Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Sub-layer rationale of anomalous layer-shrinkage from atomistic simulations of a fluorinated mesogen.

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Parameterisation Plots

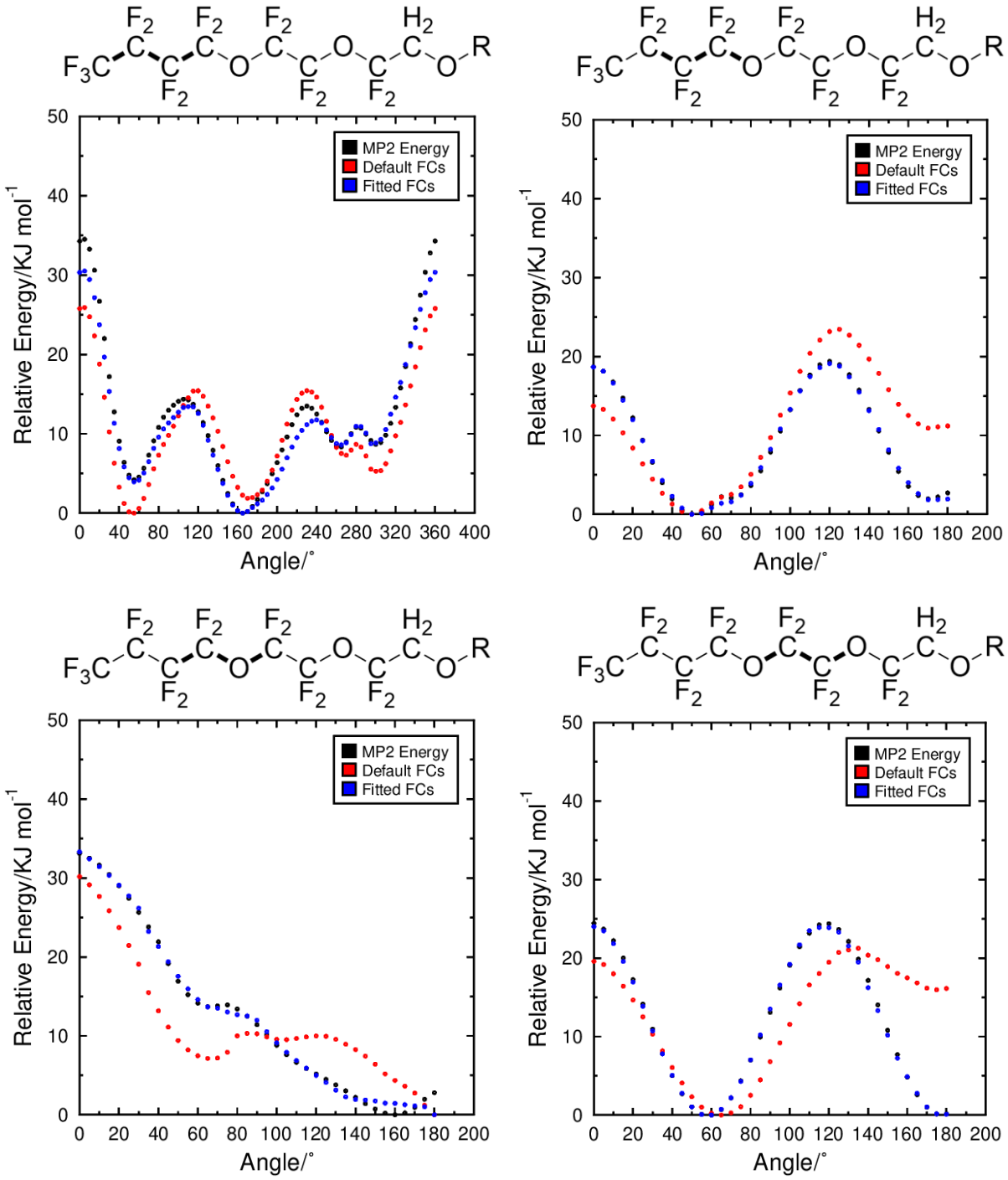


Figure S1 Structure of the perfluoropolyether chain of 3M 8422 with parameterised dihedrals shown in bold (top), and graphical comparison (bottom) of the MP2 energy (black) versus the MD energy with default force constants (red) and fitted force constants (blue), calculated at 5° intervals. The fitted force constants were applied to all equivalent dihedrals in the perfluoropolyether chain.

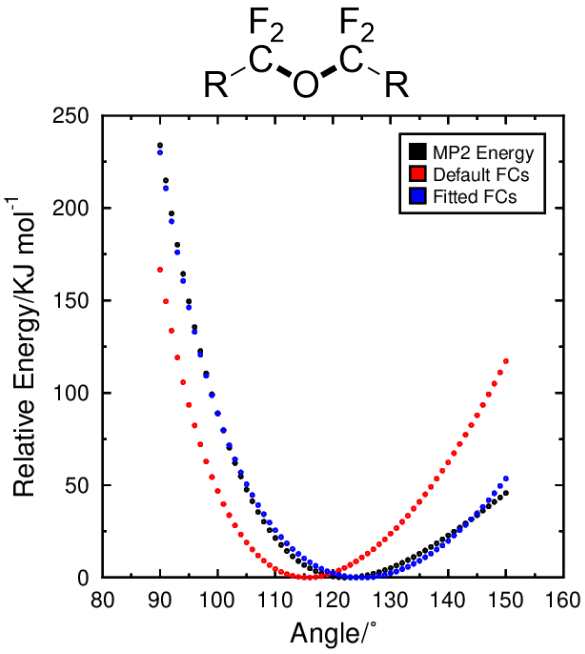


Figure S2 Structure of the perfluoropolyether chain of 3M 8422 with the parameterised bend angle shown in bold (top), and graphical comparison (bottom) of the MP2 energy (black) versus the MD energy with default force constants (red) and fitted force constants (blue), calculated at 1° intervals between 90° and 150°. The fitted force constants were applied to all equivalent bend angles in the perfluoropolyether chain.

Initial configurations

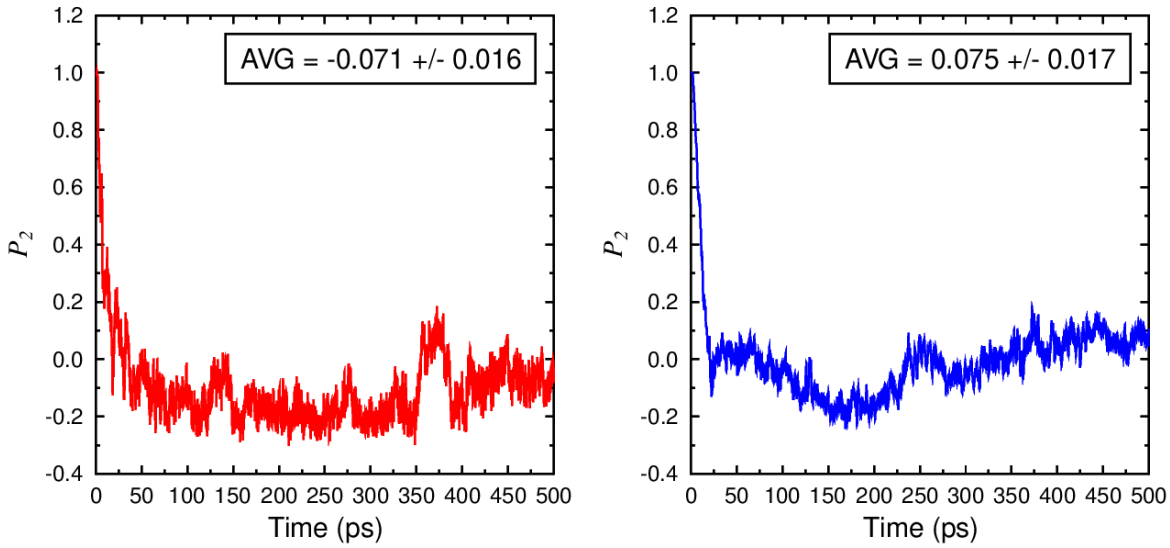


Figure S3 plots of orentational order parameters, P_2, determined during the compression from the initial gas-phase density lattice to a condensed-phase density, with the molecular axes defined as the minimum MOI axis of the atoms in the aromatic core (left) and the minimim MOI axis of all atoms in each molecule (right). The average values close to zero indicate the unbiased, isotropic nature of the starting configurations.

Orientational order parameters

Table S1 Orientational order parameter, P_2, determined with respect to **k**, of the aliphatic chain, aromatic core, and the perfluoropolyether chain from simulations of 3M 8422 at 10 K intervals between 280 K and 330 K.

	Aliphatic		Aromatic		Perfluoro	
T / K	P_2	+/-	P_2	+/-	P_2	+/-
280	0.6947	0.0153	0.7032	0.0160	0.3694	0.0052
290	0.6904	0.0034	0.6977	0.0038	0.3752	0.0050
300	0.7146	0.0072	0.7691	0.0098	0.3104	0.0043
310	0.7250	0.0070	0.7884	0.0102	0.2845	0.0027
320	0.6902	0.0066	0.7719	0.0087	0.2358	0.0048
330	0.6434	0.0048	0.7421	0.0058	0.1947	0.0037

Interdigitation

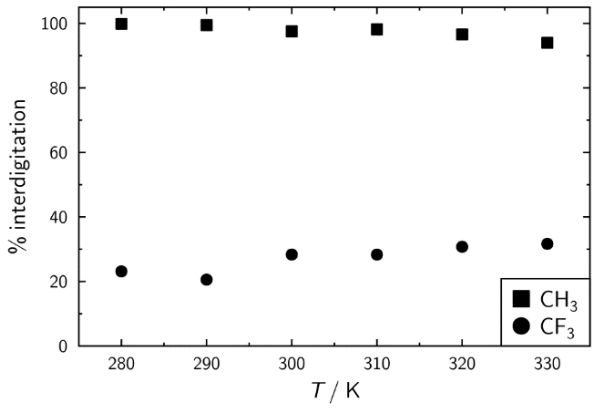
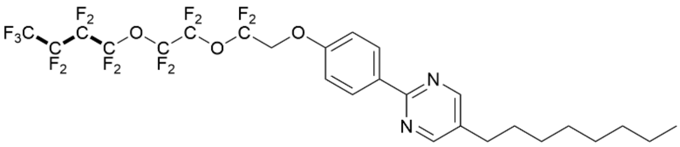
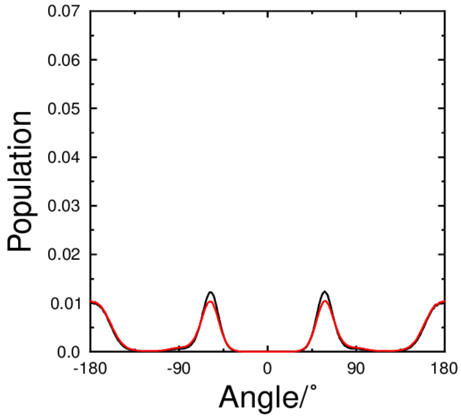
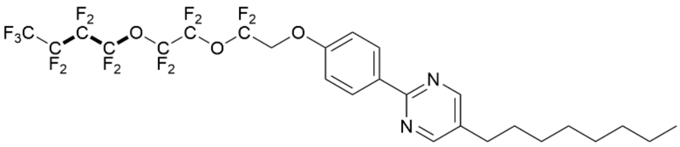


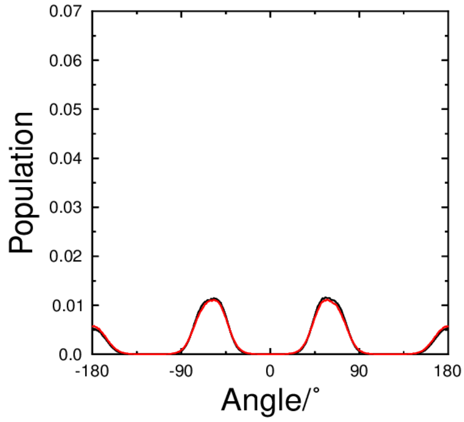
Figure S4 Degree of interdigitation of the perfluorinated end-groups and aliphatic end-groups calculated over 50 ns windows of the simulations.

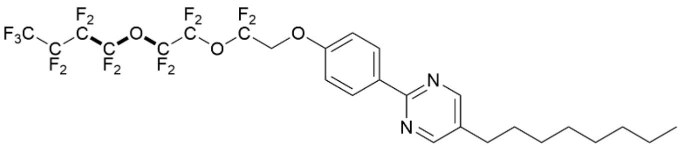
Dihedral populations from simulations at 280K (SmC) and at 330K (SmA)

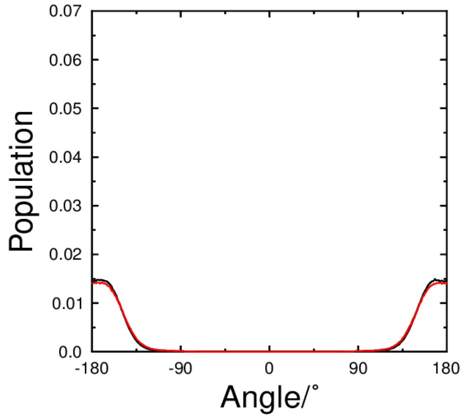


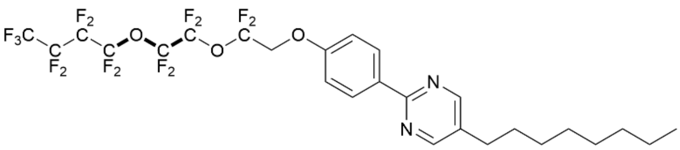


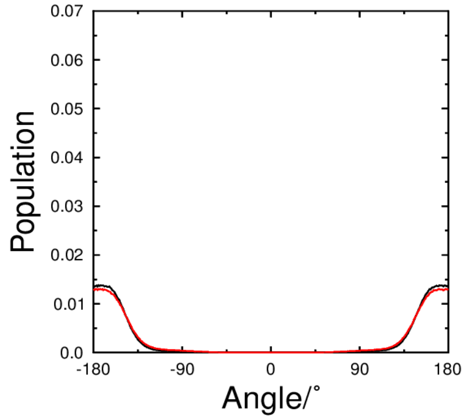


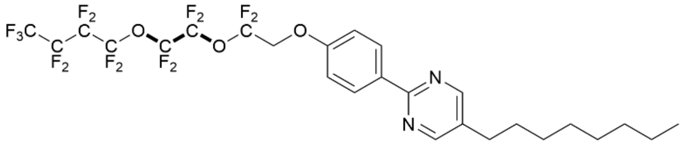


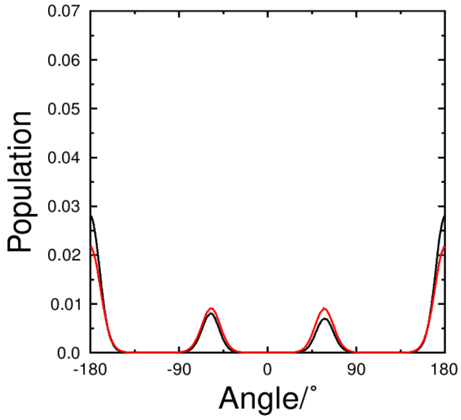








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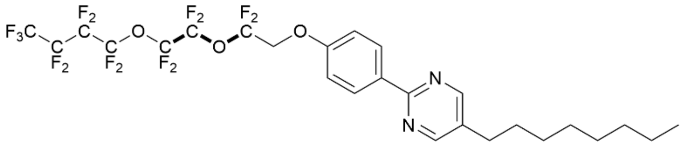

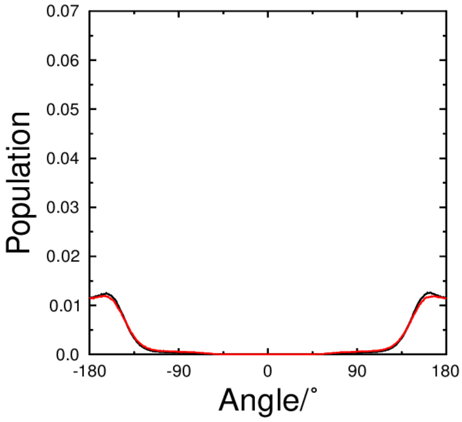
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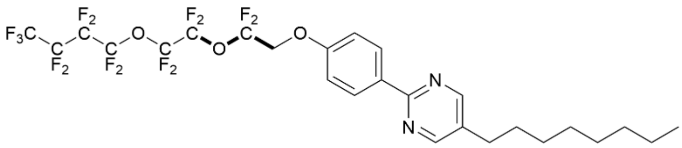

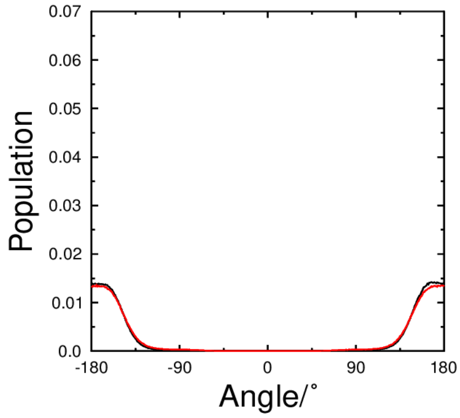
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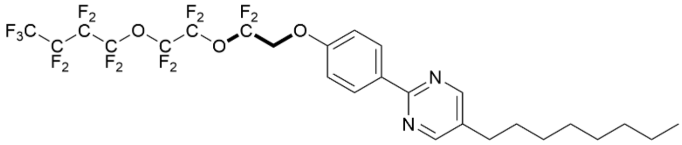

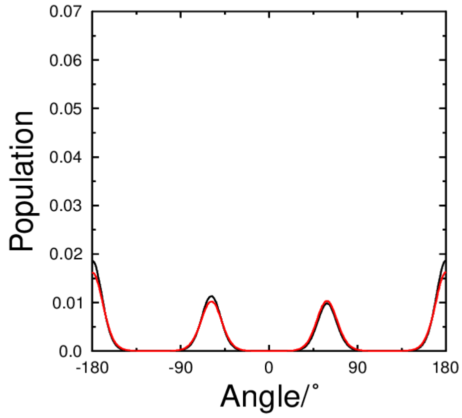
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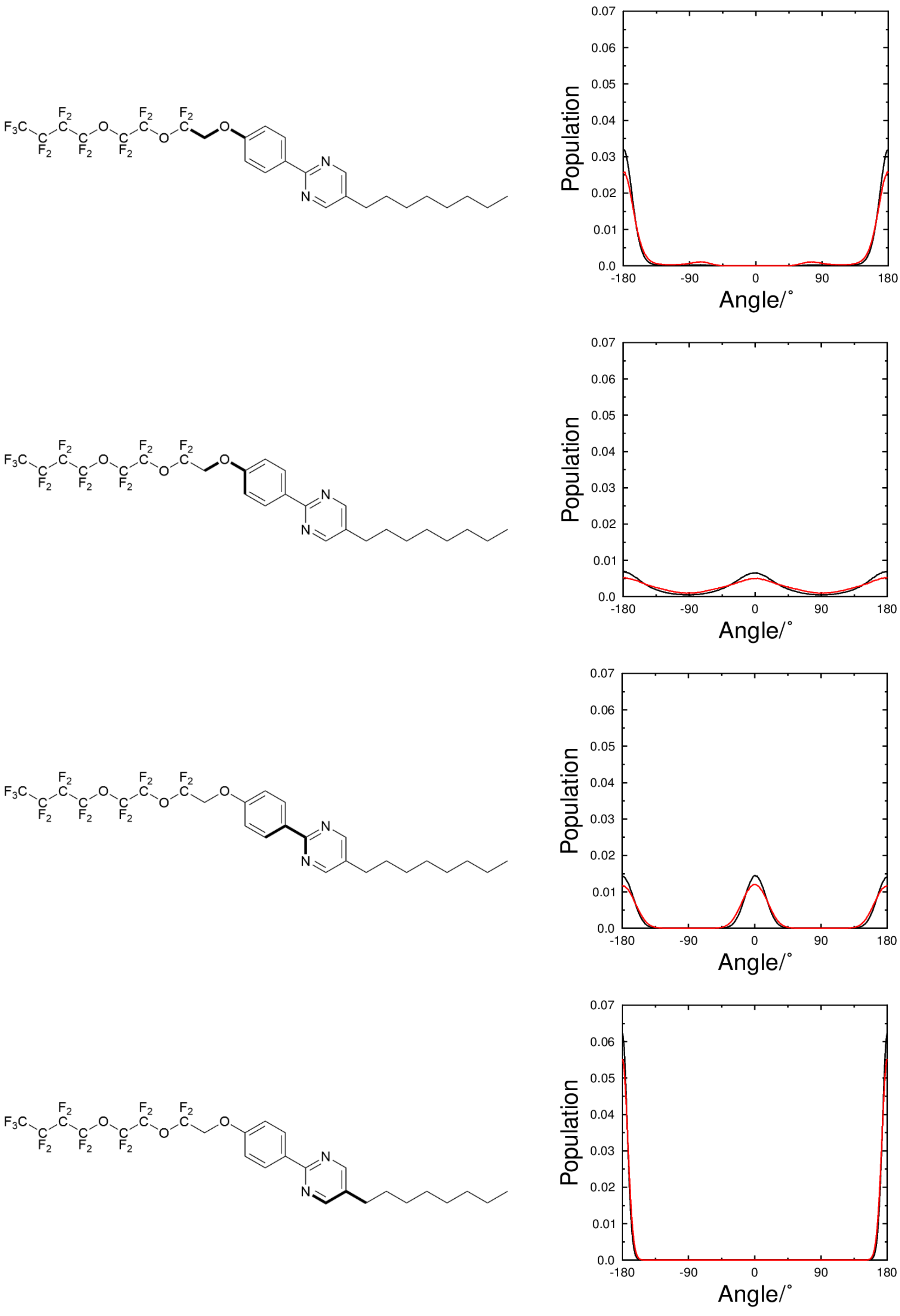

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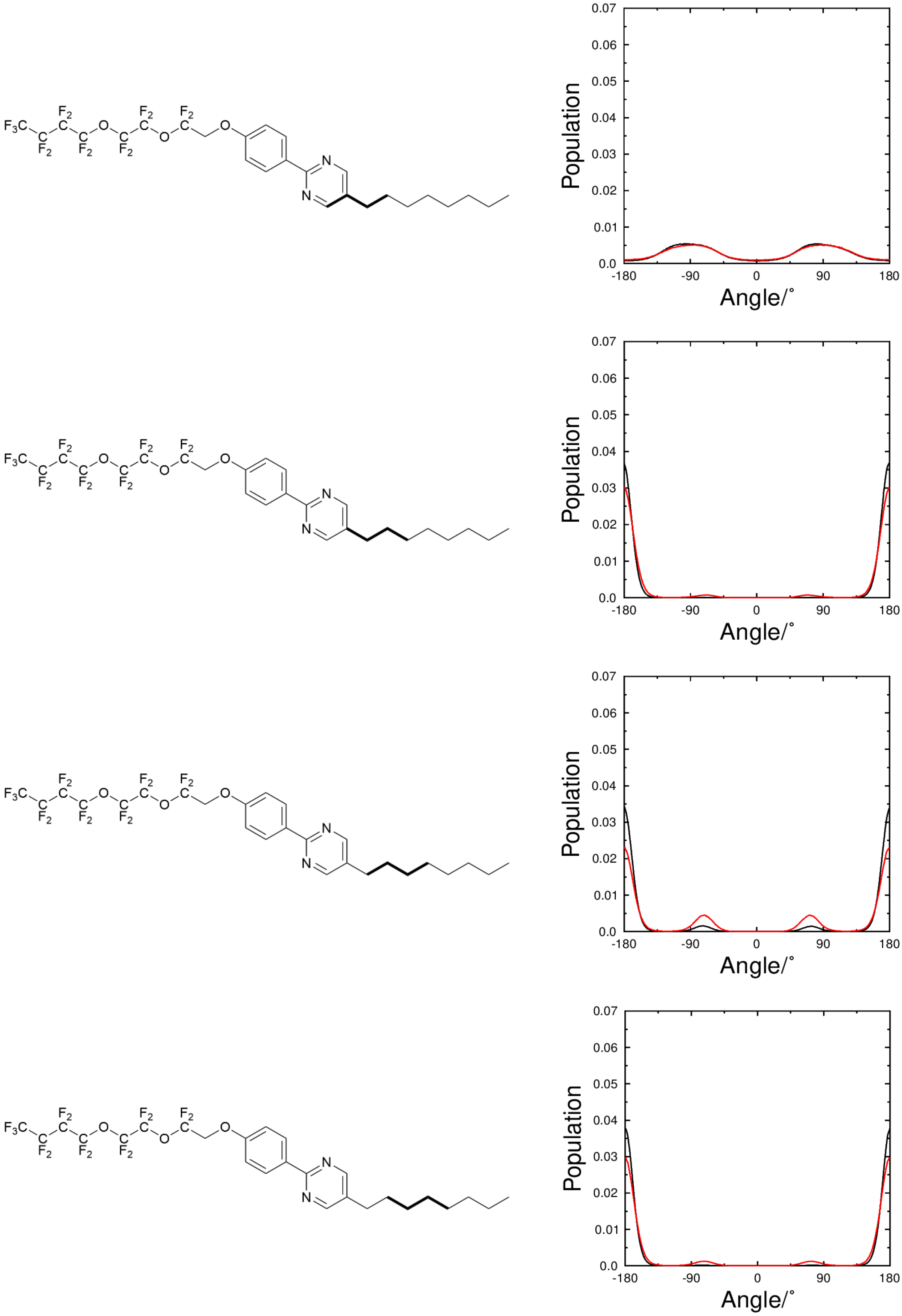

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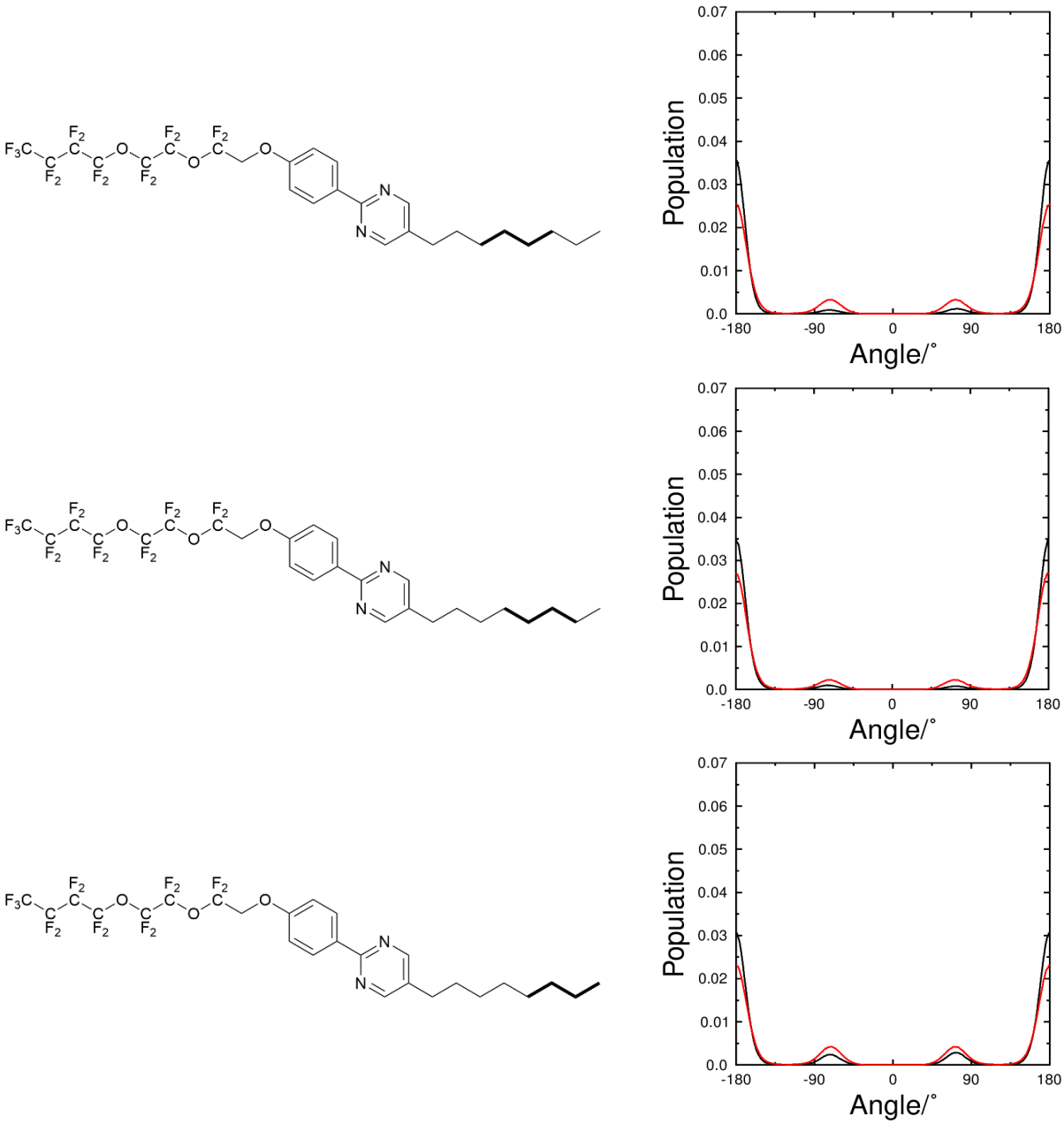

Figure S5 Populations of dihedral angles (shown in bold) in 3M 8422 at 280 K (SmC; black) and at 380 K (SmA; red).