

## Supporting information for

# N-alkyl substituted *1H*-benzimidazoles as improved n-type dopants for a naphthalene-diimide based copolymer

### Thermogravimetry of selected dopants

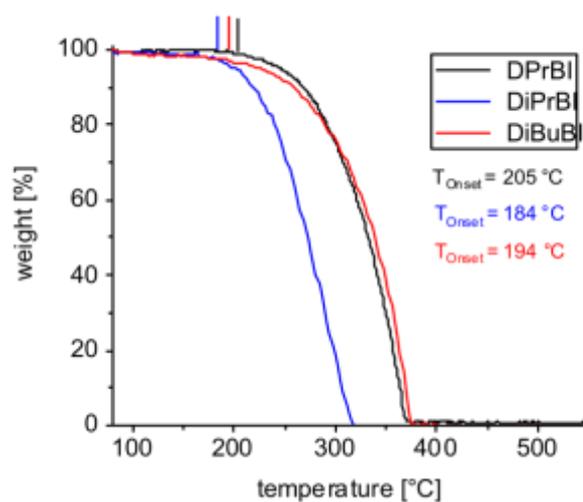


Fig. S1 TGA of DPrBI, DiPrBI and DiBuBI

### Differential Scanning Calorimetry

Analysis are carried out with a Perkin-Elmer DSC 8500 equipped with a liquid nitrogen cooling system, Perkin-Elmer CLN2 under N<sub>2</sub> flux at 40 mL/min end set at -45 °C.

### DMBI

Method used is the following:

- 1) Heating from 40 °C to 130 °C at 10 °C/min (—)
- 2) Isotherm for 1 min at 130 °C
- 3) Cooling from 130 °C to 40 °C at 10 °C/min (—)
- 4) Isotherm for 1 min at 40 °C
- 5) Heating from 40 °C to 130 °C at 10 °C/min (—)

Sample weight: 2.841 mg

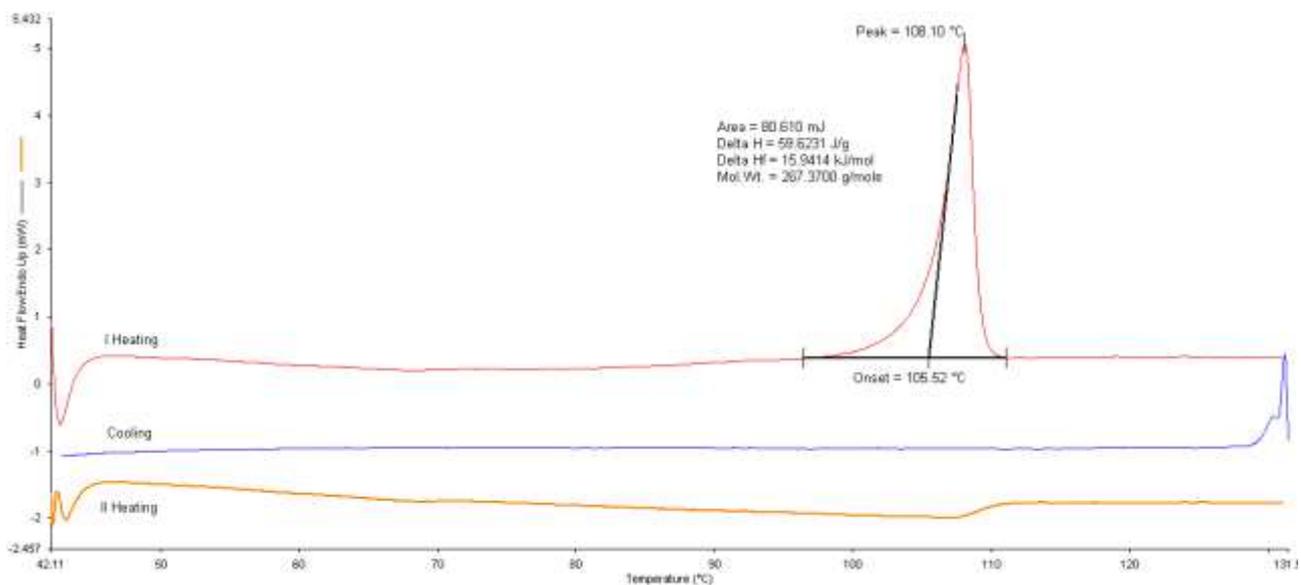


Fig. S2 Thermogram of DMBI

### DEtBI

Sample weight: 2.674 mg

Method used is the following:

- 1) Heating from 25.00 °C to 200.00 °C to 10.00 °C/min (—)
- 2) Isotherm for 1 min at 200.00 °C
- 3) Cooling from 200.00 °C to 25.00 °C to 10 °C/min (as DMBI sample, not shown)
- 4) Isotherm for 1 min at 25.00 °C
- 5) Heating from 25.00 °C to 200.00 °C to 10.00 °C/min (—)
- 6) Isotherm for 1 min at 200.00 °C

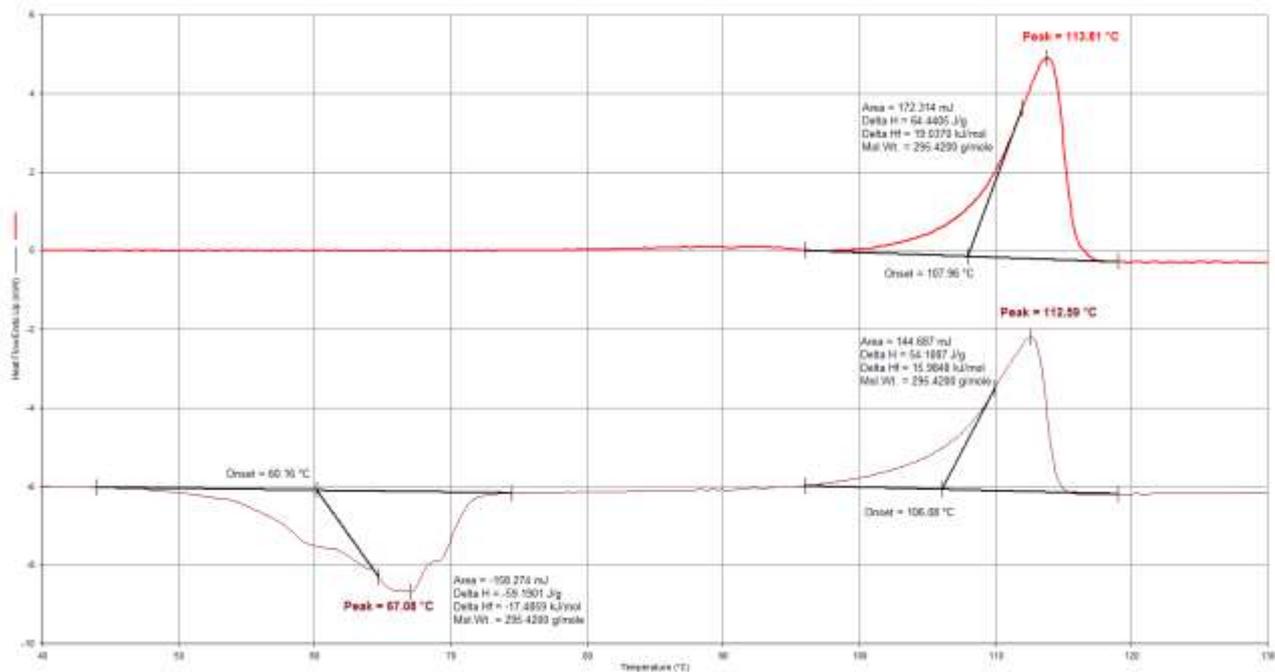


Fig. S3 Thermogram of DEtBI

## DPrBI

Method used is the following:

- 1) Heating from 0 °C to 100 °C at 10 °C/min (—)
- 2) Isotherm for 1 min at 100 °C
- 3) Cooling from 100 °C to -20 °C at 10 °C/min (as DMBI sample, not shown)
- 4) Isotherm for 1 min at -20 °C
- 5) Heating from -20 °C to 100 °C at 10 °C/min (no phase transition are observed, not shown)

Sample weight: 2.070 mg

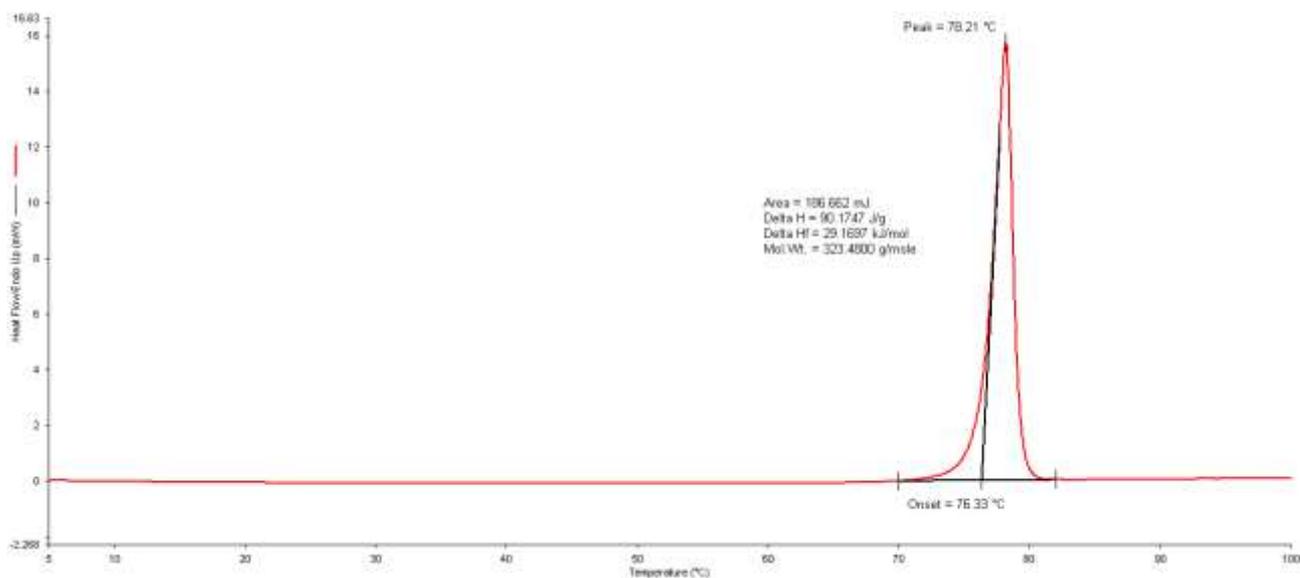


Fig. S4 Thermogram of DPrBI

## DBuBI

Method used is the following:

- 1) Heating from 0 °C to 80 °C to 10 °C/min (—)
- 2) Isotherm for 1 min at 80 °C
- 3) Cooling from 80 °C to -20 °C at 10 °C/min (—)
- 4) Isotherm for 1 min at -20 °C
- 5) Heating from -20 °C to 80 °C at 10 °C/min (—)

Sample weight: 1.246 mg

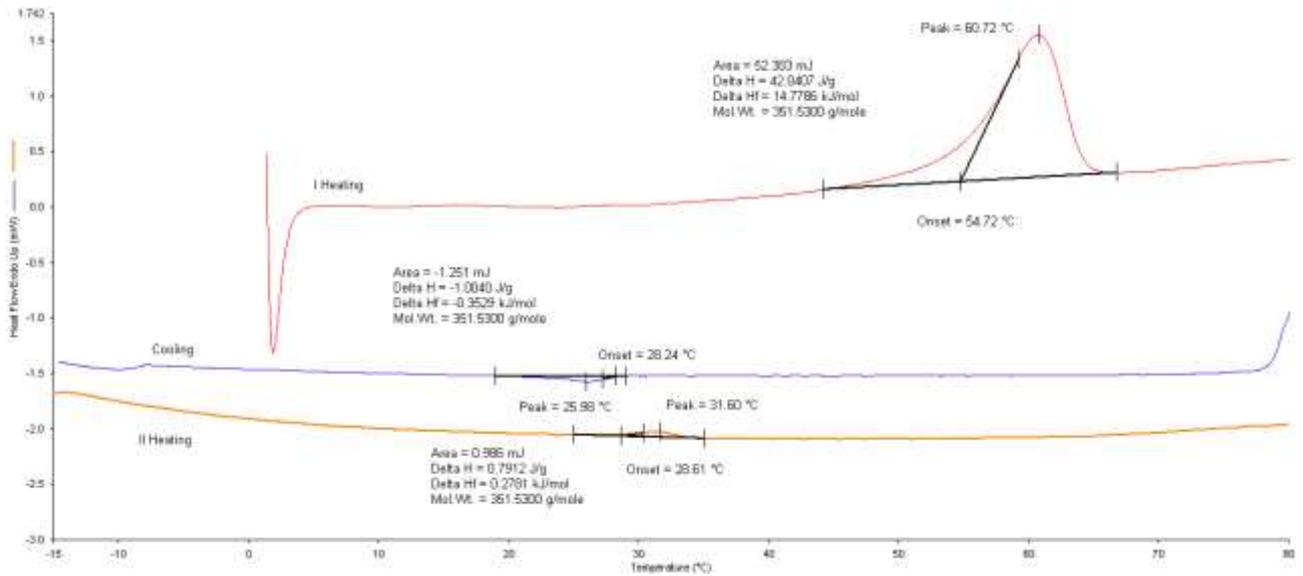


Fig. S5 Thermogram of DPrBI

DiPrBI

Method: same as for sample DPrBI

Sample weight: 0.510 mg

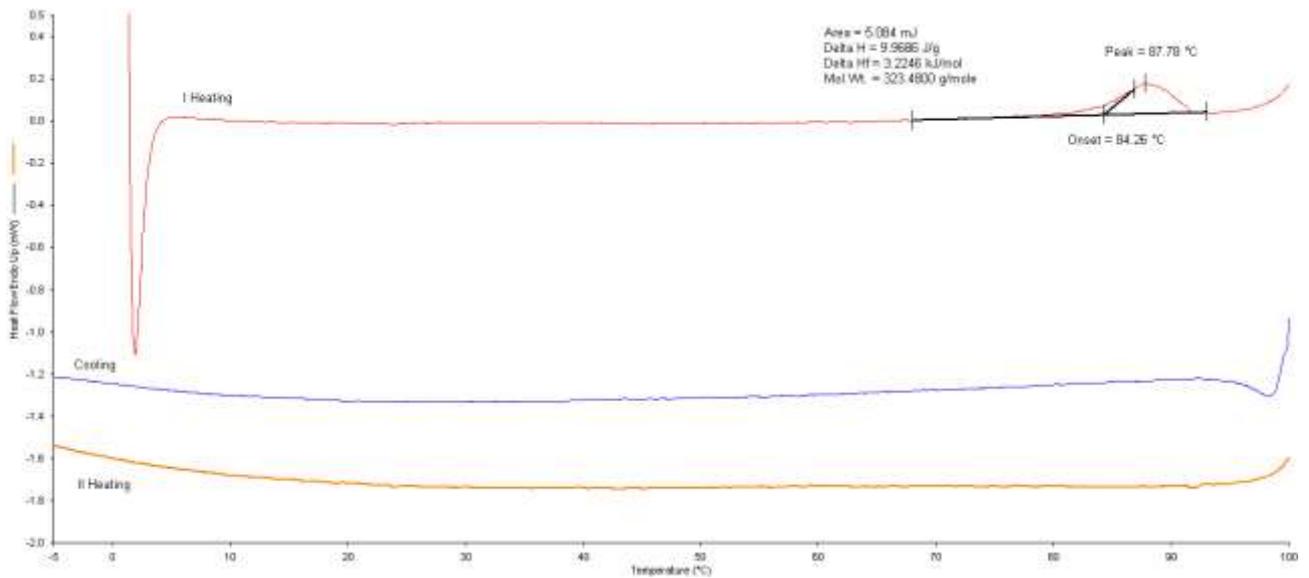


Fig. S6 Thermogram of DiPrBI

DiBuBI

Method: same as for sample DPrBI

Sample weight: 1.441 mg

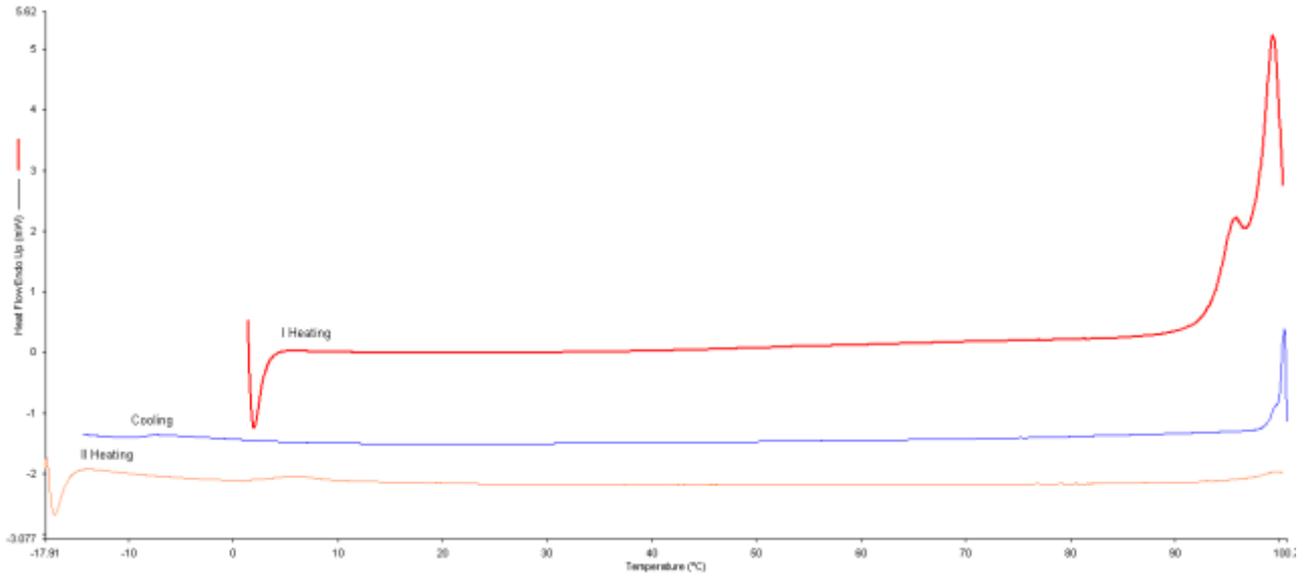
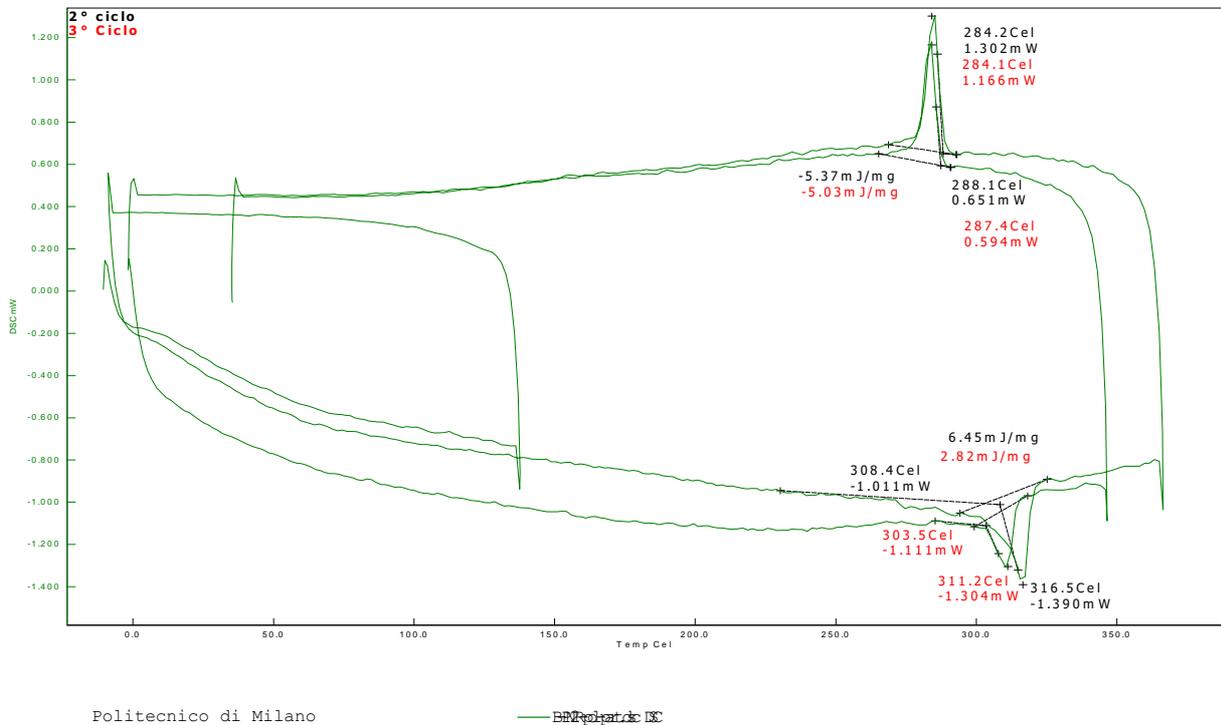


Fig. S7 Thermogram of DIBuBI

Pristine P(NDI2OD-T2)

Module:	DSC	Temperature Program:		Comment:
Data Name:	B-PN2R-pol-part.dsc			Operator: Valerio
Measurement Date:	19-Nov-12	1* -20 140 10 0 0.5		Gas1: Nitrogen
Sample Name:	PN2R polimero di partenza	2* 140 -20 10 0 0.5		Gas2: Air
Sample Weight:	4.050 mg	3* -20 370 10 0 0.5		Pan: Aluminum
Reference Name:		4* 370 -10 10 1 0.5		Strutturale
Reference Weight:	0.000 mg	5* -10 350 10 0 0.5		
		6* 350 30 10 1 0.5		



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Fig. S8 Thermogram of pristine P(NDI2OD-T2)

DSC of doped polymer films

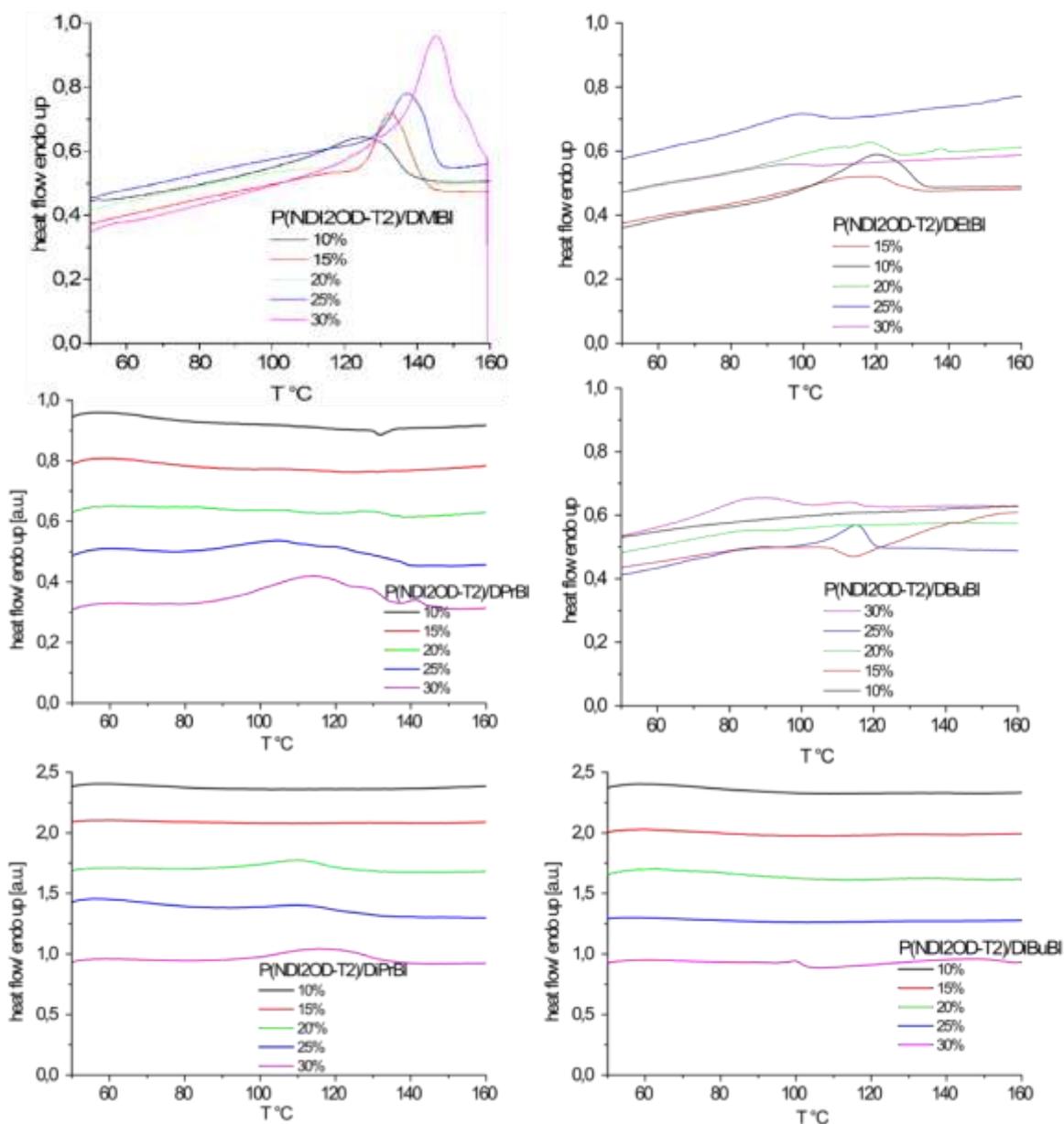


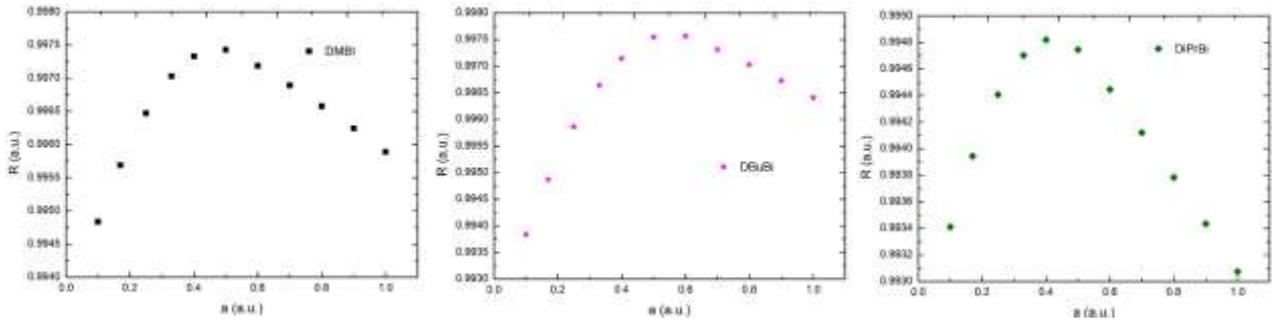
Fig. S9 Thermograms of doped polymer films for all the dopants. For every dopant, 10 %, 15 %, 20 %, 25 %, 30 % concentration were analysed. The curves shown are the first heating curves of the blends measured at 10 K/min under  $N_2$ .

## Variable Temperature Electrical Conductivity Measurements

### Instrumentation

Analysis is carried out using an Agilent Technologies semiconductor parameter analyzer (SPA) working in vacuum and equipped with a liquid nitrogen cooling system. The temperature range studied is between 200K and 300K, scanning with steps of 10K. I-V curves were taken for each step using a 4-point-probe collinear method in order to eliminate the effects of contact resistance. Then, for each curve, the value of the corresponding electrical conductivity was determined.

### Variable Range Hopping (VHR) fitting



*Fig. S1 Residual vs  $\alpha$  to determine the best fitting for the three dopant molecules*

The fitting of the Arrhenius plot for the three dopant molecules was done using Matlab Software through the linearization of the VRH model (Eq. 1) in order to calculate the value of the  $\alpha$  exponent which gives the best fitting.

$$\ln \sigma = -A \left( \frac{T_0}{T} \right)^\alpha + B$$

From the Residual calculations (Fig. S1) it appears that the best fitting corresponds to  $\alpha=0.5$ , as already reported in literature, indicating a 1D VRH transport model.

## GIWAXS

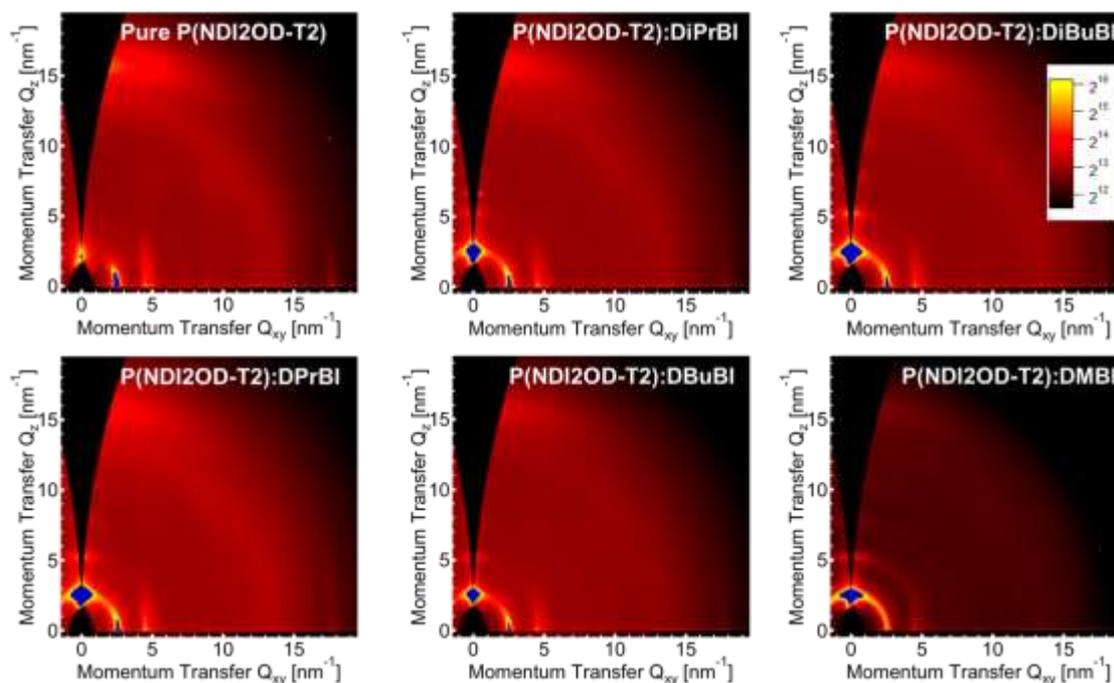


Fig. S2 2D GIWAXS patterns of P(NDI2OD-T2) thin films without and with various dopants.

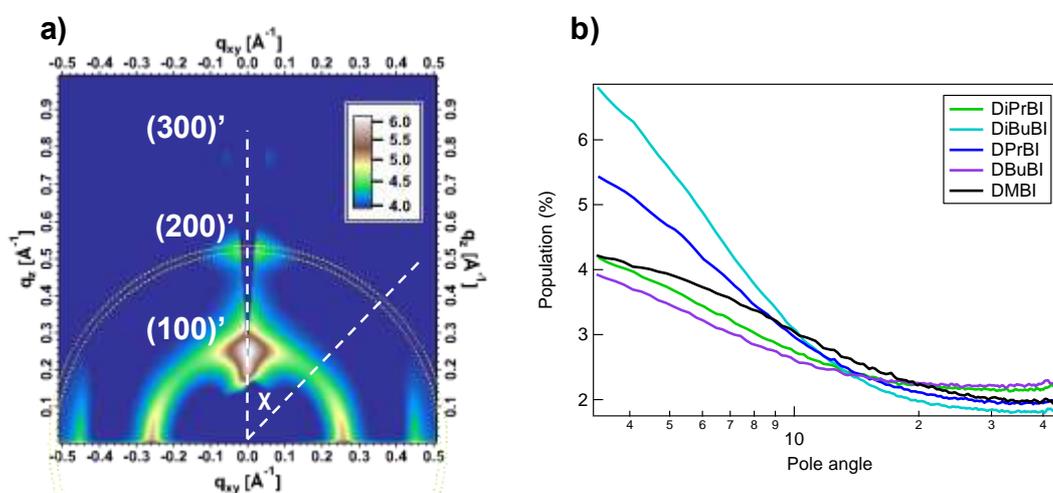


Fig. S3 a) 2D GIWAXS pattern from P(NDI2OD-T2):DiBuBI thin film. The crystallite orientation distribution (COD) profiles were extracted from the circular line cut across (200)', indicated by the thin dash lines. Pole angle  $\chi$  ranging from  $0^\circ$  to  $45^\circ$  ( $0^\circ$  denotes the direction perpendicular to the substrate) was chosen to make sure no overlays between (200)' and other diffraction features. b) COD profiles regarding P(NDI2OD-T2) (200)' under different dopants. The crystallite population was calculated by normalizing the measured diffraction intensity by the integrated total intensity within the pole angle range of interest with the assumption that crystallites from the same crystallographic direction at different pole angles are formed with similar crystallite thickness and lattice disorder.