Engineering Polymers with Improved Charge Transport Properties from Bithiophene-Containing Polyamides

Electronic Supplementary Information

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1. Supplementary Figures S1-S8



Supplementary Figure S1. *a*) Representative ¹H NMR spectra for **PA6T2** in non-deuterated HFIP with acetone-d⁶ as the internal standard showed the expected proton signals, including those of the amide protons. The ¹H-NMR chemical shifts in the range of 5.8–6.1 ppm originated from the two chemically different thiophene protons, whereas the aliphatic protons of the diamine and the spacer gave rise to six distinct peaks below 2.5 ppm. *b*) From the cross-peaks observed in ¹H-¹H COSY experiments, the peaks at 2.33, 0.65, 0.45 ppm were attributed to the aliphatic protons of the diamine, while the peaks at 1.94, 1.39, 1.09 ppm corresponded to the protons of the propylene spacer. Distinct amide protons were also observed at around 5.2 ppm. *c*) Expanded view of the dashed area of the full spectrum in *b*).



Supplementary Figure S2. Results from DSC heating scans at 10 °C/min from **PA6T2**, **PA10T2** and **PA12T2** after isothermal crystallization from the melt at the specified temperatures.



Supplementary Figure S3. Deconvoluted WAXD pattern of *a*) even and *b*) odd polyamides **PAnT2** allowed roughly to estimate degree of crystallinity of the obtained polyamides by distinguishing the Bragg peaks from the amorphous halo. The inset showed the 2D WAXD pattern of the polyamides, suggesting absence of the preferential orientation of the crystallites.



Supplementary Figure S4. Atomic force microscopy (AFM) intermittent contact mode images of a film of **PA8T2** isothermally crystallized from the melt at 176 °C. *a*) Error signal from the center of a spherulite. *b*) Height image of the local lamellar structure. The white markers are separated by 10 nm. *c*) Optical micrograph between crossed polarizers of the spherulitic morphology showing an extinction at roughly 45 ° to the direction of the polarizer and concentric banding, consistent with the curved lamellar trajectories seen in *a*).



Supplementary Figure S5. Selected area electron diffraction (SAED) from an oriented film of **PA7T2** prepared at about 140 °C. Approximate *d*-spacings corresponding to the visible reflections are also indicated. The layer lines corresponded to the axial spacing of the methyl groups, and hence did not provide a direct indication of the unit cell dimensions. However, *b*) oriented films of **PA7T2** prepared at about 130 °C and in which the equatorial reflections were less well-resolved, showed additional meridional reflections. The spacings of these reflections suggested a repeat distance in the orientation direction of approximately 55 Å, implying the spacing given in Figure 3*c* for n = 7 to correspond to the (002) planes in the oriented films, and a putative (100) spacing of about 43 Å, which was significantly greater than the lamellar thicknesses observed for even *n*. It was hence tentatively concluded based on these results that specimens of **PAnT2** melt-crystallized under quiescent conditions showed more limited three-dimensional order when *n* was odd.



Supplementary Figure S6. Representative load-displacement curves from nanoindentation measurements on the **PAnT2** together with results from industrial-grade PA610 and PA6TI films.



Supplementary Figure S7. Absorption spectra of the **PA6T2** before and after irradiation for several minutes at 317 nm, showing the photo-bleaching effect.



Supplementary Figure S8. Orbital energy levels of 4,4'-(2,2'-bithiophene-5,5'-diyl)bis (*N*-methylbutanamide) were obtained by density functional theory (DFT) (B97-3/def2-SV(P)) calculations. The dimethyl amide bithiophene was used as proxy for **PAnT2** instead of model compound **T2a** to reduce the calculation time substantially.

2. Supplementary Tables S1-S3

Table S1. The exact positions and full-width at half maximums (FWHMs) of the characteristic IR vibrations, including the amide A, I, and II, and asym/sym CH₂ peaks, for all the bithiophene containing polyamides **PAnT2** and the model compound **T2a**.

	Amide A	FWHM Amide A	Amide I	FWHM Amide I	Amide II	FWHM Amide II	Arom. CH2	Asym. CH ₂	FWHM Asym. CH2	Sym. CH ₂	FWHM Sym. CH2
PA6T2	3301	71	1634	28	1533	39	3065	2930	39	2856	25
PA7T2	3304	83	1633	31	1532	41	3066	2928	41	2854	23
PA8T2	3300	78	1634	31	1532	39.8	3065	2925	38	2852	21
PA9T2	3306	81	1635	26	1533	38	3069	2922	36	2852	19
PA10T2	3305	71	1635	27	1534	37	3068	2922	33	2850	17
PA11T2	3292	86	1634	27	1534	45	3072	2920	32	2850	18
PA12T2	3292	81	1634	29	1535	46	3067	2920	32	2850	17
T2a	3303	30	1638	19	1540	30	3072	2950	n.a	2870	n.a

Identification code	T2a	
Empirical formula	$C_{22}H_{32}N_2O_2S_2$	
Formula weight (g/mol)	420.61	
Temperature (K)	199.99(10)	
Wavelength (Å)	1.54184	
Crystal system	Triclinic	
Space group	PĪ	
Unit cell dimensions	a = 4.9848(4) Å	$\alpha = 90.584(9)^{\circ}$
	<i>b</i> = 5.6250(5) Å	$\beta = 90.140(8)^{\circ}$
	<i>c</i> = 21.347(3) Å	$\gamma = 107.702(8)^{\circ}$
Volume (Å ³)	570.18(10)	
Z	1	
Density (calculated) (Mg/m ³)	1.225	
Absorption coefficient (mm ⁻¹)	2.261	
F(000)	226	
Crystal size (mm ³)	0.742 x 0.271 x 0.034	
Theta range for data collection (°)	4.142 to 75.947	
Index ranges	-6 ≤ h ≤ 3, -6 ≤ k ≤ 7, -26 ≤ l ≤ 26	
Reflections collected	3263	
Independent reflections	$2231 [R_{int} = 0.0356]$	
Completeness to θ = 67.684°	99.1 %	
Absorption correction	Analytical	
Max. and min. transmission	0.925 and 0.392	
Refinement method	Full-matrix least-squares on $ F ^2$	
Data / restraints / parameters	2231 / 100 / 166	
Goodness-of-fit on $ F ^2$	1.063	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0585$, $wR_2 = 0.1532$	
<i>R</i> indices (all data)	$R_1 = 0.0675$, $wR_2 = 0.1617$	
Largest diff. peak and hole (e.Å-3)	0.519 and -0.418	

 Table S2. Crystallographic and refinement data for compound T2a.

	X	У	Ζ	Ueq
S(1)	6366(1)	7959(1)	4429(1)	43(1)
0(1)	3725(5)	3493(7)	1975(2)	83(1)
N(1A)	-981(14)	2484(14)	1862(4)	57(2)
N(1B)	-720(18)	3180(20)	1672(4)	59(2)
C(1)	9224(5)	10259(5)	4736(1)	38(1)
C(2)	9661(6)	12408(5)	4406(2)	46(1)
C(3)	7709(6)	12183(5)	3911(2)	48(1)
C(4)	5775(6)	9898(5)	3858(2)	42(1)
C(5)	3426(6)	9000(6)	3387(2)	47(1)
C(6)	3652(6)	6828(6)	2985(2)	46(1)
C(7)	1408(6)	6156(7)	2476(2)	51(1)
C(8)	1536(7)	4034(8)	2057(2)	58(1)
C(9A)	-1414(16)	247(15)	1467(3)	63(2)
C(9B)	-728(18)	1452(18)	1152(5)	68(2)
C(10A)	-2920(20)	301(19)	872(4)	81(2)
C(10B)	-3180(20)	-811(18)	1200(5)	80(2)
C(11A)	-3100(50)	-2020(30)	473(7)	105(4)
C(11B)	-3630(60)	-2650(30)	650(8)	96(5)

Table S3. Fractional atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters (Å² × 10³) for **T2a**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

3. NMR Spectra







