# **Supporting Information**

# Effects of PNDIT2 end groups on aggregation, thin film structure, alignment and electron transport in field-effect transistors

Rukiya Matsidik,<sup>a,b</sup> Alessandro Luzio,<sup>c</sup> Sophie Hameury <sup>a</sup>, Hartmut Komber<sup>d</sup>, Christopher R. McNeill<sup>e</sup>, Mario Caironi<sup>c</sup> and Michael Sommer <sup>a,b,f</sup>

<sup>a</sup>Universität Freiburg, Makromolekulare Chemie, Stefan-Meier-Str. 31, 79104 Freiburg, Germany

<sup>b</sup>Freiburger Materialforschungszentrum, Stefan-Meier-Str. 21, Universität Freiburg, 79104 Freiburg, Germany

<sup>c</sup>Center for Nanoscience and Technology @PoliMi, Instituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

<sup>d</sup>Leibniz Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

<sup>e</sup>Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia

<sup>f</sup>Freiburger Institut für interactive Materialien und bioinspirierte Technologien, Georges-Köhler Allee 105, 79110 Freiburg

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**Figure S1**. UV-vis absorption spectra of (a) PNDIT2 made in toluene and (b) made in 2-MeTHF with varying MW at RT in 1-chloronaphthalene

# 2. Thermal characterization



**Figure S2** DCS curves of PNDIT2 samples with increased molecular weight. Dash line: reference samples made in toluene (table 2); Solid line: samples made in MeTHF

PNDIT2-OH-1	Peak: 295.0 °C, 0.6244 mW/mg	PNDIT2-OH-2	Peak: 294.5 °C, 0.6472 mW/mg
	Area: 2.396 J/g		Area: 3.132 J/g
	Area: -3.208 4/3 Peak: 279.5 °C, -0.3462 mW/mg		Area: -3.369 J/g Peak: 281.0 °C, -0.6679 mVV/mg
PNDIT2-OH-3	Peak: 297.1 °C, 0.7168 mW/mg	PNDIT2-OH-4	Peak: 301.0 °C 0.657 mW/mg
	Area: 3.936 J/g		Area: 5.038 J/g
	Area: -4.008 J/g Peak: 283.3 °C, -0.7895 mW/mg		Area: -5.43.0rg Peak: 287.7 °C, -0.7635 mW/mg
PNDIT2-tol-1	Peak: 291.9 °C, 0.5607 mW/mg	PNDIT2-tol-2	Peak: 300.8 °C, 2.077 mW/mg
	Area: -2.253 4/9 Peak: 279.6 °C, -0.4644 mW/mg		Area: -3.643 J/g Peak: 285.0 °C, -2.197 mW/mg
PNDIT2-tol-3	Peak: 300.9 °C, 0.6873 mW/mg Area: 4.917 J/g	PNDIT2-tol-4	Peak: 303.1 °C, 0.7451 mW/mg
	Area: -7.228 yc		Area: -6.312 Jrc Peak: 289.1 °C, -0.9275 mW/mg

**Figure S3** Evaluation of melting and crystallization temperatures and enthalpies of samples from Figure S2

#### 3.<sup>1</sup>H NMR spectra



**Figure S4.** Full <sup>1</sup>H NMR spectra of PNDIT2 (a) made in MeTHF (entry 25) and (b) reference PNDIT2 made in tol (PNDIT2 tol-4). The spectra are enlarged for better visibility of end group signals. In addition to the signals assigned in Figure 3, the OH signal of the NDI-OH end group (a) and the methyl signals of the isomeric NDI-tolyl end groups (b) are assigned (cf. R. Matsidik, H. Komber and M. Sommer, *ACS Macro Lett.*, **2015**, *4*, 1346–1350). # marks signals of impurities. Spectra were measured at 120 °C in  $C_2D_2CI_4$ .

#### 4. Additional AFM images



**Figure S5** (a) Schematic of spin coating off-centre deposition: film topography is checked at a distance of ~ 5 cm from the centre of the spin, where the flow is dominated by centrifugal force field; AFM topography images of PNDIT2-tol-4 (b) PNDIT2-OH-4 (c) deposited from toluene using off-centre spin coating; domains directionality is highlighted through 2D Fast Fourier Transform (FFT) images (insets) extracted from the same AFM images; centrifugal forces direction is also indicated (white arrows).

#### 5. Additional OFET characterization



**Figure S6** plots of saturation mobility ( $\mu_{sat}$ ) as a function of the applied gate bias ( $V_{GS}$ ) for off-centre spin coated films, in case of transport parallel (a) and perpendicular (b) to the backbones/fibrils direction; the relative difference of mobility between the batch from MeTHF and the batch from toluene is also reported.

### 6. 2D GIWAXS images



Figure S7 2D GIWAXS images taken of the (a) toluene sample and the (b) MeTHF sample spin-coated from DCB.