Supporting information

Direct detection of molecular hydrogen upon p- and n-doping of organic semiconductors with complex oxidants or reductants.

Francesca Pallini,[a] Sara Mattiello,[a] Norberto Manfredi,[a] Sara Mecca,[a] Alexey Fedorov,[b] Mauro Sassi,[a] Khaled Al Kurdi,[c] Yi-Fan Ding,[d] Chen-Kai Pan,[d] Jian Pei,[d] Stephen Barlow,[c,e] Seth R. Marder,[c,e,f] Thuc-Quyen Nguyen,[g] Luca Beverina[a]*

[a]Department of Materials Science, Università di Milano-Bicocca, via Cozzi 55, 20125 Milan, Italy

[b]CNR-IFN and L-NESS, via Anzani 42, I-22100 Como, Italy

[c]School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

[d]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center of Soft Matter Science and Engineering and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[e]Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, CO 80303, USA

[f]Department of Chemical and Biological Engineering, Department of Chemistry, and Materials Science and Engineering Program, University of Colorado Boulder, Boulder, CO 80303, USA

[g]Center for Polymers and Organic Solids and Department of Chemistry & Biochemistry, University of California,

Santa Barbara, CA 93106-9510, USA

Content

1. Gas Chromatography – Hydrogen detection experiments

Hydrogen detection experiments on P(NDI2OD-T2) blends with N-DMBI-H were performed with an Agilent 6850 gas-chromatograph (GC) on 50 µL manual gas injections. The same instrument was used to perform experiment on 2CN-BDOPV containing sub-stoichiometric amount of N- DMBI-H. The other samples here described were analysed with an Agilent 8860 GC system on 250 µL manual gas injections. Both instruments are equipped with a Thermal Conductivity Detector (TCD) and a molecular sieve 5 Å column (2 m × 2 mmID, temperature 70 °C) and use argon as carrier gas (flow rate 25 mLmin^{-1}).

Samples were analysed through the following Gas-Chromatographic method:

- Oven temperature: 70 °C
- Hold time: 2 min
- Run time: 2 min

Argon mixtures with 100 ppm and 10000 ppm of H_2 were used for calibration. H_2 concentration values were then evaluated from each chromatogram via peak integration weighed on the obtained calibration line. A 5% error was considered for each value.

All samples were prepared in 2 mL GC glass vials with closures provided of septum. Vials were dried before use and the samples were prepared inside a glove box under argon atmosphere ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm).

1.1. Experiments on N-DMBI-H dopant

N-DMBI-H was synthesised following a previously reported literature procedure[1] and stored under inert atmosphere before use, as was (N-DMBI)$_2$[2]. P(NDI2OD-T2) was purchased from Flexterra (Mn=34.7 kDa, PDI=1.9) and used as received. Anhydrous chlorobenzene (99.8%) was purchased from ACROS and used as received.
NDI-C8 and 2CN-NDI-C6 acceptors were synthesised according to literature procedures[3-5].
2CN-BDOPV and 4CN-BDOPV were synthesised following the procedure reported in section 3.
PC$_{60}$BM was purchased from Solarmer Energy Inc.

After being sealed with parafilm, all samples reported in this section underwent thermal treatment at 150 °C for 2 h in an oil bath outside the glove box before GC analysis

1.1.1. Experiments on P(NDI2OD-T2) blends
Description of sample preparation is reported in the following paragraphs.

P(NDI2OD-T2) and N-DMBI-H blend preparation
P(NDI2OD-T2) powder (19 mg, 0.019 mmol) was mixed with 2 equivalents of N-DMBI-H (11 mg, 0.041 mmol) in a GC vial under inert atmosphere. Anhydrous chlorobenzene (40 µL) was added directly in glove box to the mixture to improve blending between dopant and acceptor. The mixture was kept in the dark under inert atmosphere for 6 h before solvent evaporation under N_2 flow. The vial was then sealed and kept under argon for 18 h before thermal treatment.

N-DMBI-H control experiment preparation
N-DMBI-H powder (10 mg, 0.037 mmol) was weighed in a vial and sealed under argon. The vial was kept for 24 h in the dark under inert atmosphere before thermal treatment.

P(NDI2OD-T2) control experiment preparation
P(NDI2OD-T2) powder (14 mg, 0.015 mmol) was weighed in a GC vial and sealed under argon. The vial was kept in the dark under inert atmosphere for 36 h before thermal treatment.

P(NDI2OD-T2) and (N-DMBI)$_2$ blend preparation
P(NDI2OD-T2) powder (15 mg, 0.015 mmol) was mixed with one equivalent of (N-DMBI)$_2$ (9 mg, 0.016 mmol) in a GC vial under inert atmosphere. 3-4 droplets of anhydrous chlorobenzene were added directly in the glove box to improve blending between dopant and polymer. The blend was not dried under nitrogen flux to avoid any possible hydrogen loss, since the polymer blend had already changed colour from blue to purple after few hours, which might be due to doping of the polymer. The blend was kept under inert atmosphere for 36 h and was then subjected to thermal treatment.

1.1.2. Experiments on acceptor compound different from P(NDI2OD-T2)
All dry blends were prepared according to the following procedure.
Acceptor powder (0.015 mmol) was mixed with 2 equivalents of N-DMBI-H powder (0.03 mmol) in a GC vial. 3-4 droplets of anhydrous chlorobenzene were added directly in glove box to the mixture to improve blending between dopant and acceptor. The vial was then sealed and kept under inert atmosphere at room temperature for 18 h. Solvent was then evaporated under N$_2$ flux, and the vial was sealed again under argon and kept in the dark under inert atmosphere at room temperature for 16 h before thermal treatment.

Wet Blends preparation procedure
Previous work[6] suggests that N-DMBI-H doping can be activated also at room temperature in the presence of a solvent, with noticeable differences in process rates depending on the acceptor used. This means that when preparing blends, molecular H$_2$ might evolve also prior to solvent evaporation under N$_2$ flux. If the doping process is fast enough, most of the hydrogen evolved from the blend might get lost during the drying process. This is true in particular for BDOPV derivatives, that showed fast doping kinetics during in-solution studies preceding this work. For this reason, hydrogen formation measurements were also performed on undried wet blends in the presence of small amount of chlorobenzene.

All wet blends were prepared according to the following procedure. Acceptor powder (0.011 mmol of 4CN-BDOPV, 0.015 mmol of the other acceptors) was mixed with 2 equivalents of N-DMBI-H powder (0.022 mmol with 4CN-BDOPV, 0.030 mmol with the other acceptors) in a GC vial. 3-4 droplets of anhydrous chlorobenzene were added directly in glove box to the mixture to improve blending. The vial was then sealed under Argon and kept in the dark, under inert atmosphere at room temperature for one day before thermal treatment.
Figure S1 shows chromatograms obtained from analysis of wet blends. **Table S1** reports results obtained from peak integration of the chromatograms.

Table S1: concentration of hydrogen detected from injections of gas mixtures coming from wet blends samples. H$_2$ concentration values were obtained from area integration of hydrogen related peaks and evaluated according to calibration lines. *This sample was prepared with 0.011 mmol of 4CN-BDOPV and 0.022 mmol of N-DMBI-H.

Acceptor	H$_2$ Concentration
2CN-NDI-C6	108 ppm
NDI-C8	1620 ppm
PC$_{60}$BM	-
2CN-BDOPV	18 ppm
4CN-BDOPV*	18 ppm

Obtained values confirm formation of hydrogen after thermal treatment in both samples obtained from NDI derived acceptors (2CN-NDI-C6 and NDI-C8). Integration values still suggest the hydrogen evolution process to be more efficient with NDI-C8 acceptor. Hydrogen concentration values detected are lower for NDI-C8 sample in comparison to those obtained with dry blends. Values obtained from 2CN-NDI-C6 are instead higher. These variations can be connected to the effects of solvent presence and sample preparation procedure, but also to differences in blends homogenization and dopant distribution in the samples.

Values obtained from both BDOPV derivatives show higher production of hydrogen in comparison to dry samples. These differences are relevant and can be interpreted as sign of hydrogen evolution before thermal treatment (H_2 lost in dry samples due to exposition to N_2 flux) or faster doping rates induced by chlorobenzene presence during heating.

The efficiency of hydrogen production is slightly higher for 4CN-BDOPV blends than for 2CN-BDOPV blends, when considering the lower amount of 4CN-BDOPV used. The concentration of H_2 detected are 6 times lower than those obtained with 2CN-NDI-C6 and 90 times lower than those obtained with NDI-C8. This can point out either that doping efficiency is lower compared to NDI derivatives (at least in our working conditions) or that hydrogen evolution from BDOPV derivatives is probably not the main pathway in the doping process.

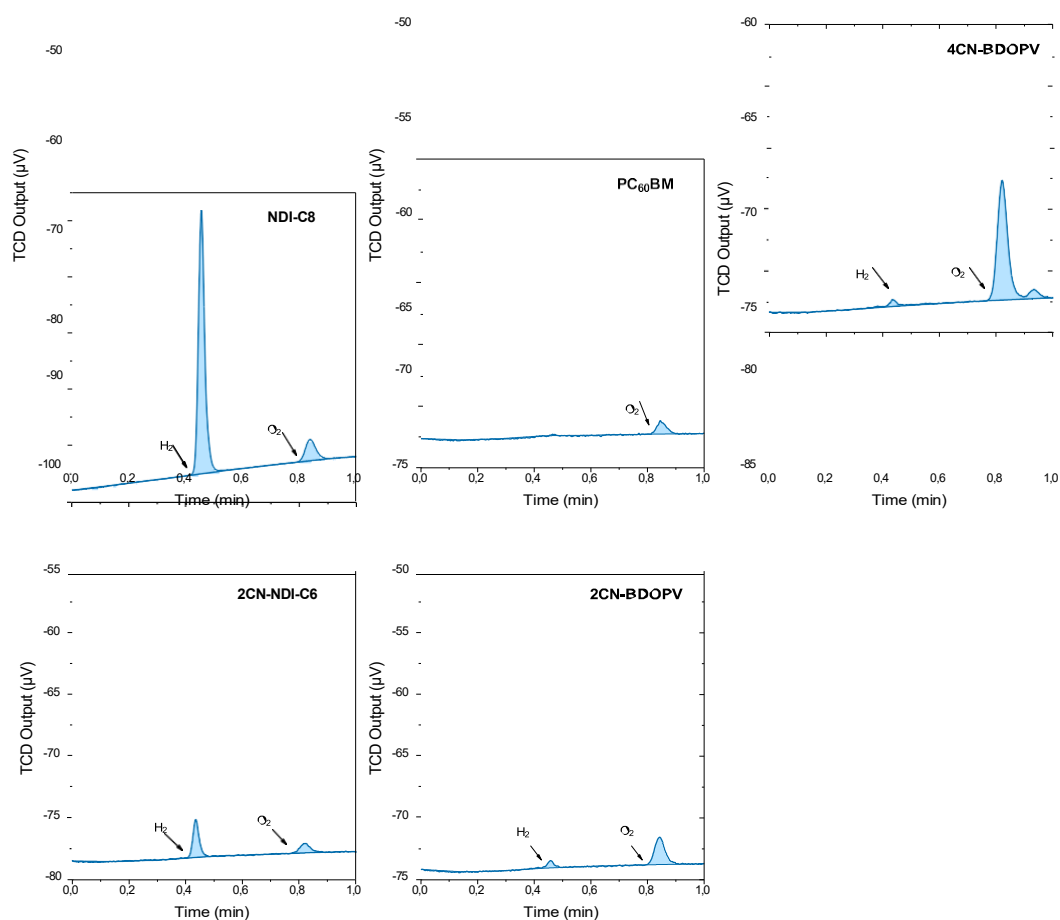PCBM still showed no evident sign of hydrogen evolution.

Figure S1: chromatograms obtained from wet blends of acceptor and N-DMBI-H (N-DMBI-H: acceptor = 2:1 mol:mol). Hydrogen and oxygen retention times are of 0.44 and 0.88 min respectively. A third apparent peak caused by back pressure on the injection syringe is present in 4CN-BDOPV analysis at 0.9 min.

1.1.3. Experiment on 2CN-BDOPV in the presence of sub-stoichiometric N-DMBI-H
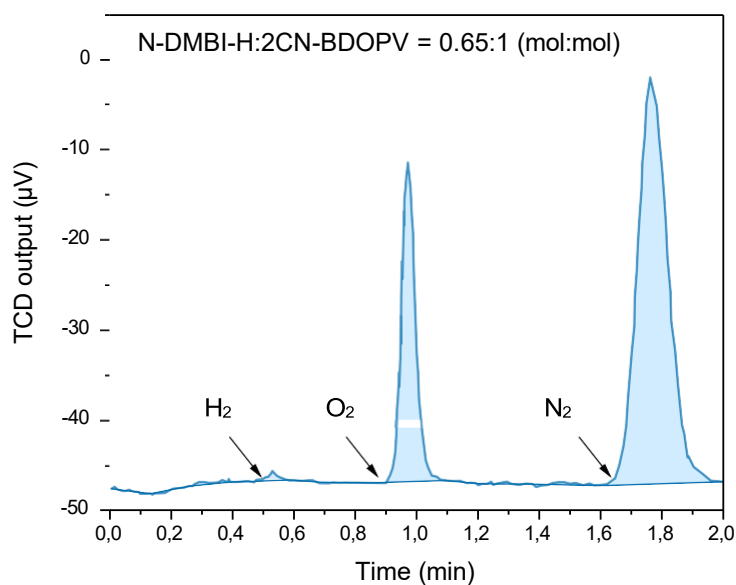

Figure S2: chromatograms obtained from wet blends of 2CN-BDOPV and N-DMBI-H (N-DMBI-H: 2CN-BDOPV = 0.65:1 mol:mol). Hydrogen, oxygen, and nitrogen related peaks are highlighted with black arrows.

Previous work demonstrated that formation of BDOPV derivatives radical anions in solution depends on the amount of N-DMBI-H with which the acceptor reacts.[6] In particular, the supposed doping mechanism suggest initial formation of hydrogenated BDOPV-H species that can then interact, following an unknown mechanism, with a neutral BDOPV molecule to give the anion radical BDOPV$^{\bullet-}$. This process is favoured when the dopant is added in sub-stoichiometric amount with respect to the acceptor, otherwise the hydrogenation step is so efficient that mostly no available neutral BDOPV is present in the reaction environment and the acceptor radical anion is not formed. As our experiments on dry and wet blends were performed using twice as much dopant as the acceptor counterpart, the reason behind the low amount of H_2 detected could be connected to the complete reaction of BDOPV derivatives to form the hydrogenated counterpart, which is stable under inert atmosphere. We then decided to repeat a test on a wet blend of 2CN-BDOPV containing sub-stoichiometric amount of N-DMBI-H to see if this is the case. We thus prepared a sample containing 0.65 equivalents of N-DMBI-H with respect to 2CN-BDOPV. The sample was prepared using 14 mg of 2CN-BDOPV and following the procedure reported in the paragraph describing wet blend preparation. **Figure S2** shows the obtained chromatogram. No evident sign of H_2 formation was detected which is line with the results obtained in the previous experiments. The experimental results again suggest that the doping processes of BDOPV derivatives does not happen prevalently via H_2 formation, at least in our working conditions.

.

1.2. Hydrogen leakage measurements

Hydrogen detection leakage experiments were performed to investigate the air tightness of 2 mL GC vials used during the experiments. Leakage was measured over a one-day period.

Procedure
All the 2 mL gas-chromatography vials used were introduced in the same vacuum bag. The bag was then put under vacuum to remove most of the air inside. A gaseous mixture of argon and molecular hydrogen (molecular hydrogen concentration around 1%) was cannulated inside the bag. The bag was then sealed with a

thermoplastic adhesive and the vials were closed directly inside the bag. This procedure should ensure all the samples to be in the same initial condition.

The vials were then collected outside of the vacuum bag and parafilm was used to ensure better sealing to follow the same procedure of N-DMBI-H related H_2 detection experiments. H_2 detection measurements were performed immediately after sample preparation and then after 1, 4 and 24 h (two samples for each collection time). Two samples were kept at room temperature for 22 h after preparation and then heated for 2 hours at 150 °C in an oil bath, to simulate effect of thermal treatment on the H_2 content.

Results

Figure S3 shows hydrogen concentration variation inside the samples. Data were obtained as average value between two samples analysed at each collection time. Value corresponding to heated samples is highlighted in red.
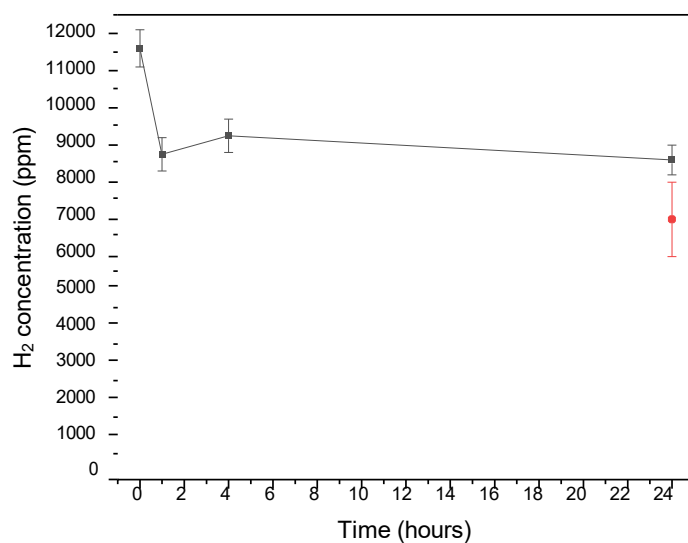

Figure S3: concentration of hydrogen in the GC vials over time. Values obtained from samples kept at room temperature are reported in black. The value relating to samples heated at 150 °C is reported in red.

Experimental results report an overall hydrogen loss of around 25 % after 24 h for a sample kept at room temperature, mostly happening during the first hour of storage. Leakage seems not to evidently affect the samples after the first hour, as differences in the values measured after 1, 4 and 24 h are minimal ($\leq$5%). Considering the sample preparation procedure, initial overpressure of the gaseous mixture inside the vials cannot be excluded: this could have caused a higher hydrogen loss in the first hour.

Samples heated at 150 °C for 2 h contained an average H_2 concentration value of 7000 ± 1000 ppm. This implies an overall hydrogen loss of 40 ± 9 % with respect to initial average value (11600 ppm). Hydrogen loss is around 20 ±10 % with respect to samples analysed after 24 hours but not subjected to thermal treatment (average value: 8600 ppm).

These results suggest that on the overall, previous measurements should have been affected by hydrogen leakage lower than 50 %.

1.3.   Experiments on BCF dopant

BCF dopant was purchased from Sigma-Aldrich and used as received. PCPDTBT was purchased from 1-Material and used as received.

P3HT was purchased from Sigma-Aldrich (regioregular, average Mw 20-45 kDa, PDI ≤ 6.0). Unless otherwise stated, all samples were prepared using anhydrous chlorobenzene saturated with degassed water as solvent.

1.3.1. Experiments testing water impact on doping efficiency

7 mg (0.009 mmol) of PCPDTBT were weighed inside a GC vial. 0.53 mL of chlorobenzene and 0.47 mL of a 20 mg/mL stock BCF solution were added to the vial to obtain a polymer concentration of 7 mg/mL (BCF:PCPDTBT = 2:1 in molar ratio): chlorobenzene was added as first step, the vial was closed, then BCF solution was added via syringe and eventually the septum was sealed with a thermoplastic adhesive. The sample was analyzed after 24 hours. 4 different GC injections were performed. The one giving the highest H_2 concentration value is here reported. The procedure was repeated twice, in one case using degassed chlorobenzene saturated with degassed water, in the other case using anhydrous chlorobenzene as solvent.

1.3.2. Experiments analysing doping of P3HT and PCPDTBT in time

Sample containing P3HT in 9×10^{-3} M concentration (1.5 mg/mL)
A 5mg/ml stock solution of P3HT in chlorobenzene was prepared. This solution, chlorobenzene, and a 20 mg/mL stock BCF solution were added in different amounts to a GC vial to obtain samples containing 1 and 2 molar equivalents of BCF with respect to the polymeric repeating unit. P3HT solution was added as first step, then chlorobenzene, the vial was closed, BCF solution was added via syringe and eventually the septum was sealed with a thermoplastic adhesive.

Sample containing PCPDTBT in 9×10^{-3} M concentration (7 mg/mL)
7 mg of PCPDTBT were weighed in each GC vial. Chlorobenzene and a 20 mg/mL stock BCF solution were added in different amounts to the samples to obtain 1 and 2 molar equivalents of BCF with respect to the polymeric repeating unit. Chlorobenzene was added as first step, the vial was closed and shaken to help the polymer dissolution. BCF solution was then added via syringe and eventually the septum was sealed with a thermoplastic adhesive.

For both samples, the first GC injection was performed 30 min after sample preparation. After the first GC injection, H_2 detection experiments were repeated after 1 h, 24 h, and 48 h. After each GC injection, samples were again sealed with thermoplastic adhesive and kept at room temperature under air before the following experiment.

1.3.3. Control experiments

Control experiments were performed on solutions containing only P3HT, only PCPDTBT and only BCF to confirm H_2 evolution to be the results of the doping process. Each sample was kept in a glove box under argon atmosphere for 24 hours before being analyzed. Preparation of the samples is described in the following paragraph.

PCPDTBT control experiment sample preparation
7 mg of PCPDTBT were weighed in a GC vial. 1mL of Chlorobenzene was added to the samples to obtain a PCPDTBT 9×10^{-3} M solution (7 mg/mL). The vial was closed and shaken to help the polymer dissolution and eventually the septum was sealed with a thermoplastic adhesive.

P3HT control experiment preparation
5mg/ml stock solution of P3HT in chlorobenzene was prepared. This solution (0.31 ml, 1.55 mg) and chlorobenzene (0.69 mL) were added in different amounts to a GC vial to obtain a sample containing P3HT in 9×10^{-3} M concentration. P3HT solution was added as first step, then chlorobenzene, the vial was closed and eventually the septum was sealed with a thermoplastic adhesive.

BCF control experiments (test A and B) preparation

A 20 mg/mL stock solution of BCF in chlorobenzene was prepared. 0.47 mL of this solution were added to a GC vial, followed by 0.53 mL of chlorobenzene. The vial was closed and eventually the septum was sealed with a thermoplastic adhesive.
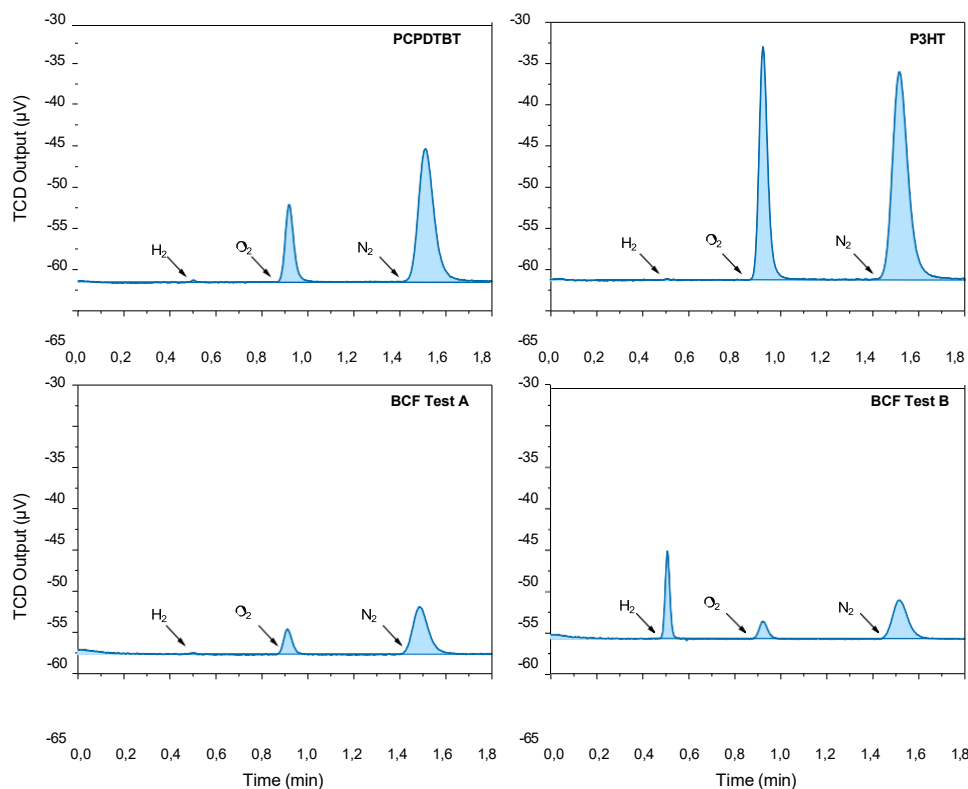

Figure S4: chromatograms obtained from GC analysis of control experiments containing only PCPDTBT, only P3HT or only BCF (test A and B). Retention times related to H_2, O_2 and N_2 are highlighted with black arrows.

Results

Figure S4 collects the Gas chromatograms traces of the performed control experiments. Both PCPDTBT and P3HT polymers do not show H_2 related peaks in the chromatogram, which demonstrates that H_2 evolution is not possible when the polymer is the only specie present in the solution. Interpretation of results related to BCF control experiments is instead not straightforward. If **Test A** does not show any evidence of H_2 formation, chromatogram related to **Test B** highlights presence of an intense peak at the retention time corresponding to molecular H_2. Further analysis of the phenomenon is reported in the following paragraph.

1.3.4. Analysis of H_2 production from BCF control experiments

As the unknown process behind molecular hydrogen evolution during control experiments on BCF might have affected the outcome of the H_2 detection experiments performed on P3HT and PCPDTBT polymers as well, we performed different tests to better understand the phenomenon. We repeated the control experiments with BCF several times, keeping the same conditions of the doping tests performed on polymers, to see the if the average amount of detected H_2 is, statistically, in the same range of values detected with P3HT and PCPDTBT. We then evaluated the influence of different factors, like solvent, presence of water and contact with materials of the septum of the GC vial or the thermoplastic adhesive used to seal samples on the amount of detected

hydrogen. The obtained data are shown in **Figure S5A.**

Results on BCF control experiments show that the H_2 detected values are mostly below 100 ppm, with only two values in the range of 200-250 ppm. Experiments performed using anhydrous toluene saturated with water instead of chlorobenzene again show random values of H_2, which suggest that the H_2 evolution is not due to the presence of chlorobenzene. Same is for data obtained with anhydrous chlorobenzene, that confirm that interaction of BCF with H_2O is not the reason behind H_2 evolution, since molecular hydrogen is formed in levels higher than 100 ppm even in such dry condition. Both experiments performed dissolving a piece of thermoplastic adhesive in the sample show H_2 values near to 0 ppm, which confirm that the H_2 evolution is not due to contact with this material. Both experiments performed adding pieces of the vial septum show instead very high H_2 detected values, one of the samples reaching around 450 ppm of detected H_2 concentration. These results suggest that contact with the septum might be the reason behind H_2 evolution from BCF control experiments. Different works reported that H_2 evolves during BCF catalyzed attachment reactions of hydrosilanes or methylsiloxane polymers and oligomers to silica[7,8]. As part of the GC-Vial septum is made of polydimethylsiloxanes, we speculate that presence of residual methylsiloxanes oligomers might be the reason behind the H_2 evolution detected during the control experiments.
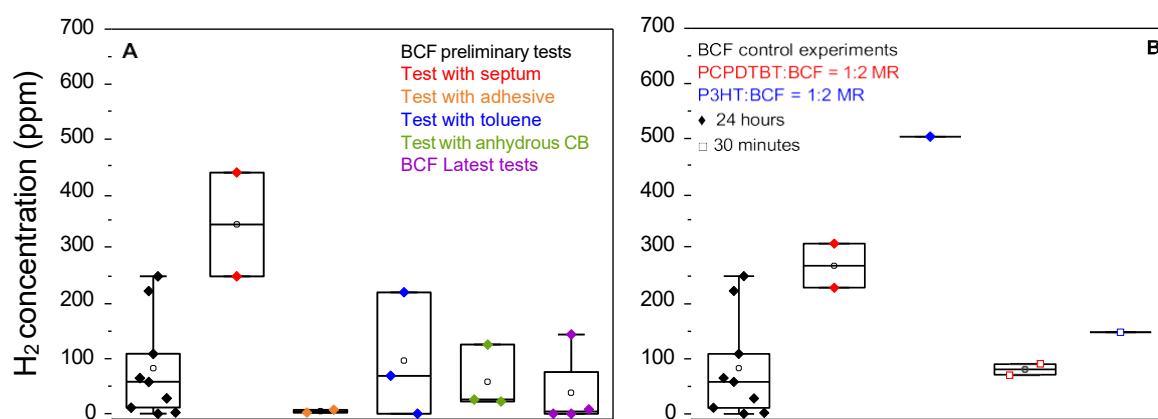

Figure S5: **A)** Collection of H_2 concentration values detected via GC from control experiments on BCF; The graph shows preliminary results obtained during analysis of BCF control experiments performed in chlorobenzene saturated with water (♦), results of test performed with toluene (♦), test performed in presence of septum inside the solution (♦), test performed in presence of thermoplastic adhesive inside the solution (♦), test obtained with anhydrous chlorobenzene (♦)and latest test performed reducing at minimum contact with septum (♦). **B)** Comparison of H_2 concentration values detected via GC during control experiments on BCF (♦) and data obtained during doping experiments on PCPDTBT (♦) and P3HT (♦) after 24 hour from sample preparation and during doping experiments performed on PCPDTBT and P3HT after 30 minutes (□,□) from sample preparation. In both graphs mean H_2 concentration value is highlighted with a white circle (○).

Four other BCF control experiments were then performed with the same conditions used during doping experiments, but closing the vials after addition of the solutions instead of adding solution through syringes to already sealed vials. In this way, contact with septum fragments should be minimised. Syringes were also rinsed with clean solvent before use, to avoid contact with possible unknown lubricants. Following this procedure, 3 over 4 samples showed no H_2 detection or H_2 concentration below 10 ppm. nevertheless, one sample still showed H_2 concentration values higher than 100 ppm. Such results hints that complete avoidance of H_2 evolution with this experimental setup is hard. However, a comparison between H_2 concentration values obtained during doping experiments performed on P3HT and PCPDTBT polymer and those obtained during BCF control experiment, show that H_2 values detected in presence of a semiconductor are always higher with respect to the average value obtained during the latter (see Figure S5B). This is true in particular for P3HT polymer, whose doping allows to detect H_2 concentration value around 500 ppm. Moreover, experiments performed on P3HT and PCPDTBT 30 minutes after samples preparation show H_2 concentrations equal or higher with respect to average H_2 concentration values obtained during control experiments. These

considerations, together with the fact that H_2 values detected from BCF control experiments are very random, suggest that there might be a contribution from these unknown side reactions on the total amount of hydrogen detected during doping processes of p-type semiconductor with BCF, but that the process of doping itself produces molecular Hydrogen.

2. Residual Gas Analysis – Hydrogen detection experiments

Deuterated N-DMBI-D was synthesised according to the literature[9]. P(NDI2OD-T2) was synthesised following a literature reported procedure[10]. RGA-MS measurements were performed using the setup showed in **Figure S6**.

A vacuum chamber was directly connected to a Residual Gas Analysis (RGA) quadrupole mass spectrometer (SPECTRA, Microvision Plus) equipped with dual Faraday and electron multiplier detector and capable of discriminating masses in the order of 2, 3 and 4 amu. The sample container was covered with a heater (lamp with reflector) connected to an external Sorensen adjustable DC power supply and controller. Temperature inside the chamber was monitored through a thermocouple.
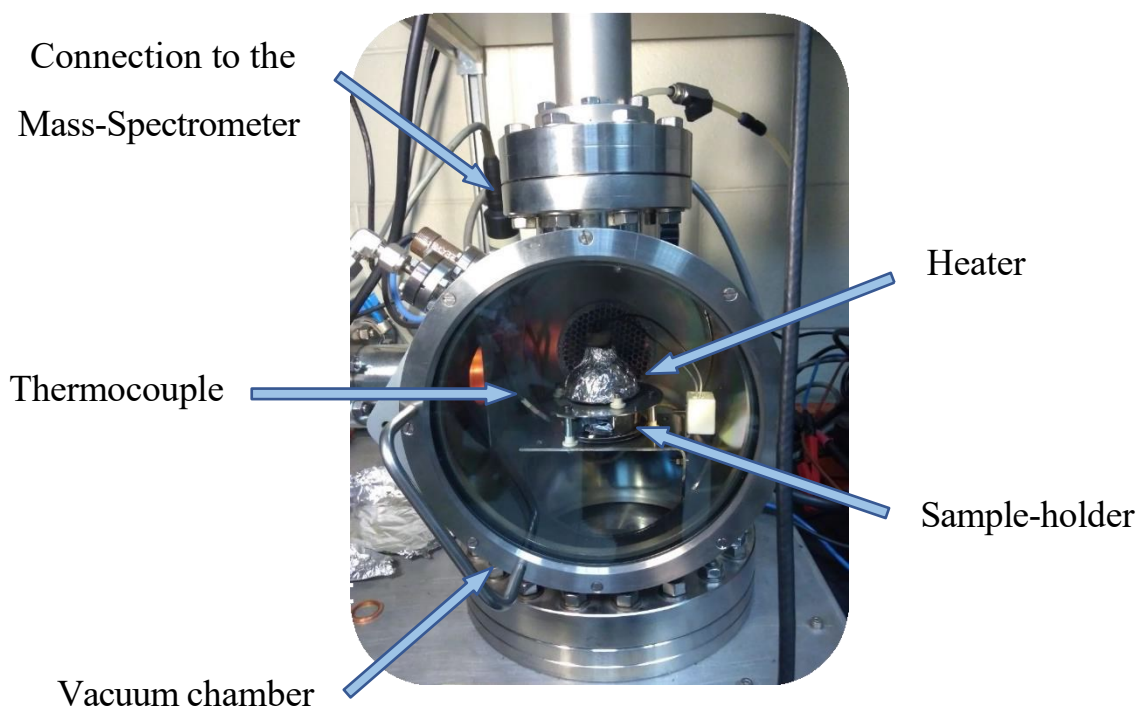

Figure S6: RGA-MS experimental setup: a vacuum chamber is connected directly to a quadrupole mass spectrometer; a tantalum sample holder is placed inside the chamber. The sample is heated by a lamp heater and the internal temperature is monitored via thermocouple.

Sample powder was placed inside aluminum foil. Holes in the foil were placed to let formed gases flow freely from the sample during the detection experiment. The sample was then placed inside a tantalum container positioned in the vacuum chamber. The chamber pressure was reduced to 2×10^{-6} Torr before starting the experiments. The sample was then heated with a rate of 10 °C/min from an initial temperature of around 50 °C to a final temperature of 160 °C. While heating, partial pressure of D_2, H_2, and H-D ions inside the chamber were monitored over time through the RGA mass spectrometer via conversion of their respective ion current against mass (vacuum pumping speed: 50 L/s).

P(NDI2OD-T2) and N-DMBI-H blend preparation
Polymer and dopant blend was prepared according to the following procedure: P(NDI2OD-T2) (38.5 mg, 0.0389 mmol) was weighed in an anhydrous glass vial. N-DMBI-D (21 mg, 0.078 mmol) was weighed and dissolved in 0.3 mL of anhydrous chlorobenzene in glove box under inert atmosphere. Such solution was then added to the polymer (N-DMBI-D: P(NDI2OD-T2) = 2:1 in molar ratio) and the mixture was left resting for

3 hours under argon, in the dark at room temperature before evaporating the solvent under nitrogen flux. 49 mg of this blend were used for the RGA-MS experiment.

P(NDI2OD-T2) control experiment sample preparation

60 mg of P(NDIOD-T2) were weighed in an anhydrous glass vial. 0.3 mL of anhydrous chlorobenzene were added to the sample inside a glovebox under argon atmosphere to keep consistency with the P(NDI2OD-T2) and N-DMBI-H blend preparation condition. The mixture was left resting for 3 h under argon, in the dark at room temperature before evaporating the solvent under nitrogen flux. 50 mg of this powder were used for the RGA-MS control experiment.

P(NDI2OD-T2) Control experiments results

As H_2 molecules can desorb from the vacuum chamber walls when heating under high vacuum[11], control experiments involving only P(NDI2OD-T2) was performed to analyze the impact of such phenomenon on the H_2 partial pressure values detected during RGA-MS detection experiments. Results of this control experiment are collected in **Figure S7**. As expected, since a deuterium source is missing, the graph shows no detection of deuterium and H-D (partial pressure levels below 1.4×10^{-8} Torr). The maximum detected difference in H_2 partial pressure with respect to initial partial pressure inside the vacuum chamber is 6.45×10^{-8} Torr, a value an order-of-magnitude lower with respect to the 3.5×10^{-7} Torr maximum value detected during experiment on blend of the polymer with N-DMBI-D. This implies that the H_2 detected during experiments performed on polymer and dopant blend is mostly due to doping processes.
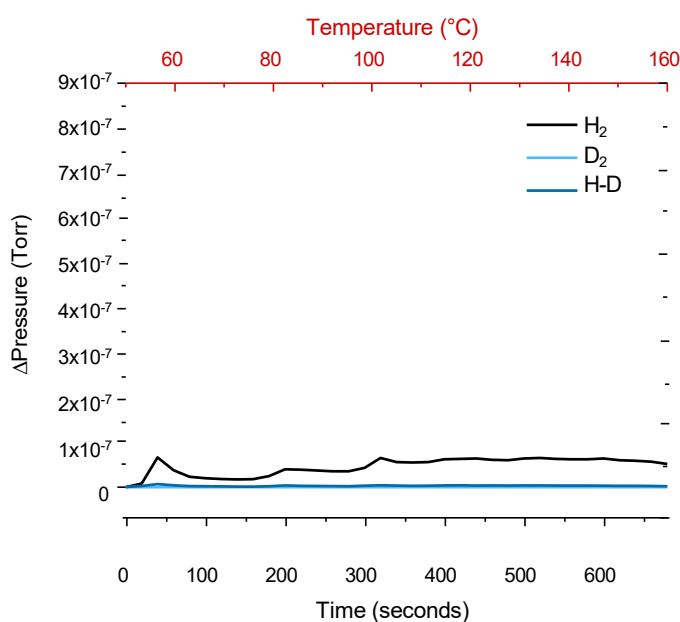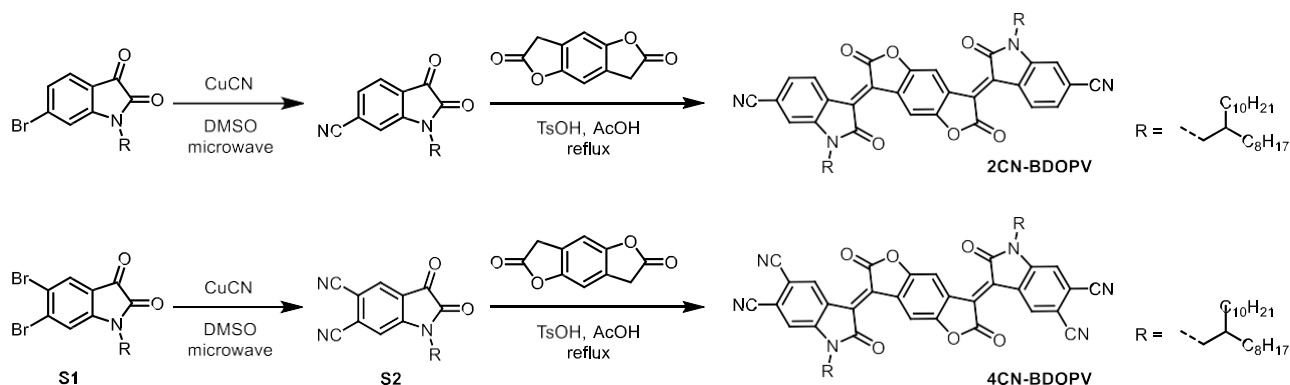

Figure S7: Selective detection of D_2 (light blue line), D-H (blue line), and H_2 (black line) in P(NDI2OD-T2) control sample as the function of time while heating at the constant rate of 10 °C/min.

3. Synthesis of BDOPV acceptors

The synthetic pathway for the synthesis of BDOP acceptors is reported in the following scheme.

2CN-BDOPV was synthesised according to the literature[6].

Details on 4CN-BDOPV synthesis are reported in the following paragraph

Synthesis of 1-(2-Octyldodecyl)-2,3-dioxoindoline-5,6-dicarbonitrile (**S2**)

5,6-Bromo-1-(2-octyldodecyl)indoline-2,3-dione (1.17 g, 2 mmol), was sealed in a microwave vessel with CuCN (0.90 g, 10 mmol) and DMSO (15 mL) under a nitrogen atmosphere. The vessel was then heated in a microwave reactor at 170 °C for 5 min, and then at 190 °C for 1 h. The reaction mixture was then poured into chloroform (100 mL) and then filtered. The filtrate was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography, eluting with chloroform to afford an orange solid.

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.94 (s, 1H), 7.25 (s, 1H), 3.65 (d, J = 7.4 Hz, 2H), 1.83 (m, 1H), 1.36–1.23 (m, 32H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 180.43, 156.90, 153.96, 129.33, 124.18, 119.35, 114.96, 114.56, 114.50, 110.90, 45.72, 31.42, 40.01, 29.69, 29.41, 26.30, 22.77, 22.74, 14.21, 14.19

Synthesis of (3E,3'E)-3,3'-(2,6-Dioxobenzo[1,2-b:4,5-b']difuran-3,7(2H,6H)-diylidene)bis(1-(2 octyldodecyl)-2- oxoindoline-5,6-dicarbonitrile). (4CN-BDOPV)

3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (0.19 g, 1 mmol), and p-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) were added to a solution of **S2** (0.95 g, 2 mmol) in acetic acid (15 mL). The mixture was stirred at 115 °C under a nitrogen atmosphere for 24 h. Then the mixture was poured into methanol (100 mL) and then filtered. After washing with methanol to remove the acetic acid, the solids were purified by silica gel chromatography, eluting with hot chloroform to give 4CN-BDOPV as a dark green solid (0.49 g, 0.44 mmol, 44%).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.57 (s, 2H), 9.21 (s, 2H), 7.16 (s, 2H), 3.74 (d, J = 7.4 Hz, 4H), 1.87 (m, 2H), 1.37-1.24 (m, 64H), 0.86 (t, J = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz): δ 166.61, 166.09, 153.11, 148.89, 134.62, 133.12, 131.22, 127.87, 123.89, 119.83, 115.58, 115.23, 112.70, 112.55, 109.74, 45.57, 36.48, 31.98, 31.88, 31.57, 30.09, 29.76, 29.64, 29.40, 26.43, 26.38, 22.79, 22.75, 14.25, 14.21
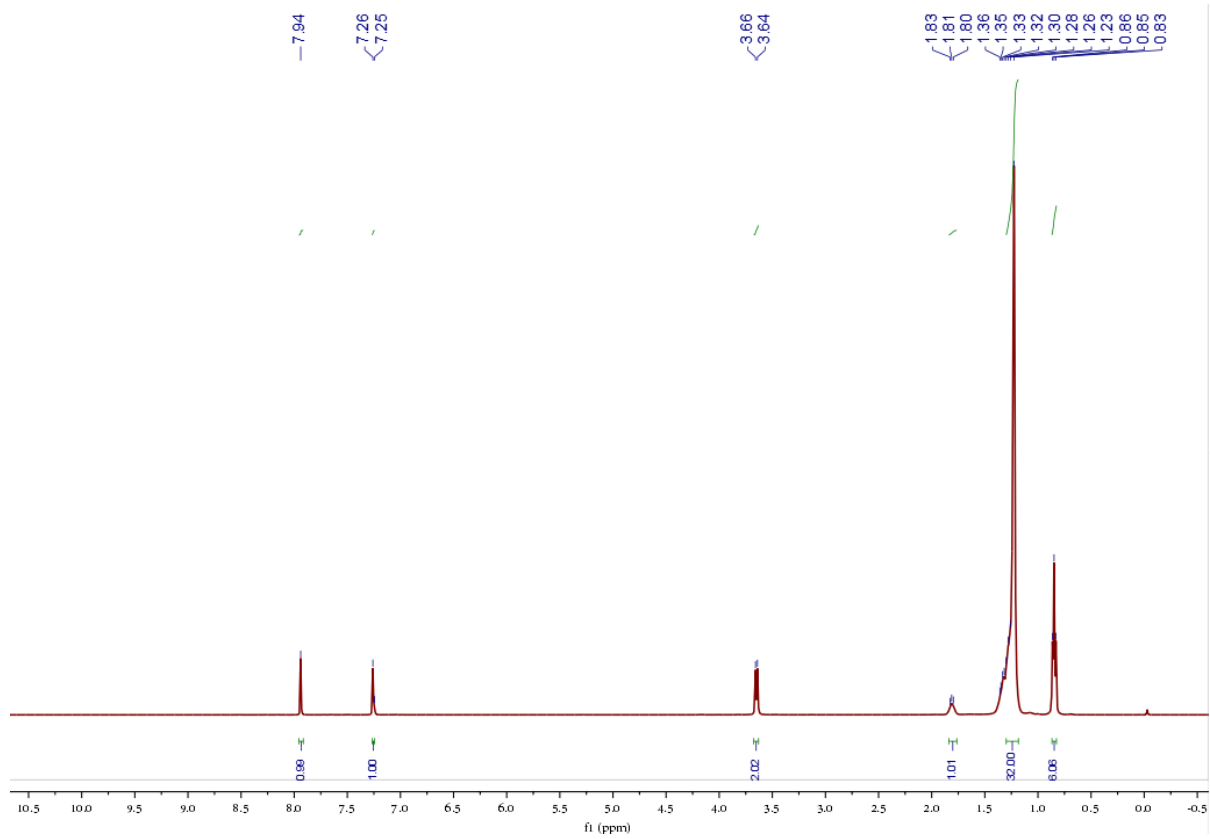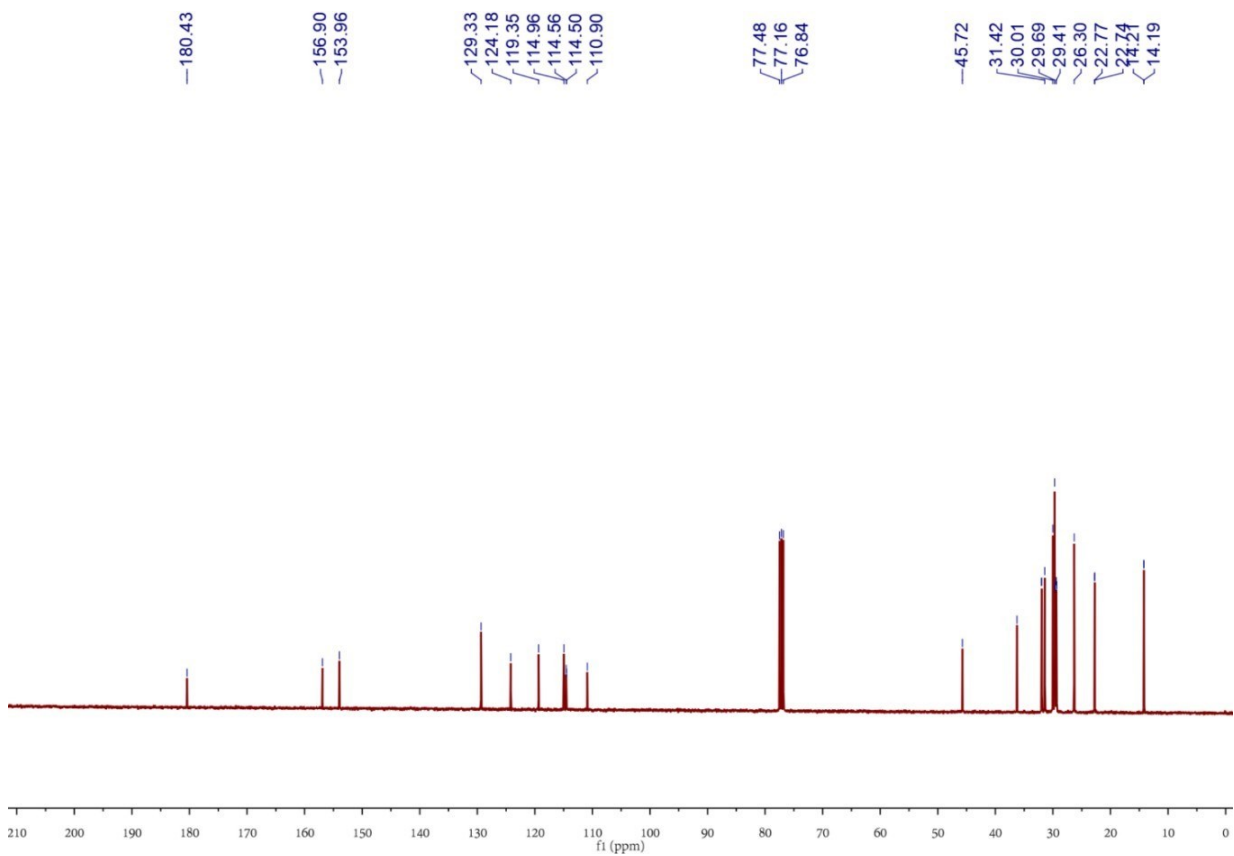
Figure S8: ^{1}H NMR of **S2** in CDCl$_3$

Figure S9: ^{13}C NMR of **S2** in CDCl$_3$

17

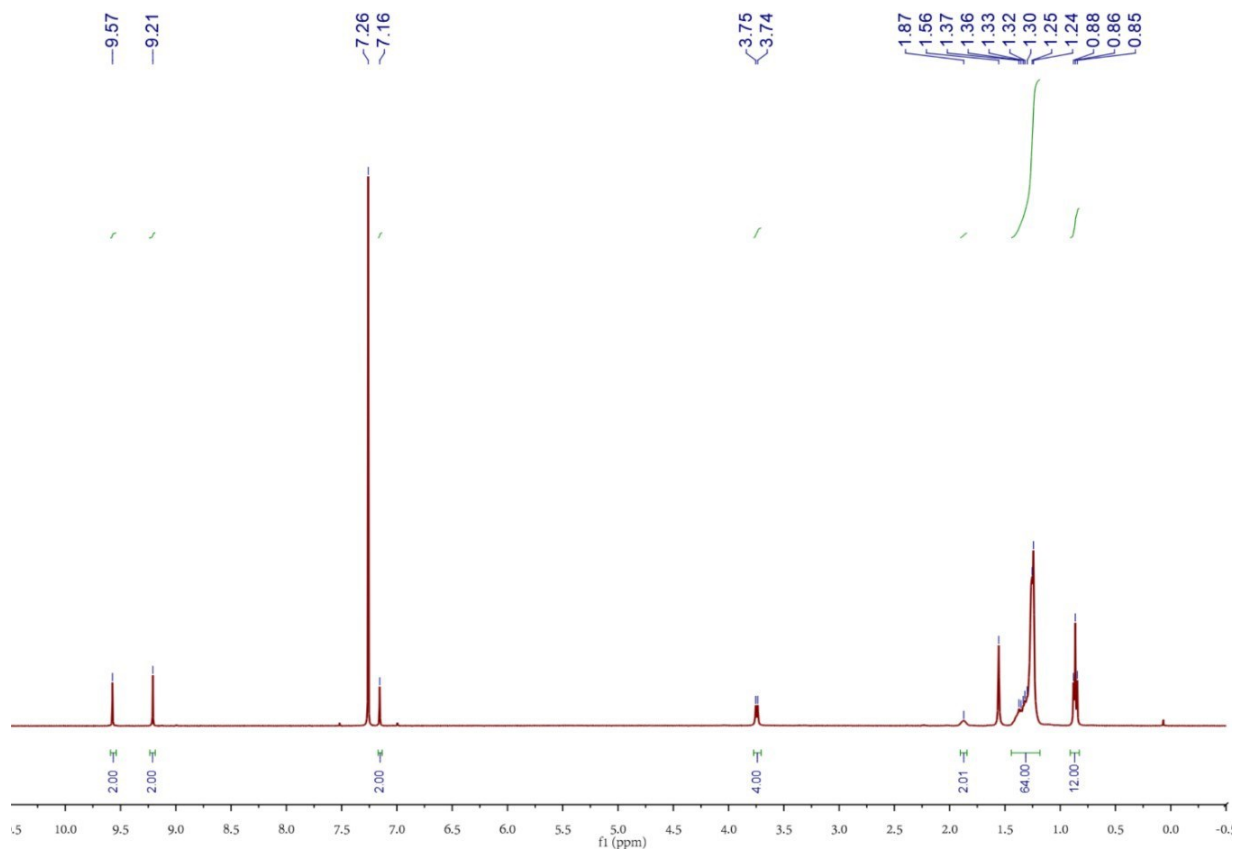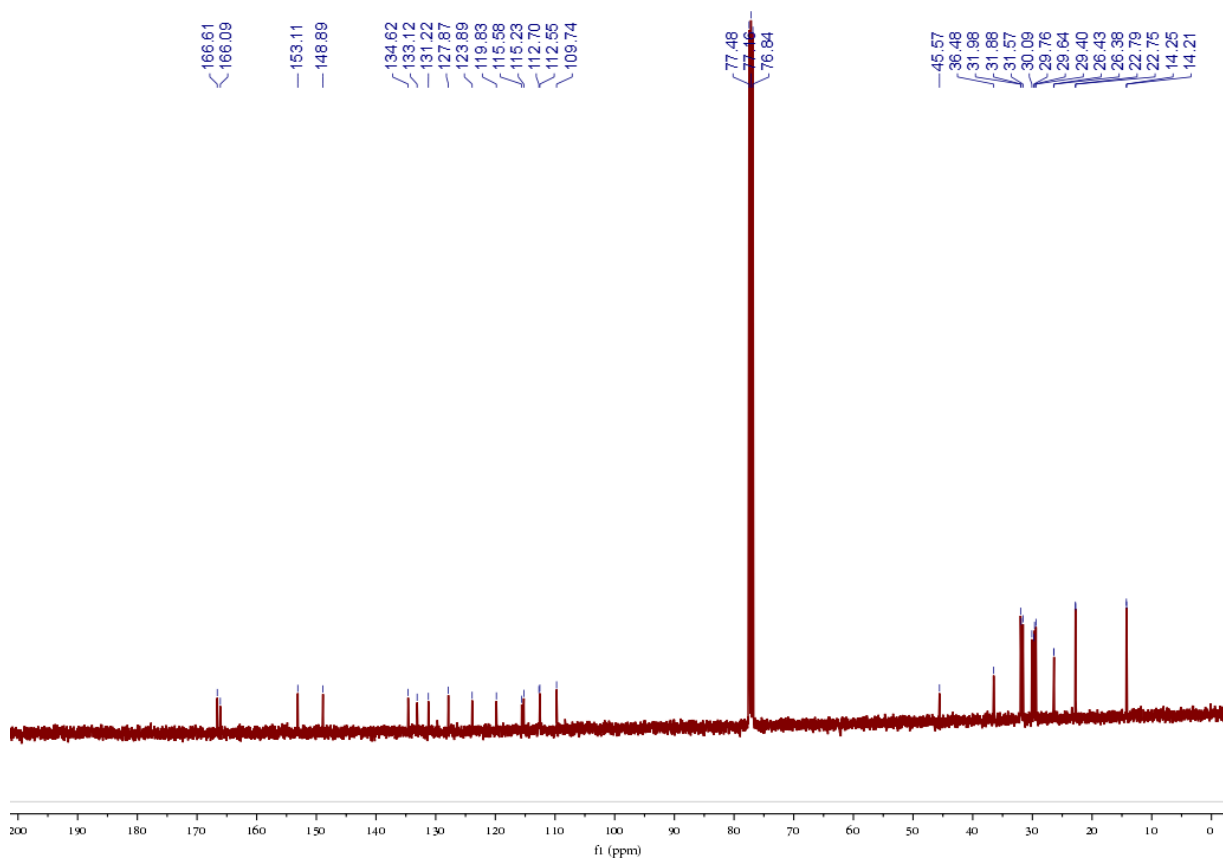**Figure S10**: ^{1}H NMR of **4CN-BDOPV** in CDCl$_3$

Figure S11: ^{13}C NMR of *4CN-BDOPV* in CDCl$_3$

References for the Supporting Information

1. Pallini, F. *et al.* Unexpected Enhancement of Molecular n-Doping Efficiency in Polymer Thin Films by a Degradation Product. *ACS Appl. Energy Mater.* **5**, 2421–2429 (2022).

2. Un, H. I. *et al.* Understanding the Effects of Molecular Dopant on n-Type Organic Thermoelectric Properties. *Adv. Energy Mater.* **9**, 1–10 (2019).

3. Greenfield, S. R., Svec, W. A., Gosztola, D. & Wasielewski, M. R. Multistep Photochemical Charge Separation in Rod-like Molecules Based on Aromatic Imides and Diimides. *J. Am. Chem. Soc.* **118**, 6767–6777 (1996).

4. Gryko, D. T. *et al.* Unprecedented 1,3-Dipolar Cycloaddition: From 1,4,5,8-Naphthalene Bisimides to a New Heterocyclic Skeleton. *Org. Lett.* **12**, 2020–2023 (2010).

5. Vadehra, G. S., Maloney, R. P., Garcia-Garibay, M. A. & Dunn, B. Naphthalene diimide based materials with adjustable redox potentials: Evaluation for organic lithium-ion batteries. *Chem. Mater.* **26**, 7151–7157 (2014).

6. Jhulki, S. *et al.* Reactivity of an air-stable dihydrobenzoimidazole n-dopant with organic semiconductor molecules. *Chem* **7**, 1050–1065 (2021).

7. Flagg, D. H. & McCarthy, T. J. Rapid and Clean Covalent Attachment of Methylsiloxane Polymers and Oligomers to Silica Using B(C6F5)3 Catalysis. *Langmuir* **33**, 8129–8139 (2017).

8. Moitra, N. *et al.* Surface functionalization of silica by Si-H activation of hydrosilanes. *J. Am. Chem. Soc.* **136**, 11570–11573 (2014).

9. Naab, B. D. *et al.* Mechanistic Study on the Solution-Phase n-Doping of 1,3-Dimethyl- 2-aryl-2,3-dihydro-1H-benzoimidazole Derivatives. *J. Am. Chem. Soc.* **135**, 15018–15025 (2013).

10. Matsidik, R., Komber, H., Luzio, A., Caironi, M. & Sommer, M. Defect-free Naphthalene Diimide Bithiophene Copolymers with Controlled Molar Mass and High Performance via Direct Arylation Polycondensation. *J. Am. Chem. Soc.* **137**, 6705–6711 (2015).

11. Redhead, P. A. Hydrogen in Vacuum Systems: An Overview. *AIP Conf. Proc.* **671**, 243 (2003).