Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information to

Increased charge carrier mobility and molecular packing of a solution sheared diketopyrrolopyrrole-based donor-acceptor copolymer by alkyl side chain modification

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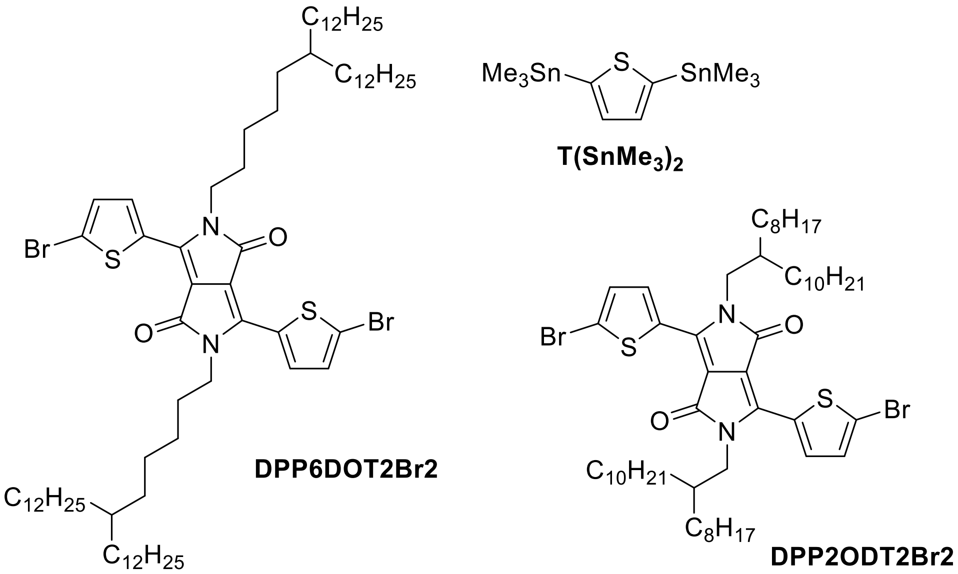
Materials



$T(SnMe_3)_2$

DPP6DOT2Br2

DPP2ODT2Br2

Fig. S1 *Molecular structure of the DPP- and thiophene-based co-monomers used in this work.*

Thermal properties

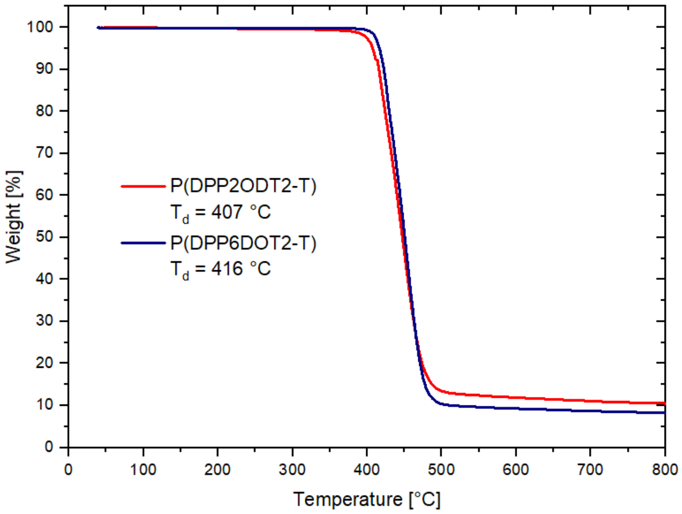


Fig. S2 *TGA curves of P(DPP2ODT2-T) and P(DPP6DOT2-T). Decomposition temperatures T_d were determined at 5 % weight loss.*

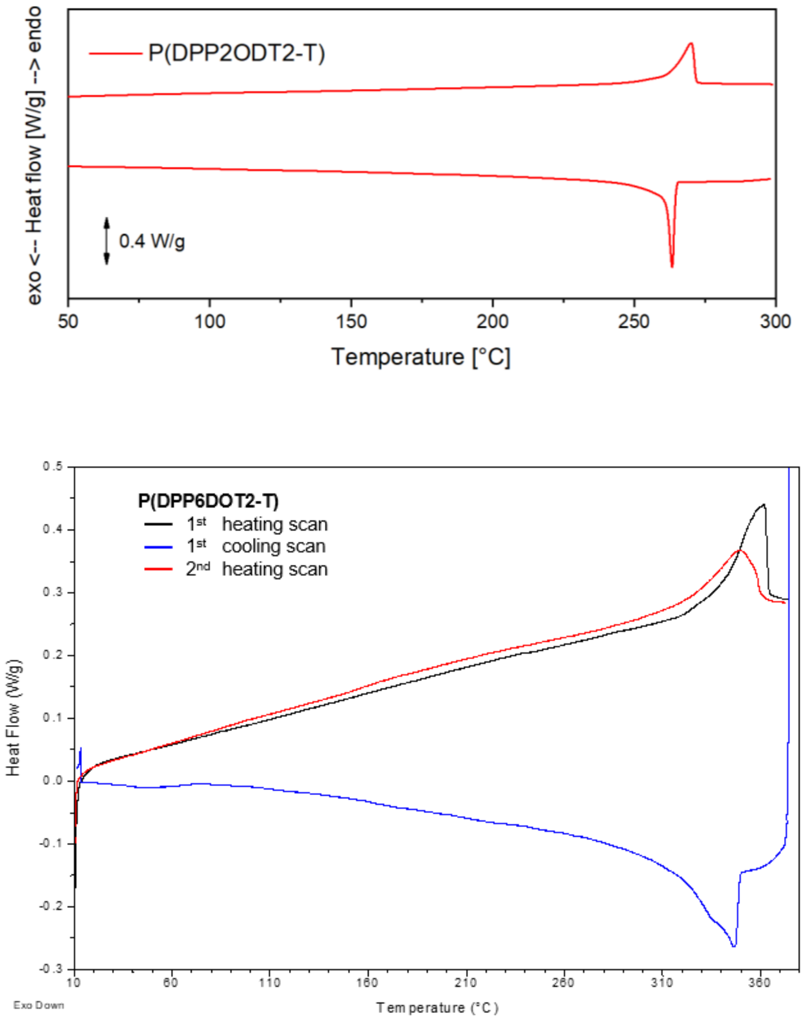


Fig. S3 *Differential scanning calorimetry curves of P(DPP2ODT2-T) (2nd heating and 1st cooling scan) and P(DPP6DOT2-T).*

The following comparison of the discussed DPP-based polymer pair to pairs of hydrocarbons, potentially representing the polymers side-chains, shows that the large difference in melting temperatures between the polymers cannot be solely explained by the increase in molecular weight (**Table S3**) and that the absolute mass of the respective hydrocarbons must be taken into consideration. The reason for the latter can be seen by the non-linear increase of melting temperatures within the homologous series of linear hydrocarbons (**Figure S4**) and by the therefore resulting decrease in ΔTm with chain-length (**Figure S5**). This points to a not linear but weakening gain in London dispersion forces with increasing the chain length due to a weakening relative influence on the polarizability with increasing chain-length for the homologous series of n-alkanes.

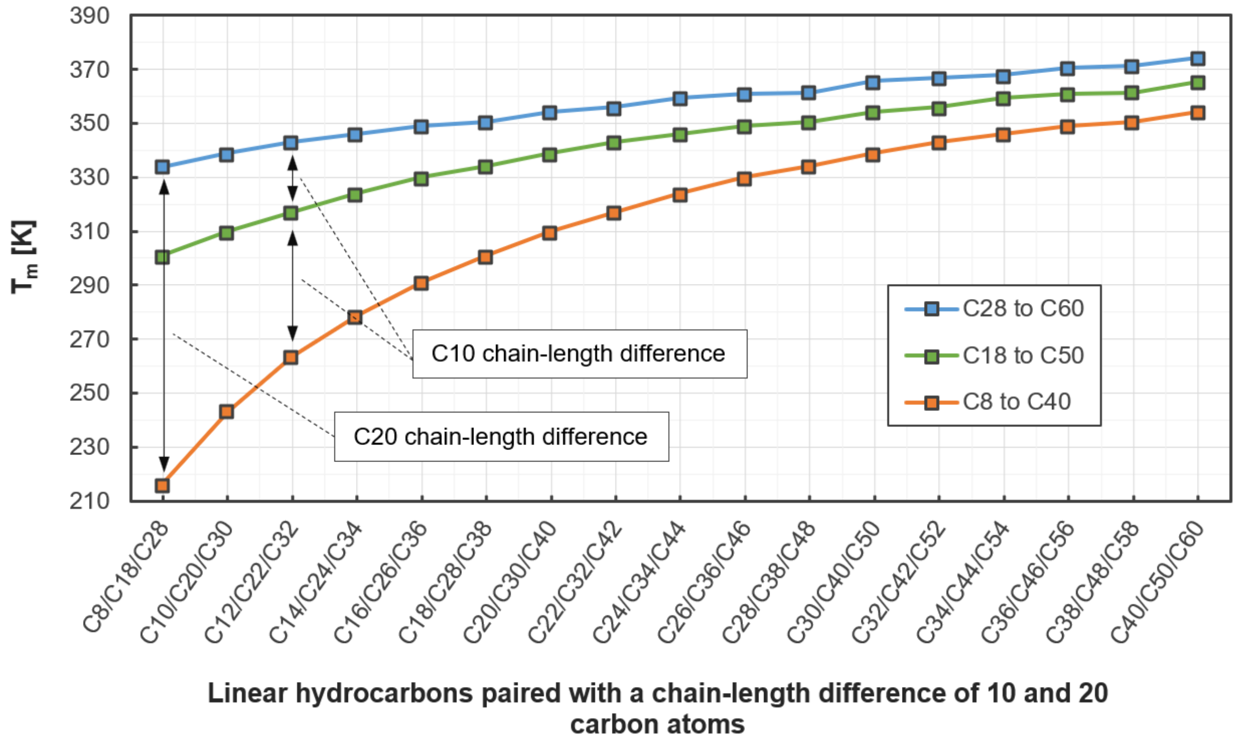


Figure S4 *Melting temperature of linear hydrocarbons stacked to have a relative chain-length difference of 10 (orange↔green / green↔blue) or 20 carbon atoms (orange↔blue) along the vertical. Data listed by NIST (for C56 by Sigma Aldrich).*

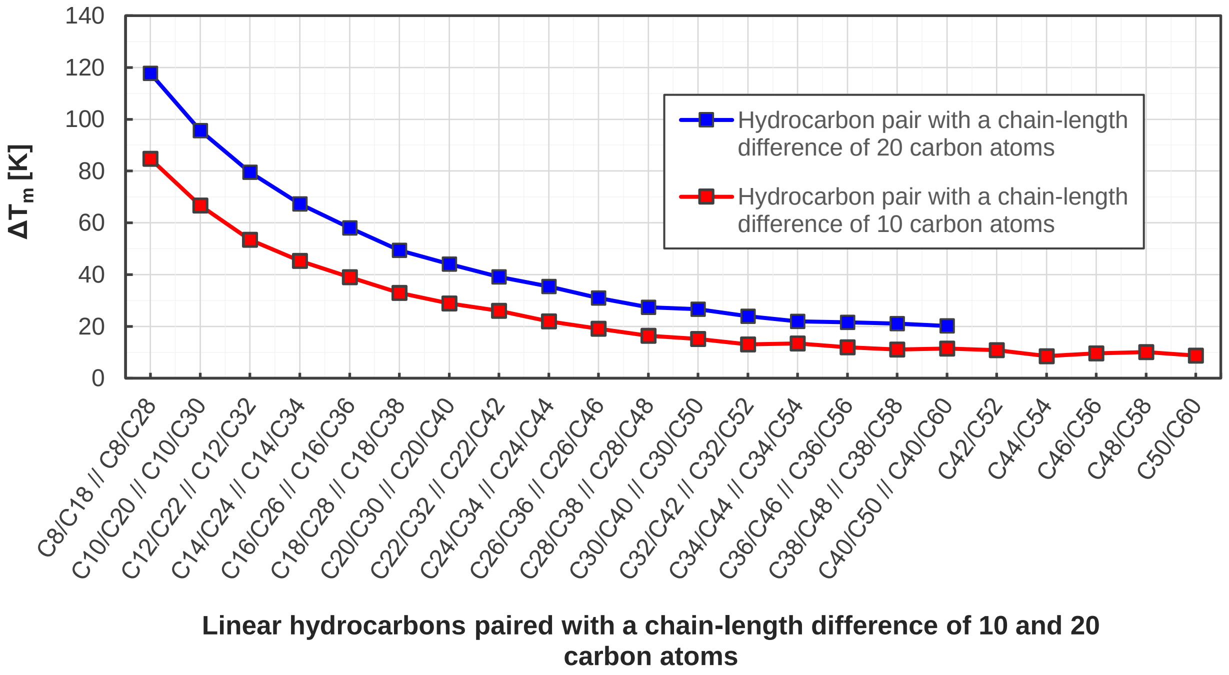


Figure S5 *Chain-length dependence of the melting temperature difference of hydrocarbon pairs having a relative chain-length difference of 10 (red) or 20 carbon atoms (blue). For instance, the first data point of the red graph is the melting temperature difference (ΔT_m) between hydrocarbon C_8H_{18} and $C_{18}H_{38}$ and the first blue datapoint ΔT_m between C_8H_{18} and $C_{28}H_{58}$.*

Optoelectronic properties

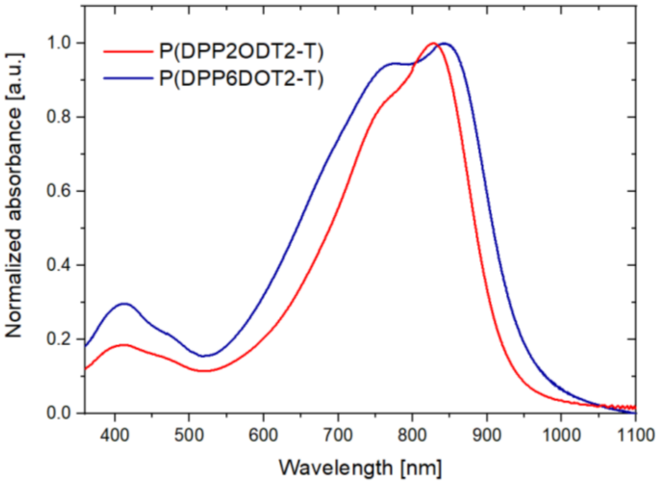


Fig. S6 *Thin-film UV-Vis absorption spectra of P(DPP2ODT2-T) and P(DPP6DOT2-T).*

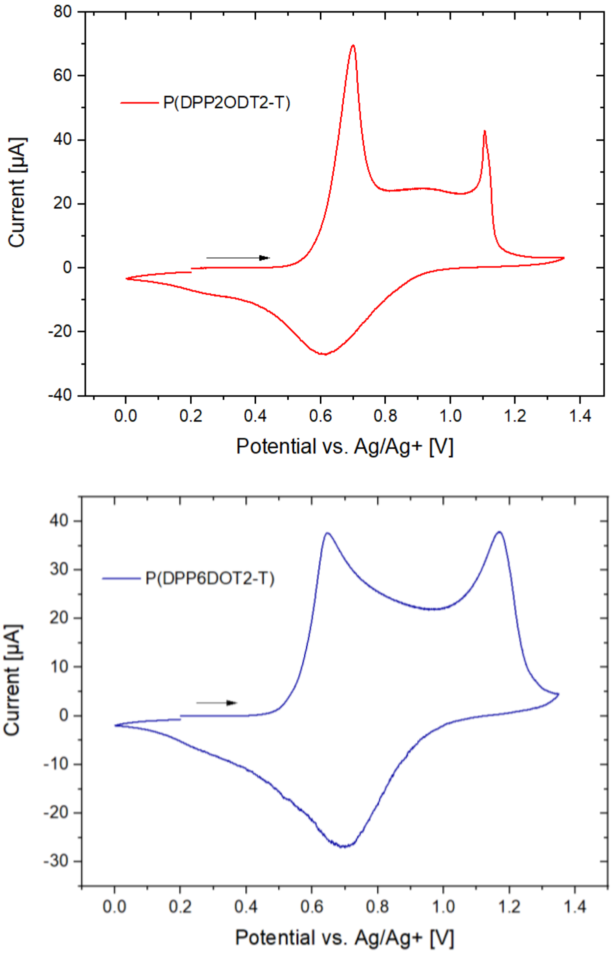


Fig. S7 *Cyclic voltammogram of a P(DPP2ODT2-T) and P(DPP6DOT2-T) thin film.*

Transistor characteristics

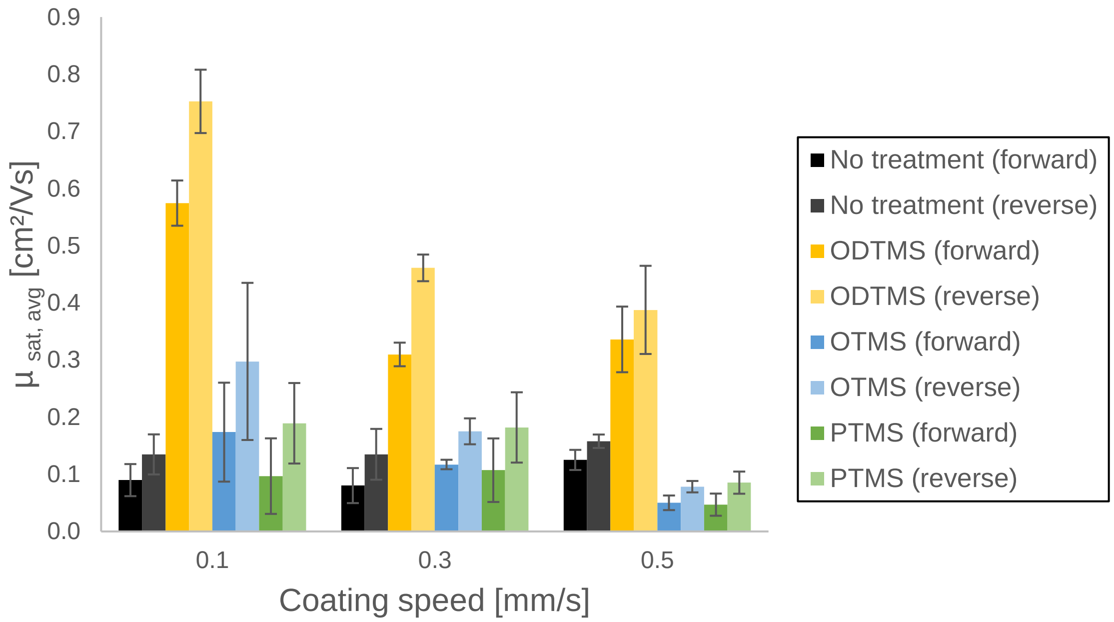


Fig. S8 *Average saturation mobility of P(DPP6DOT2-T) transistors with solution sheared films on different SAMs and for different coating speeds.*

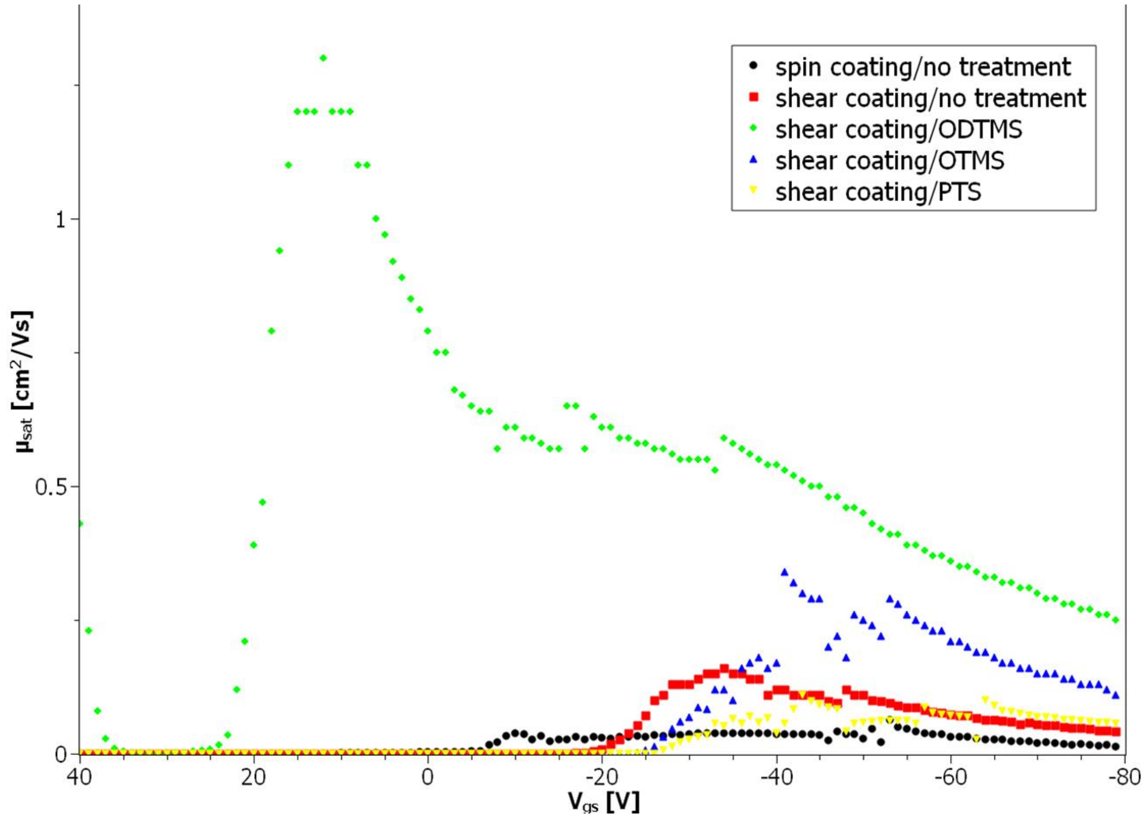


Fig. S9 *Gate voltage dependent saturation mobility for spin coated and solution sheared P(DPP6DOT2-T) transistors for different SAMs. It can be seen that the mobility is dependent on the gate voltage especially for the high mobility devices on the ODTMS SAM.*

NMR spectroscopy and GPC results

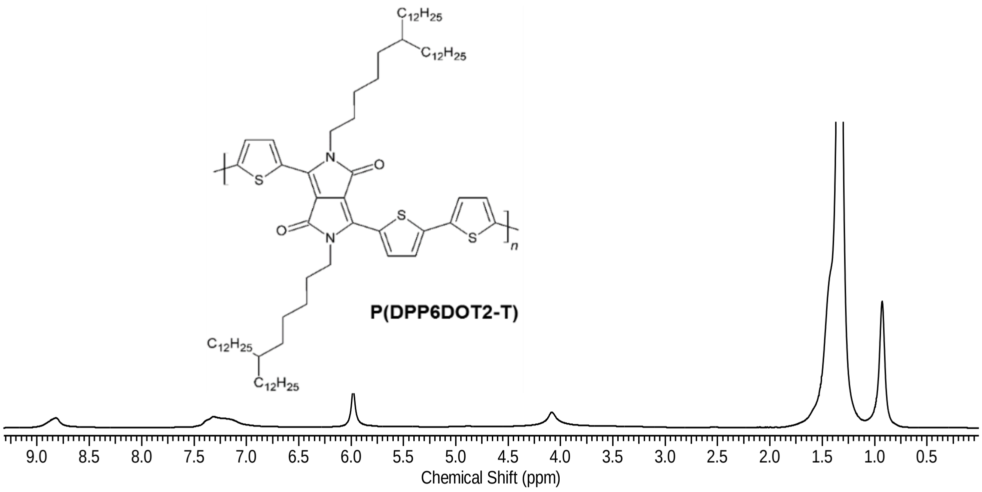


Fig. S10 *^{1}H NMR spectrum of P(DPP6DOT2-T) in $C_2D_2Cl_4$ at 393 K.*

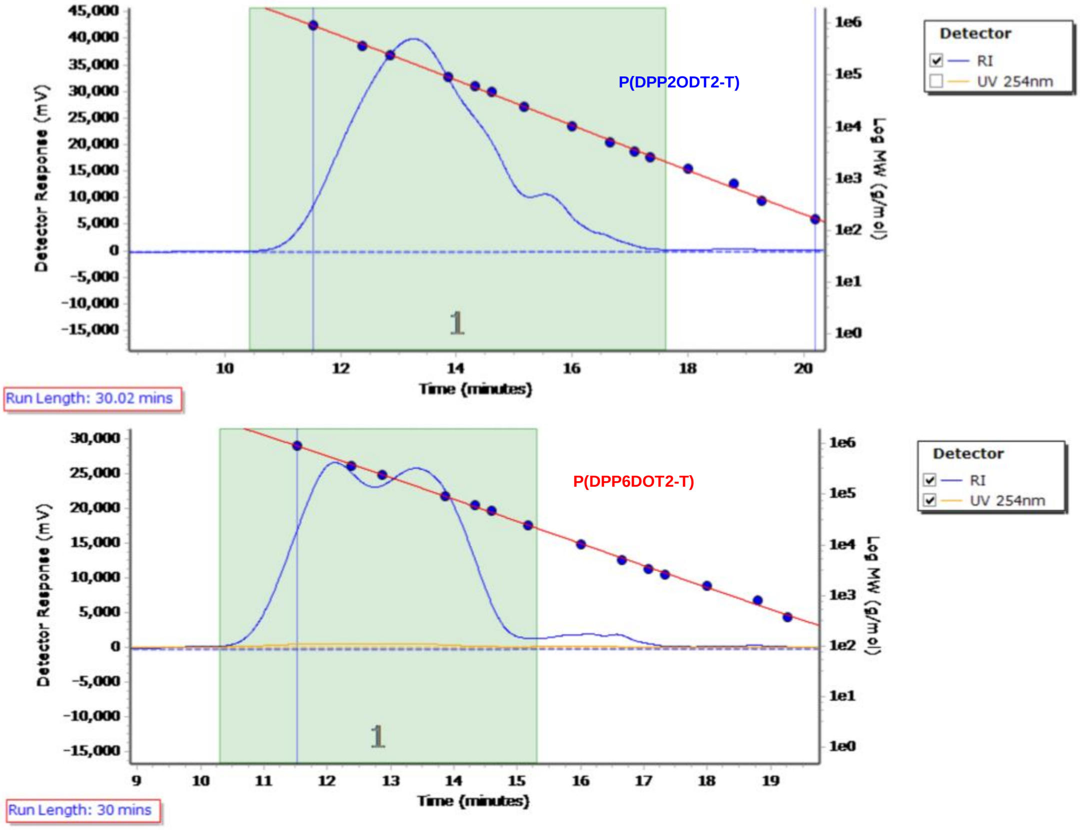


Fig. S11 *GPC curves of P(DPP2ODT2-T) and P(DPP6DOT2-T) in $CHCl_3$ at 40 °C.*

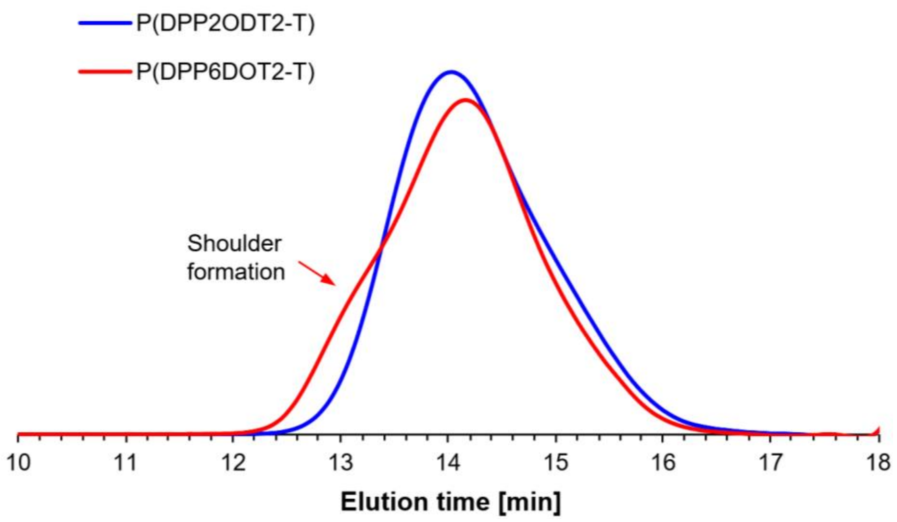


Fig. S12 *HT-GPC curves of P(DPP2ODT2-T) and P(DPP6DOT2-T) in 1,2,4-trichlorobenzene at 150 °C.*

Table S1 *Electrochemical properties of P(DPP2ODT2-T) and P(DPP6DOT2-T).*

	$\bar{E}_{1/2,\ Fc/Fc+}$ [V][a]	**$\bar{E}_{onset,\ ox}$ [V][b]**	**λ_{onset}^{abs} [nm][c]**	**E_g [eV][d]**	**E_{HOMO} [eV][e]**	**E_{LUMO} [eV][f]**
P(DPP2ODT2-T)	0.095	0.600	924	1.34	-5.60	-4.26
P(DPP6DOT2-T)	0.087	0.548	948	1.31	-5.55	-4.24

[a] Average half-wave potential of Fc/Fc^+ vs. Ag/Ag^+-reference electrode calculated from 3 scans before and after the CV measurement series. [b] Average onset oxidation (ox) potential determined from at least 3 individual CV scans. [c] Estimated from the absorption edge to high wavelengths. [d] Calculated by $E_g \approx 1240\ nm/\lambda_{onset}^{abs}$[eV]. [e] Calculated by $E_{HOMO} = -(5.09 + \bar{E}_{onset,ox} - \bar{E}_{1/2,Fc/Fc^+})$[eV]. [f] Calculated by $E_{LUMO} = E_{HOMO} + E_g$.

Table S2 *Parameters of solution sheared P(DPP6DOT2-T) transistors measured at various times after fabrication.*

Time of measurement	Initial	2 weeks	16 weeks	58 weeks
V_{th} [V]	20 ± 2	18 ± 2	17 ± 1	15 ± 1
$\mu_{sat,avg}$ [cm²/Vs]	0.6 ± 0.04	0.7 ± 0.03	0.6 ± 0.04	0.5 ± 0.03
$\mu_{sat,min}$ [cm²/Vs]	0.4 ± 0.1	0.3 ± 0.02	0.3 ± 0.03	0.3 ± 0.03
$\mu_{sat,max}$ [cm²/Vs]	1.1 ± 0.06	1.5 ± 0.3	1.3 ± 0.2	0.8 ± 0.09

I_{on}/I_{off}	$2x10^5 \pm 7x10^4$	$5x10^4 \pm 2x10^4$	$1x10^4 \pm 4x10^3$	$7x10^3 \pm 4x10^3$

Table S3: *Comparison of the melting point behavior between the discussed DDP-based polymers and selected hydrocarbons*

Compound	M of repeating unit or hydrocarbon [g/mol]	ΔM [g/mol]	Number of (side-)chain carbon atoms	Δ in number of (side-)chain carbon atoms	T_m [°C][a]	ΔT_m [K]
P(DPP6DOT2-T)	1139.95	280.54	C30 / C60[b]	10 / 20	349	79
P(DPP2ODT2-T)	859.41		C20 / C40[b]		270	
Octacosane	394.76	280.53	C28	20	61	118
Octane	114.23		C8		-57	
Triacontane	422.81	140.26	C30	10	66	29
Eicosane	282.55		C20		37	
Hexacontane	843.61	280.53	C60	20	101	20
Tetracontane	563.08		C40		81	

[a] Melting temperature as derived from DSC experiments for the polymers or as listed by the National Institute of Standards and Technology (NIST, U.S. Department of Commerce) for the hydrocarbons. [b] Taking into consideration that one repeating unit holds two side chains.