (left) and after (right) a VPI of DEZ and water.

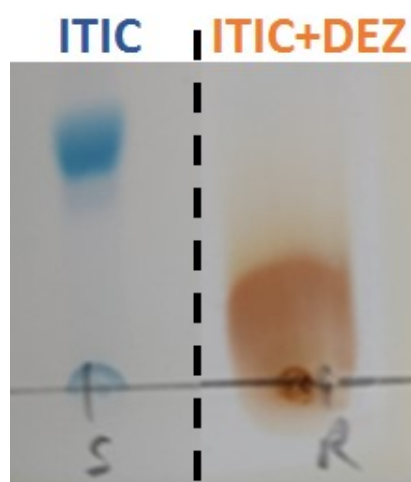
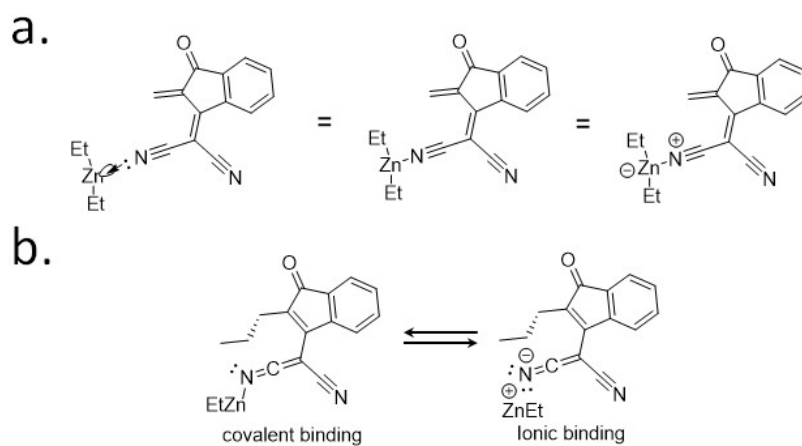
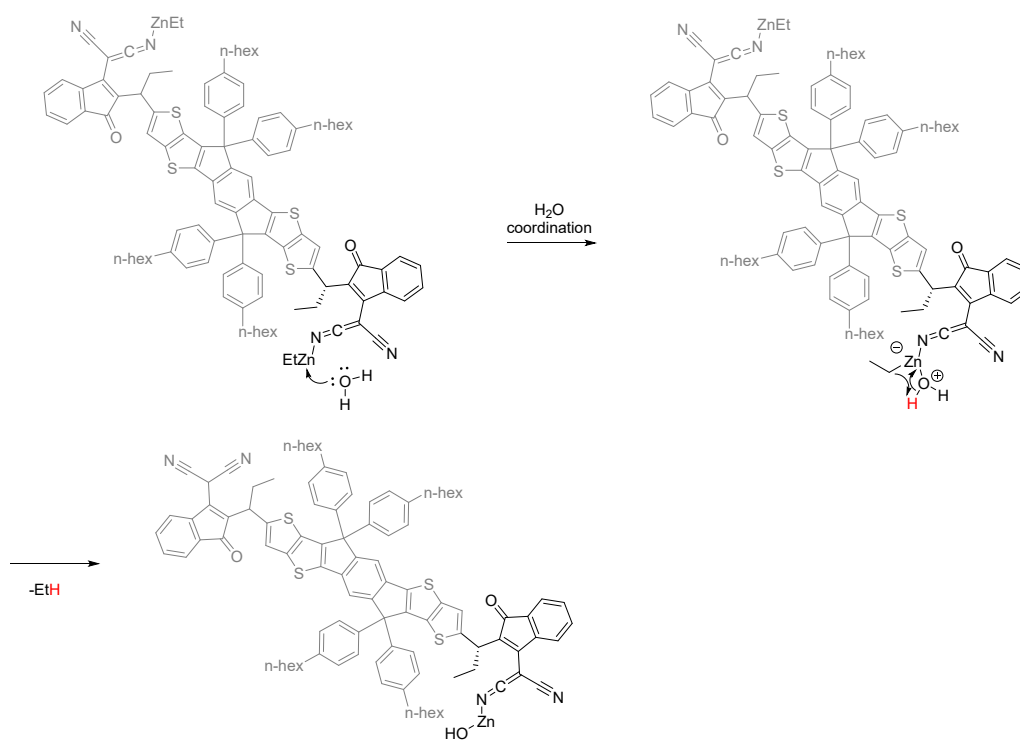


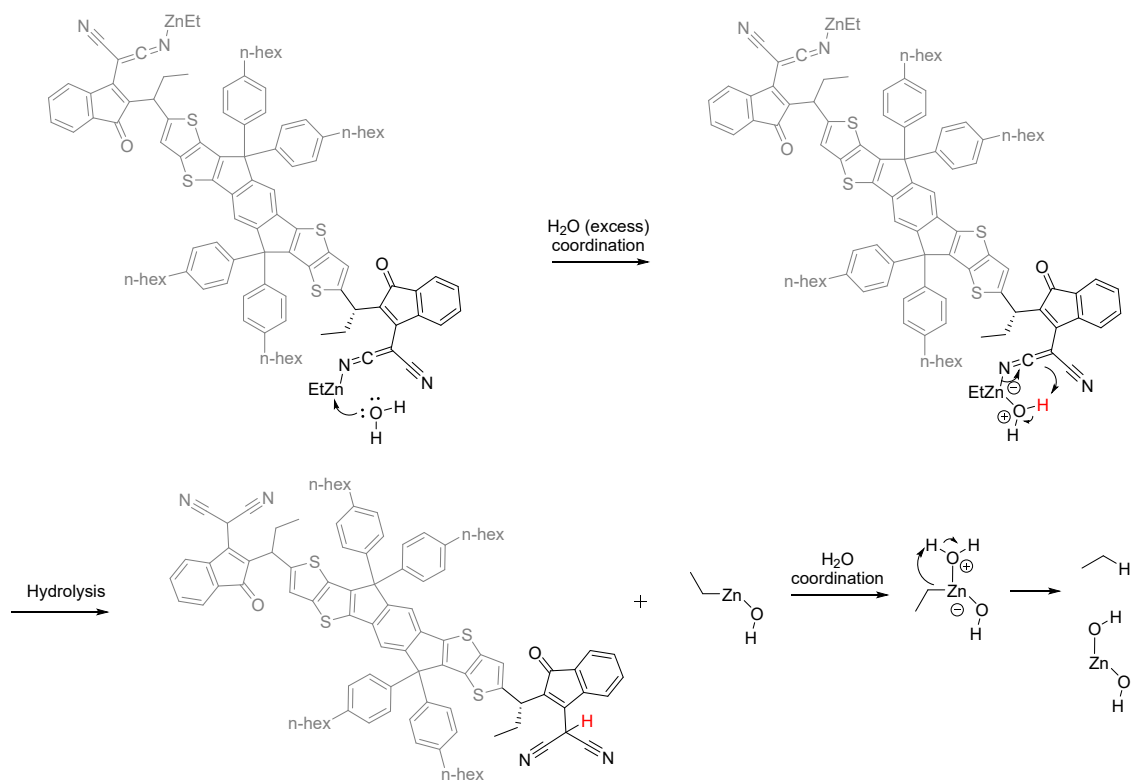
Figure S2- Optical image of the TLC test of ITIC (left) and ITIC after a reaction with DEZ in solution.



Scheme S1- Description of the (a) initial coordination bond on the neutral nitrogen atom and (b) final covalent/ionic bond on the negatively charged nitrogen atom.



Scheme S2- Suggested mechanism for sequential reaction with water vapor during the VPI.



Scheme S3- Suggested mechanism for the full hydrolysis.

NMR Analysis

The ^1H spectra of the ITIC and DEZ reaction product are shown in Figure S3 and Figure S4, respectively. Comparing the spectra indicates that a substantial shift of most signals occurred due to the reaction (a molecule schematics with letter marks is shown in Figure S4). Noteworthy are the new peaks at 3.8-4 ppm with integration corresponding to 2 hydrogens (Figure S4 a). These chemical shifts are characteristics of a conjugated malononitrile formed during the reaction. The existence of two peaks with different intensities could be correlated with products of mono and double addition on the end-capping units on each ITIC molecule. However, the double addition is the major product of the reaction, with a ratio of about 4:1 compared to the mono-addition (based on the intensity ratio of these two peaks). The peak at 3.7 ppm (Figure S4 b) is a strong indication of the addition of the ethyl nucleophile, matching the predicted high shift of a benzylic CH bond next to an extended electron-withdrawing conjugated system. The two new aliphatic peaks at 2.2 ppm and 2.35 ppm are associated with the ethyl CH_2 group that was added during the reaction (Figure S4 c and d). This assignment is further supported by the 2D COSEY NMR shown in Figure S5, showing a clear coupling between these two signals (Figures c and d). These signals also couple with a signal at 1.2 ppm (Figure S4 e) characteristic of a CH_3 group (integrated for 6H in the ^1H NMR spectrum, Figure S4), corroborating that these signals belong to an ethyl group. The presence of a stereocenter in the vicinity of this group would explain the slightly different shift of the two diastereotopic hydrogens at 2.2 and 2.35 ppm (Figure S4 c and d). It is also easily observed that all the aromatic peaks underwent a distinct upfield shift due to the complete deconjugation of the central aromatic system from the electron-withdrawing peripheral aromatic system. Furthermore, the total integration of the aromatic hydrogens is found to be 28H, as expected. The most striking change is the strong shift of the thiophene proton (Figure S4 f), originally a sharp singlet at 8.87 ppm (integration of 2H, Figure S3), to 6.75 ppm (integration of 2H, Figure S4) in the product, characteristic of the resulting electron-rich sulfur heterocycle. The upfield shift of the central phenyl ring, i.e., the doublet signal shift from 8.7 ppm to 8.1 ppm (Figure S4 h), also supports the deconjugation of the central aromatic system. Finally, the peak at 2.6 corresponds to the benzylic hydrogens of the hexyl chain in

both ITIC and the product (Figure S4 g), and the peaks at 3.48 ppm are correlated to the diethylether residue from the extraction.

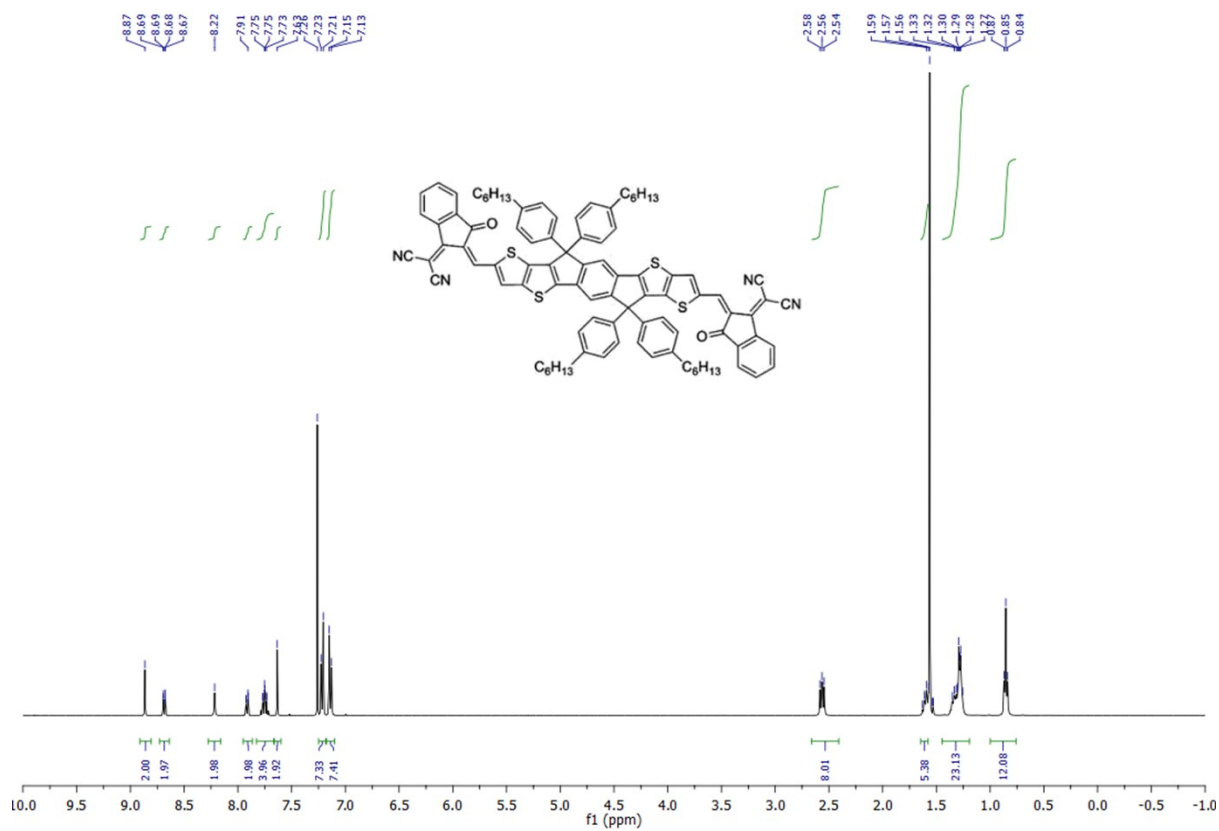


Figure S3- ^1H NMR spectrum of ITIC.

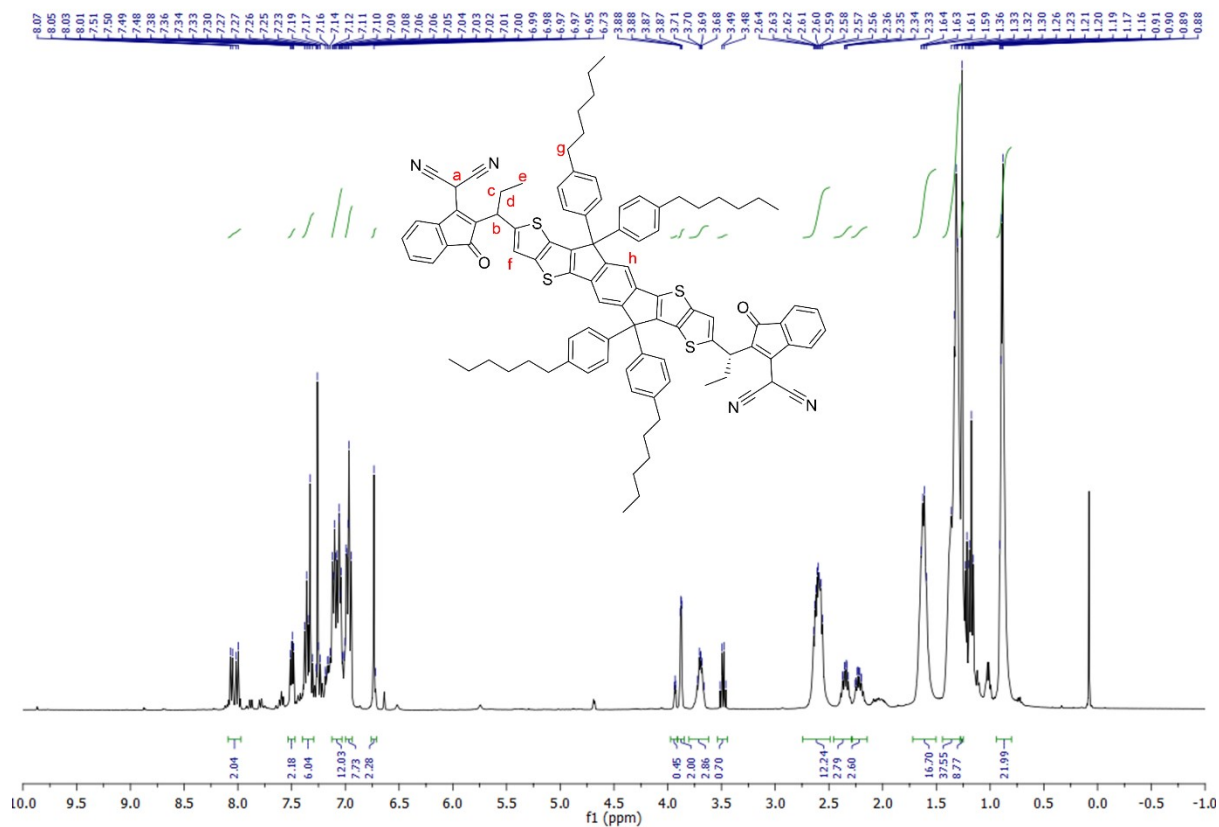


Figure S4- ^1H NMR spectrum of ITIC and DEZ reaction product. The suggested chemical structure of the product includes red letter marks for NMR interpretation. The chemical shift data is presented below

^1H NMR (400 MHz, CDCl_3):

δ 8.03 (dd, $J = 21.3, 7.9$ Hz, 2H), 7.50 (dd, $J = 7.2, 4.8$ Hz, 2H), 7.40 – 7.29 (m, 6H), 7.13 – 7.03 (m, 12H), 7.00 – 6.94 (m, 8H), 6.73 (d, $J = 5.4$ Hz, 2H), 3.97 – 3.91 (m, 1H), 3.88 (dd, $J = 3.6, 1.2$ Hz, 2H), 3.69 (dt, $J = 11.3, 7.6$ Hz, 3H), 3.49 (q, $J = 7.0$ Hz, 1H), 2.74 – 2.49 (m, 12H), 2.45 – 2.28 (m, 3H), 2.23 (ddd, $J = 9.0, 7.3, 2.4$ Hz, 3H), 1.62 (dd, $J = 12.9, 7.3$ Hz, 16H), 1.33 (dd, $J = 14.6, 8.7$ Hz, 37H), 1.26 (s, 9H), 0.90 (dd, $J = 6.7, 4.6$ Hz, 22H).

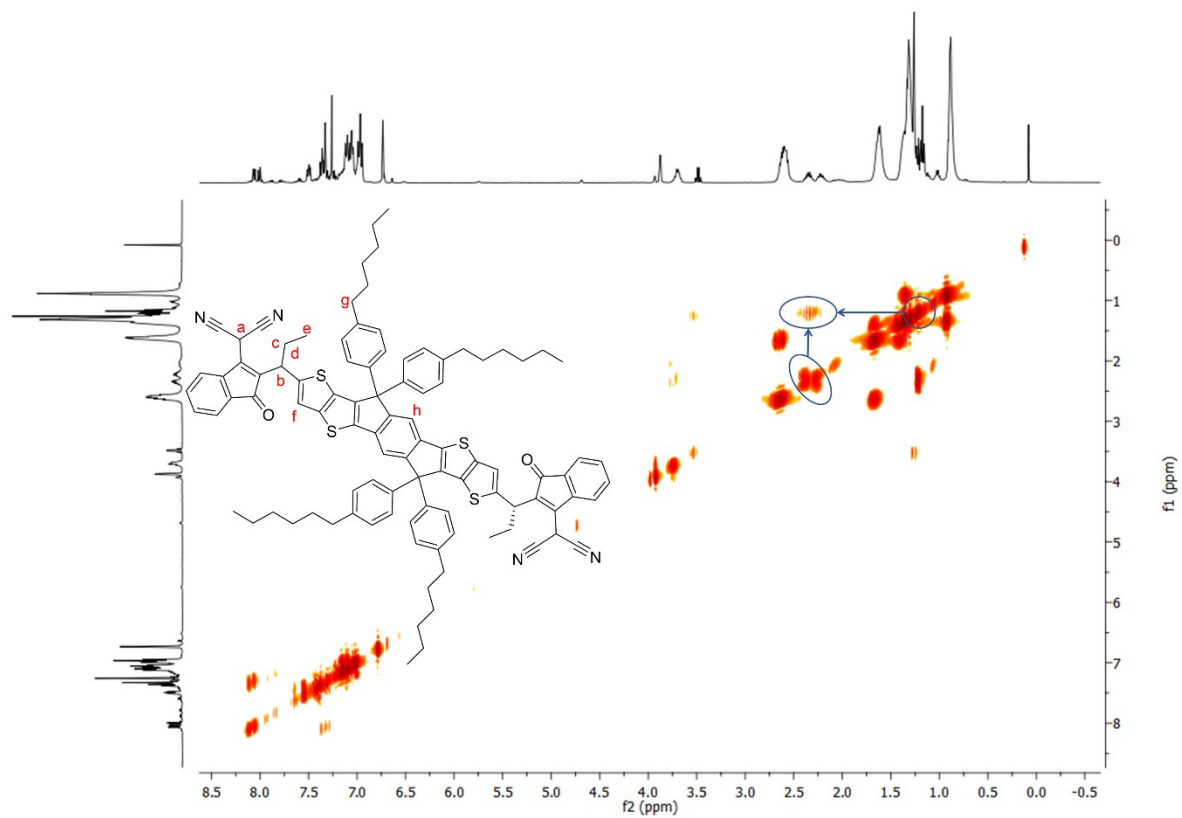


Figure S5- COSEY 2D NMR spectra of the ITIC and DEZ reaction product. Highlighted are the couplings of the added ethyl groups hydrogens.

The ^{13}C NMR spectrum in Figure S6 indicates 21 aromatic carbons (aromatic range: 110-175ppm) as predicted. For the aliphatic carbons (aliphatic range: 10-70ppm), 11 carbons are seen as expected, with the addition of 2 peaks from the diethylether (2 symmetric carbons) residue. Importantly, the carbonyl peak, present at about 200 ppm and characteristic of a ketone signal, remains unchanged, confirming it does not react with the DEZ precursor.

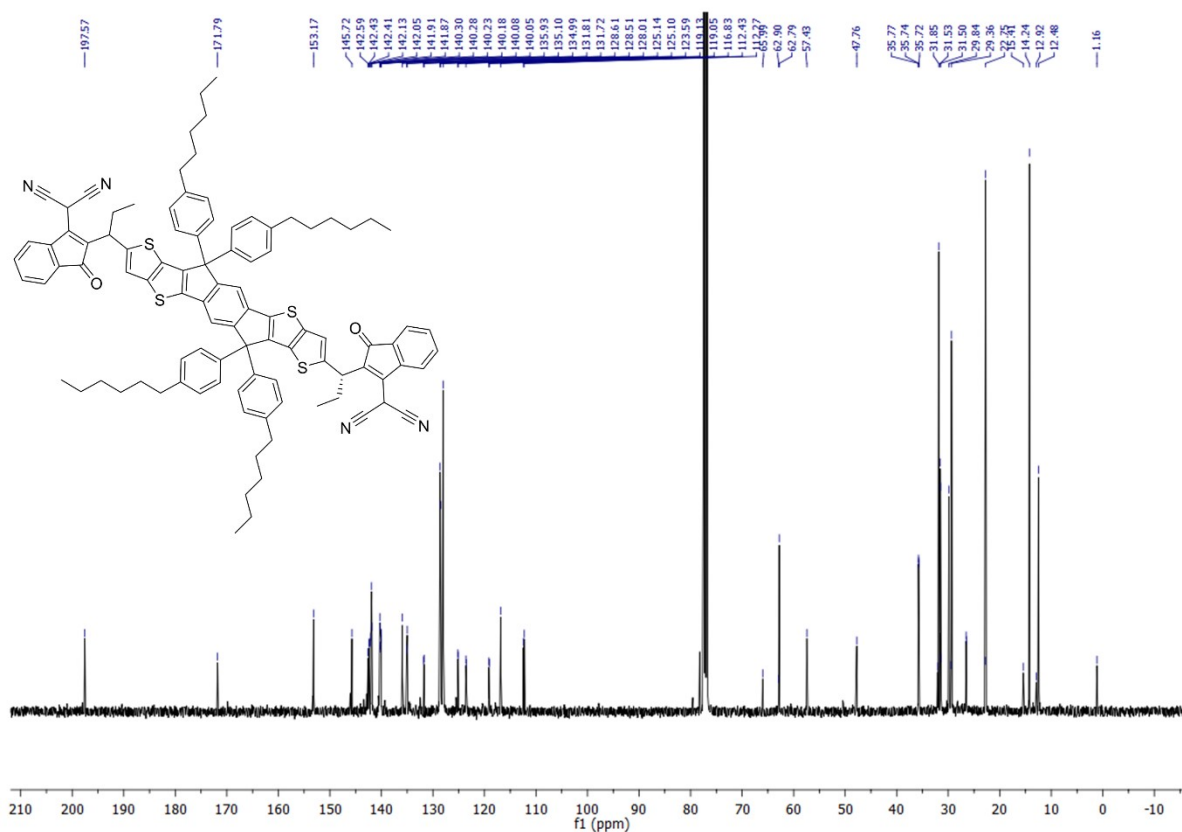


Figure S6- ^{13}C NMR spectrum of ITIC and DEZ reaction product. The chemical shift data is presented below.

^{13}C NMR (101 MHz, CDCl_3):

δ 197.57, 171.79, 153.17, 145.72, 142.59, 142.43, 142.41, 142.13, 142.05, 141.91, 141.87, 140.30, 140.28, 140.23, 140.18, 140.08, 140.05, 135.93, 135.10, 134.99, 131.81, 131.72, 128.61, 128.51, 128.01, 125.14, 125.10, 123.59, 123.50, 119.13, 119.05, 116.83, 112.43, 112.27, 65.99, 62.90, 62.79, 57.43, 47.76, 35.77, 35.74, 35.72, 32.06, 31.85, 31.53, 31.50, 31.43, 29.84, 29.50, 29.36, 26.52, 26.46, 22.83, 22.75, 15.41, 14.24, 12.92, 12.48, 1.

ITIC+DEZ reaction product MS data-

Based on the schematic structure presented in Figure S7 the MS m/z: (direct positive) [M]⁺, calculated for C₉₈H₉₄N₄O₂S₄, is 1486.6260. The spectrum shows the detected intense m/z peak at 1486.6675, confirming the suggested product structure.

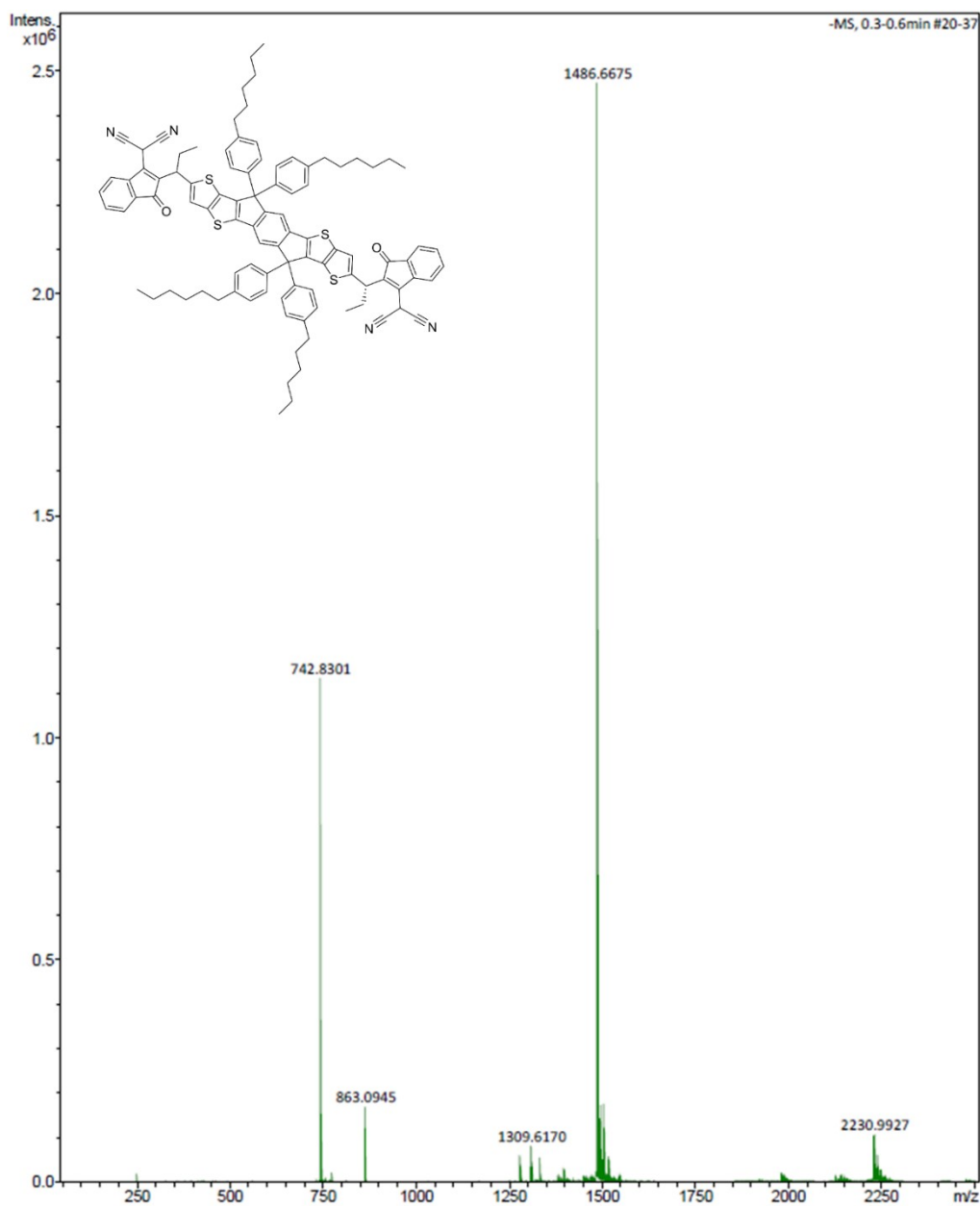


Figure S7- Mass spectroscopy of ITIC+DEZ reaction product

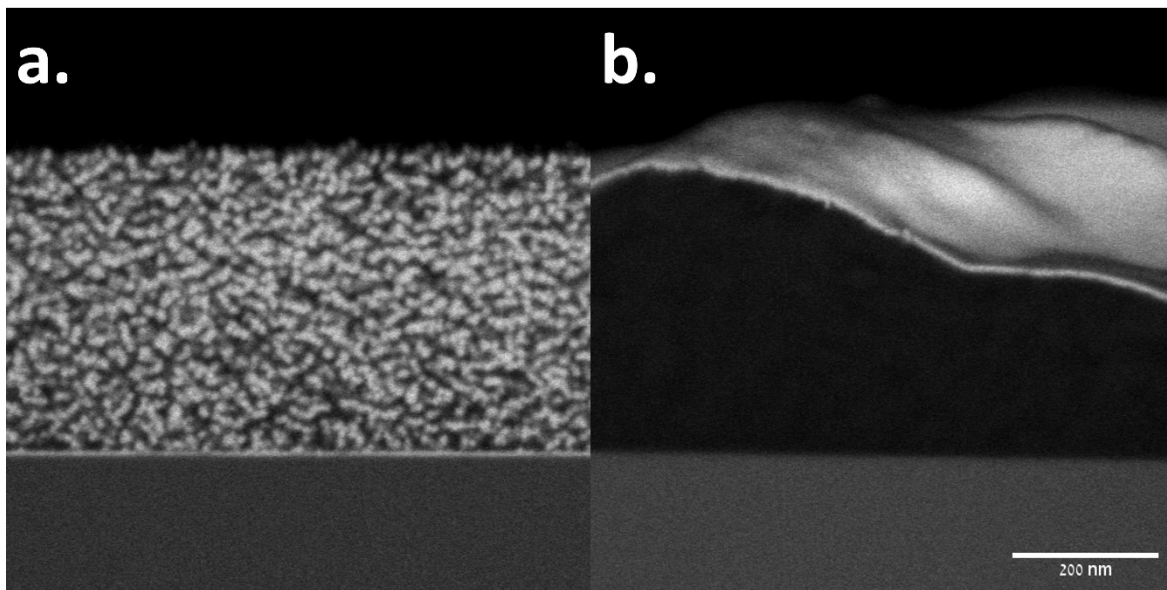


Figure S8- Cross-section HRSEM BSE micrographs of pristine P3HT (left) and ITIC (right) films after a VPI process of TDAHf and water. The process leads to the deposition of HfO₂ particles in P3HT films (bright contrast). In contrast, there is no HfO₂ deposition in ITIC, and hence, ITIC domains are generally characterized by dark contrast. The scale bar for all micrographs is 200nm.

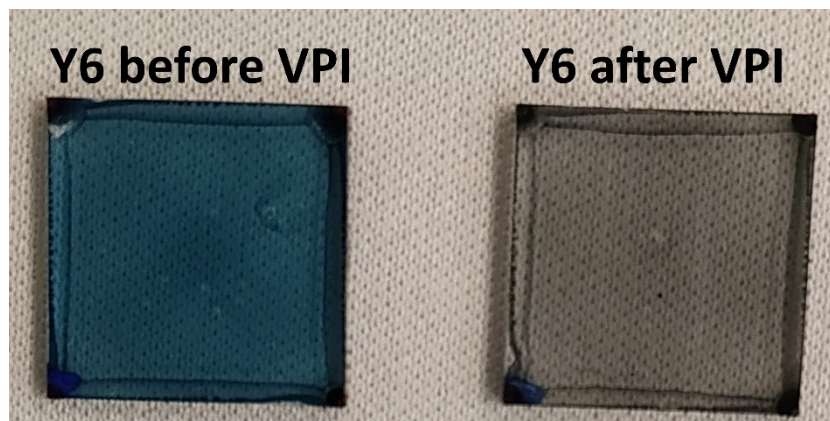


Figure S9- Optical images of Y6 films on a quartz substrate, before (left) and after (right) a VPI process of DEZ and water.