Electronic Supplementary Information

Tuning Nanostructures and Molecular Orientation of High Molecular Weight Diketopyrrolopyrrole-Based Polymers for High-Performance Field-Effect Transistors

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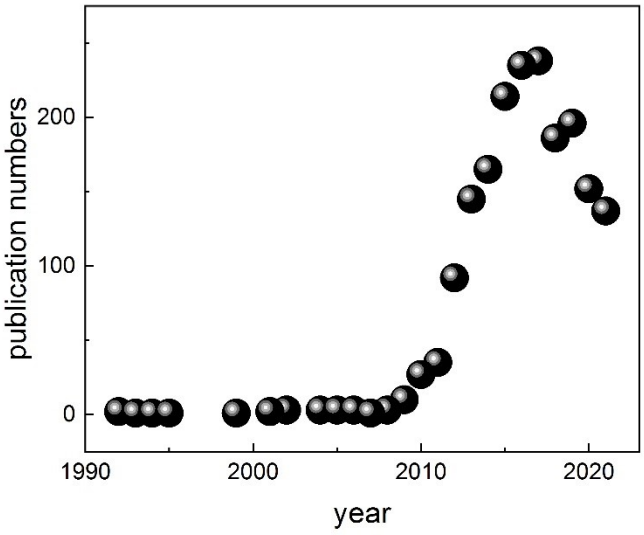

Figure S1. Annual number of scientific publications on "diketopyrrolopyrrole polymer" since 1993, searched using Web of Science.

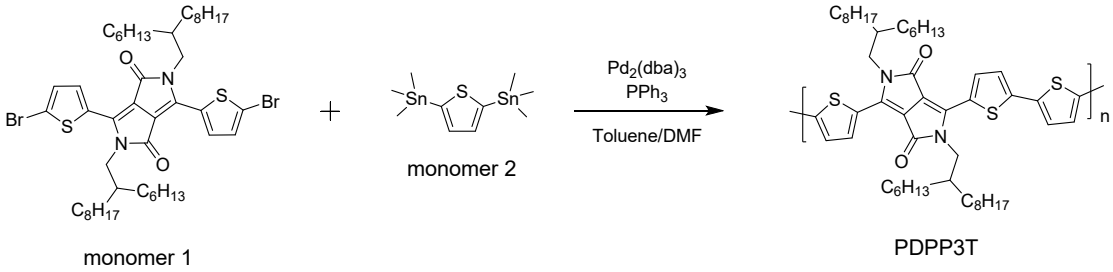

Figure S2. Polymerization reaction used for PDPP3T. Details can be found in literature[1].

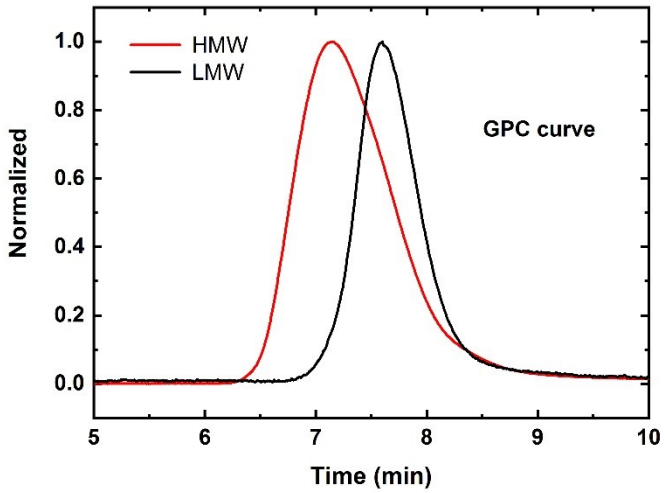

Figure S3. GPC traces of two batches of PDPP3T.

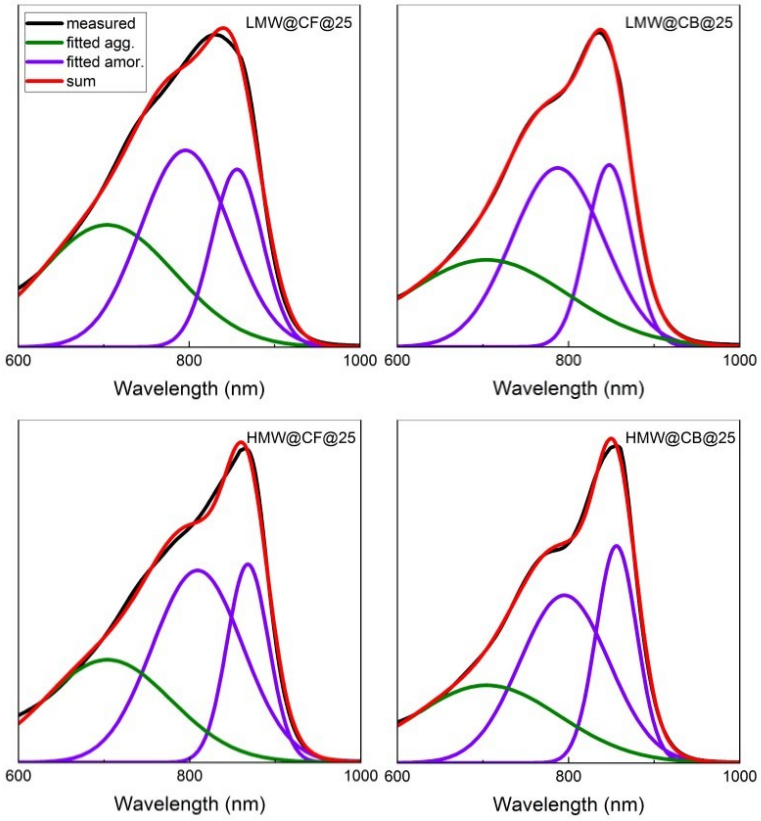

Figure S4. Decomposition analysis of representative absorption spectra in Figure 1.

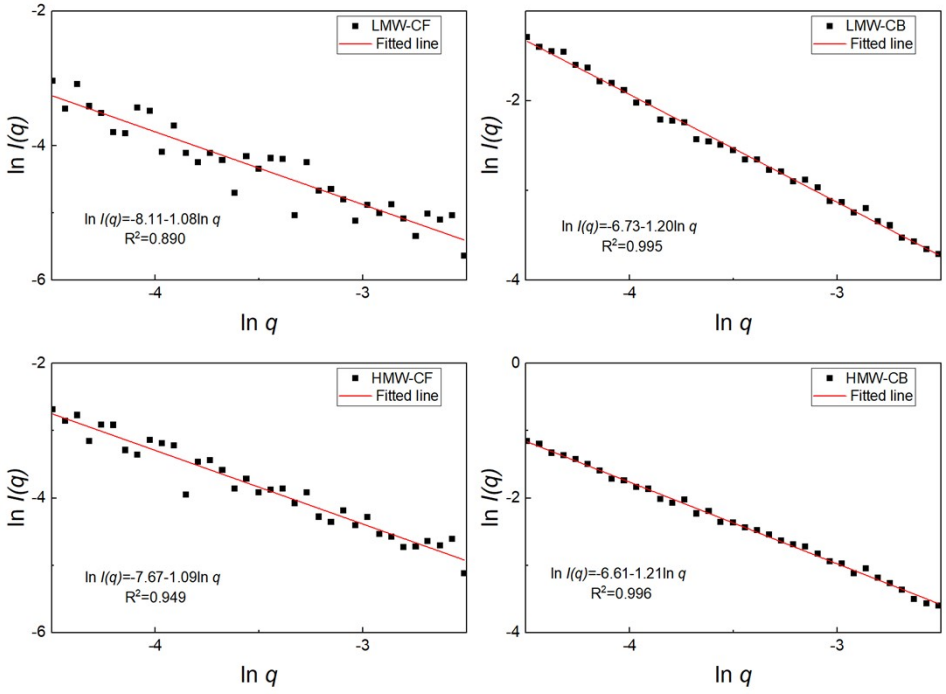

Figure S5. SANS profiles and fitted lines for PDPP3T solutions, where deuterated CF-*d* and CB-*d5* were used to dissolve polymers. The Porod law, $I(q) \sim q^{-n}$, where $I(q)$ is the scattering intensity and the Porod exponent n is the fractal dimension of scattering objects, was used for fitting.

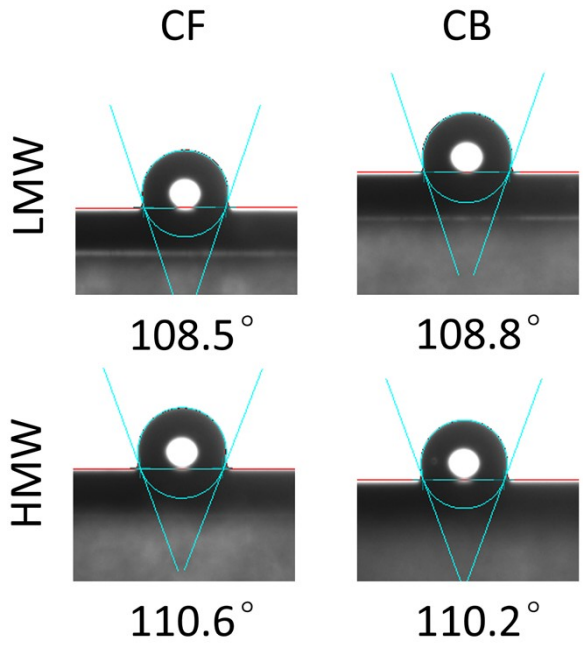

Figure S6. Contact angles of PDPP3T films with different molecular weights.

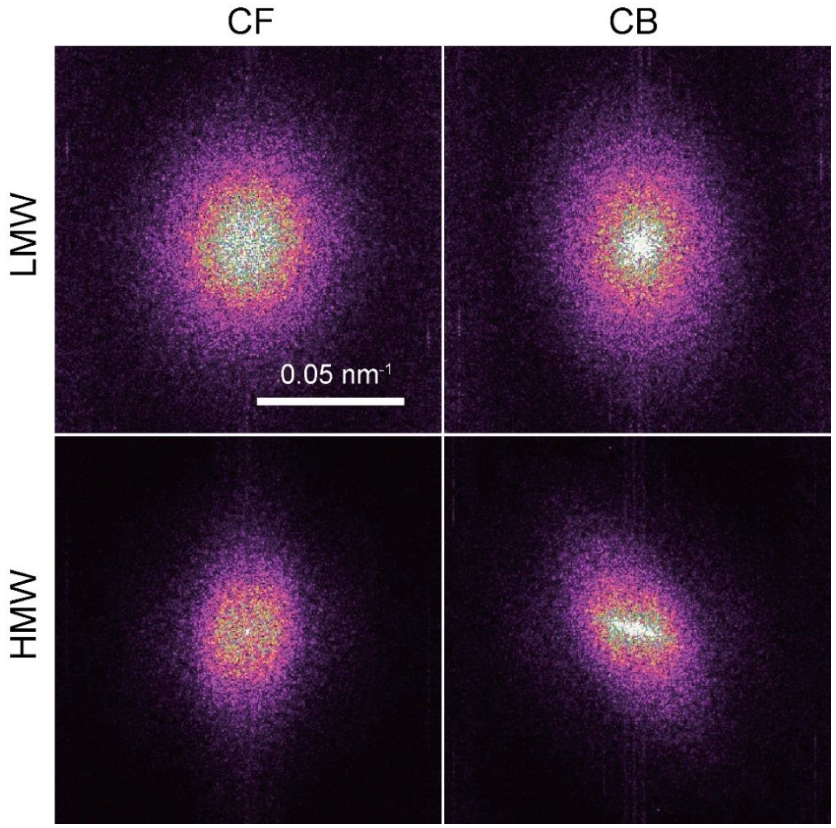

Figure S7. Fourier transform images from AFM images in Figure 3. All images share the same scale bar.

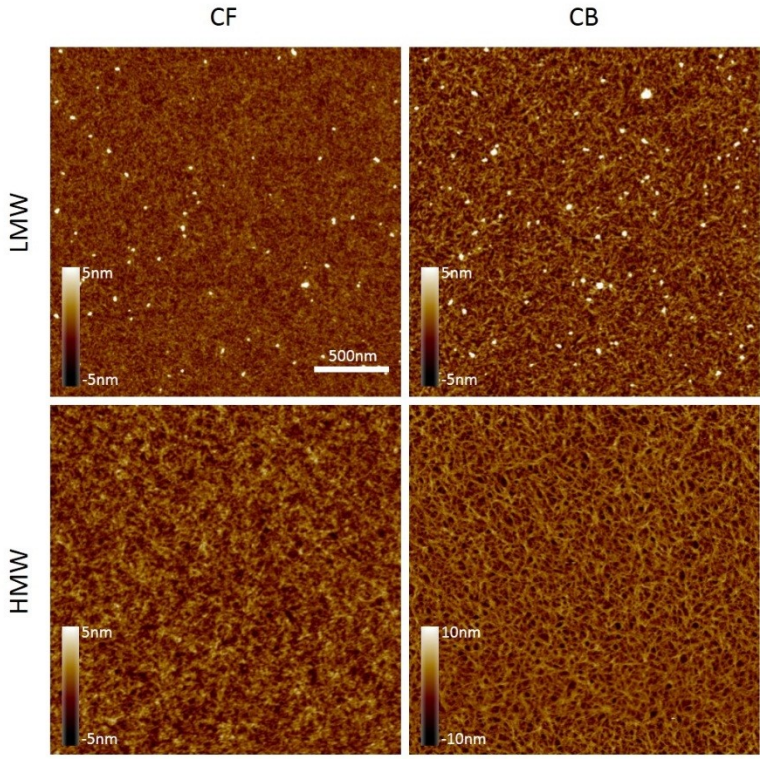

Figure S8. AFM height images of LMW and HMW PDPP3T thin films spin-coated from CF and CB. HMW films always show longer nanofibers compared with LMW one, well consistent with Figure 3.

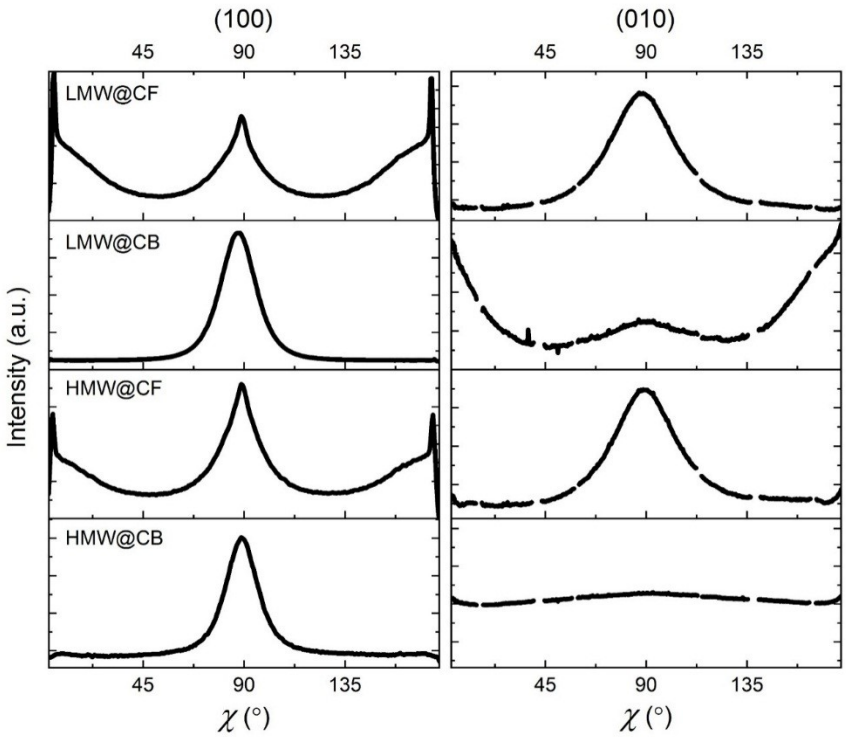

Figure S9. Intensity azimuthal pole figure plots for the (100) interlayer and (010) π–π stacking reflections.

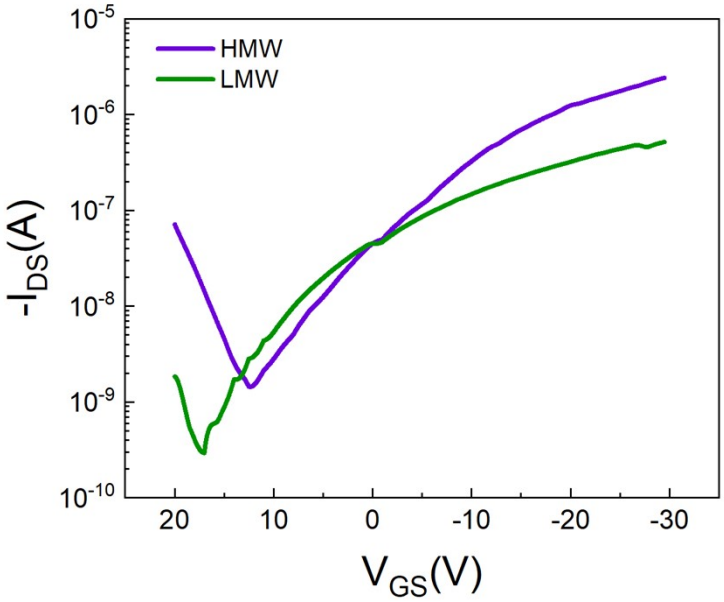

Figure S10. Transfer characteristics of PDPP3T polymer transistors from *o*-DCB. HMW polymer transistors show higher mobility (0.17 $cm^2\ V^{-1}\ s^{-1}$) compared to LMW (0.025 $cm^2\ V^{-1}\ s^{-1}$). Toluene as solvent is also tested, and LHM polymer transistors show a mobility of 0.043 $cm^2\ V^{-1}\ s^{-1}$, while HMW polymer is almost insoluble.

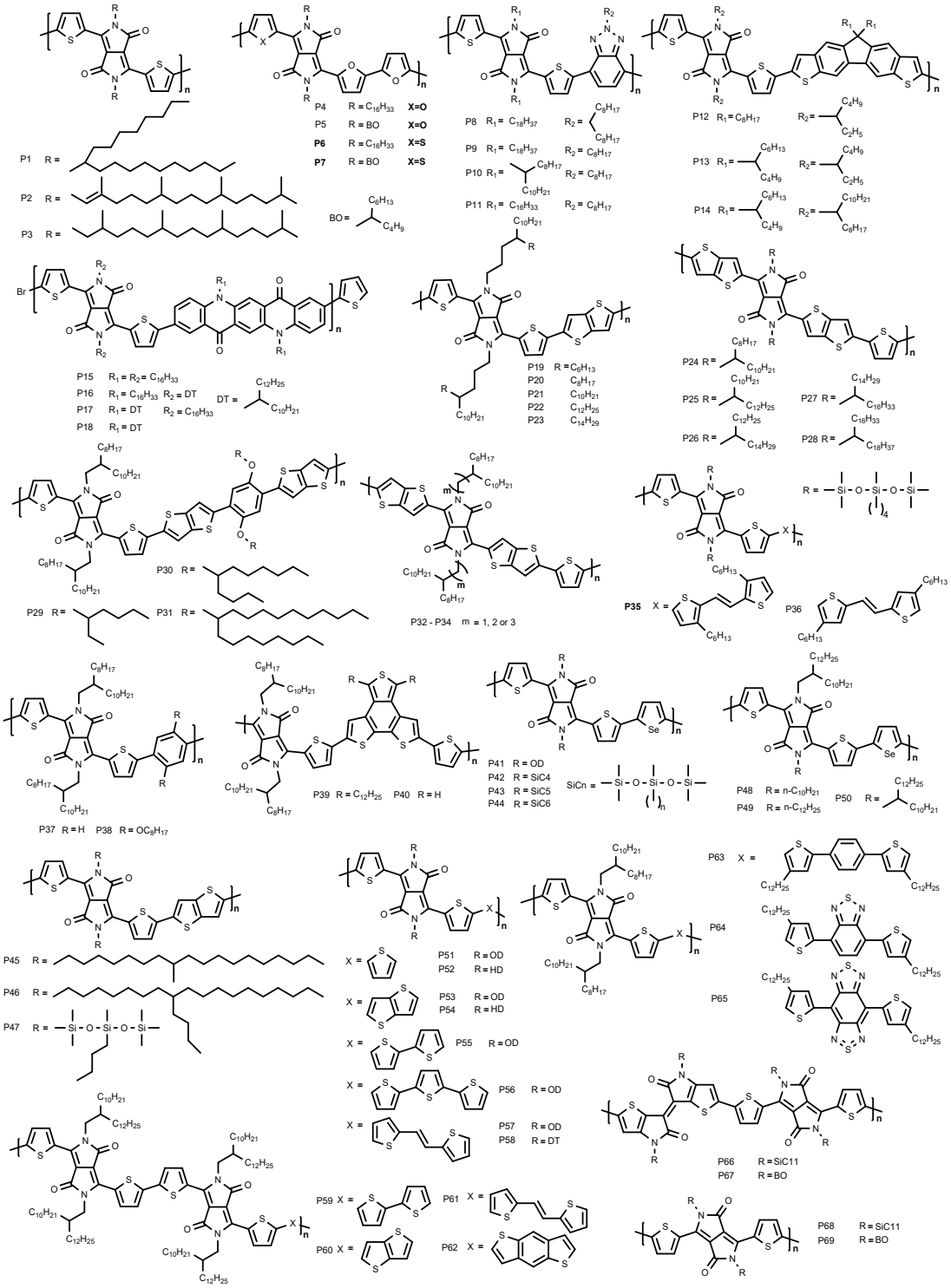

Figure S11. DPP-based polymers with tunable packing orientation through modification of chemical structures.

Table S1. The molar ratio of two monomers used for polymerization.

Polymer	Monomer 1 (equ)	Monomer 2 (equ)	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	M_{peak} (kg mol^{-1})
HMW	1	1.05	68.2	254.8	3.73	238.9
LMW	1	1.2	42.6	78.7	1.85	75.4

Table S2. Fitted parameters for solution absorption spectra using nucleation-elongation cooperative model.

polymer	solvent	ΔH_e (kJ mol^{-1})	T_e (°C)	R^2 (%)
LMW	CF	-55.2	93	99.9
	CB	-35.2	125	98.8
HMW	CF	-47.1	117	99.9
	CB	-80.6	104	98.9

Table S3. Summary of DPP based polymers with tunable packing orientation.

strategy		polymers	Orientation	Ref.
chemical structure	side chain	P1-P3	Face on/Edge on	[2]
		P4-P7	Face on/Edge on	[3]
		P8-P11	Face on/Edge on/Amorphous	[4]
		P12-P14	Face on/Edge on	[5]
		P15-P18	Face on/Edge on	[6]
		P19-P23	Face on/Edge on	[7]
		P24-P28	Face on/Edge on	[8]
		P29-P31	Face on/Edge on	[9]
		P32-P34	Edge on	[10]
		P35-P36	Edge on/Mixed	[11]
		P37-P38	Face on/Edge on	[12]
		P39-P40	Face on/Edge on	[13]
		P41-P44	Face on/Edge on/Mixed	[14, 15]
		P45-P47	Edge on	[16]
		P48-P50	Face on/Edge on	[17]
	conjugated segment	P51-P58	Face on/Edge on	[18-21]
		P59-P62	Mixed	[22]
		P62-P64	Face on/Edge on	[23]
		P65-P68	Face on/Edge on/Mixed	[24]
solvent quality		PDPP3T	Face on/Edge on	This work

Table S4. Solubility of PDPP3T in CF and CB.

	Solvent	Solubility (mg mL^{-1})
LMW	CF	>30
	CB	>30
HMW	CF	5-8
	CB	8-10

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