Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Collective Dynamics of Molecular Rotors in a Periodic Mesoporous Oganosilica: A Combined Solid-State ^{2}H-NMR and Molecular Dynamics Simulation Study.

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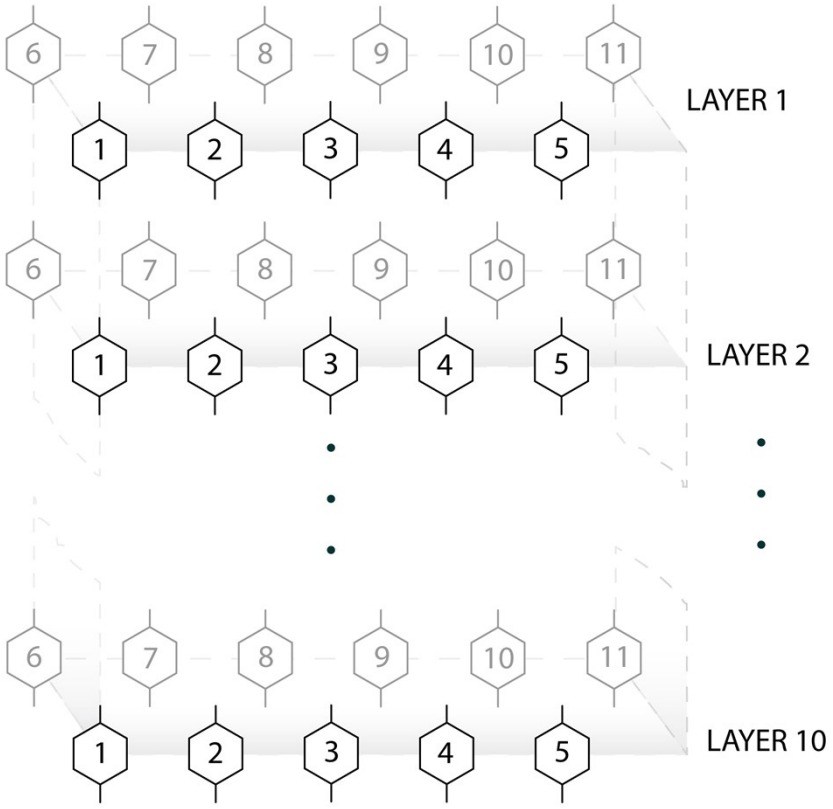
Rotators Indexing

The periodic structure of PPS material is composed of 110 *p*-phenylene units (rotators). In total, the structure composed of ten layers, each one containing two rows (eleven rotators/layer). Two indexes, *l* (layer) and *r* (row), are assigned to each rotator to identify its position in the periodic structure. According to the position of *p*-phenylene unit in a layer and in a row, each rotator is univocally identified by the indexes *l*, *r* by following the scheme reported in Scheme S1.



Scheme 1. Scheme for the assignment of label to p-phenyl units in the PPS framework.

Table S1. Total simulation time for each simulated sample.

Temp. [K]	S1 (μs)	S2 (μs)	S3 (μs)	S4 (μs)	S5 (μs)
270	2.34	2.30	2.31	2.20	2.11
293	2.12	2.01	2.03	2.06	2.11
300	2.0	1.97	1.99	2.1	2.0
400	1.39	1.44	1.32	1.41	1.41
500	1.51	1.504	1.53	1.41	1.41

Angle Distributions

A qualitative estimation of the temperature effect on the sampling of ϕ can be achieved comparing the peak width, obtained via fitting procedure. The Gaussian function (eq. S1) has been used to fit each peak as function of ϕ values at 270 K and 500 K.

$$f(x) = \sum_{i=1}^{n} a_i e^{\left(\frac{-(x-b_i)^2}{2c_i^2} \right)} \qquad \text{(S1)}$$

where a is the height of the peak, b is the centre of the peak and c is the width of the curve. In Table S1, the best fitting parameters (a, b, c) for the peaks tagged with indexes 1-5 (in Figure S1) are listed. From the comparison of the widths, an increase of the amplitude from ~<24^{O} > (at 270 K) to ~< 38^{O} > (at 500 K) is observed. From energetic point of view, the peaks no. 1 and 2 labelled in the right side of Figure S1, belong the same energetic state. In particular, the energy difference between them is about 0.02 k_BT (see the corresponding state in the ΔG distribution reported in Figure S1).

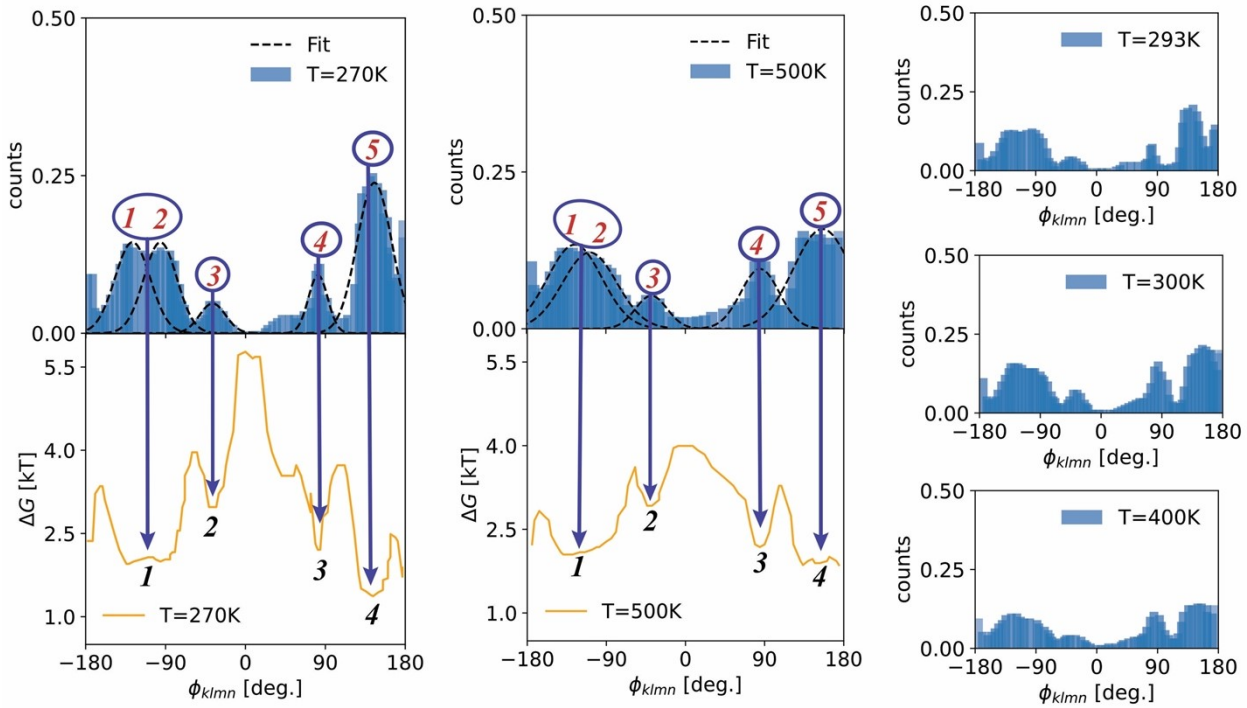


Figure S1. Probability distribution of ϕ_{klmn} calculated at: 270, 293, 300, 400 and 500 K respectively. In the right side of figure, below the distributions calculated at 270 and 500 K the corresponding Boltzmann inversion is reported. The four isoenergetic distinct states (1-4) are labelled too.

Table S2. Fitting parameters from eq. S1.

Peak No.	Temp. [K]	a [A.U.]	b [deg.]	c [deg.]
1	270	0.14 ± 0.1	-127 ± 1	28 ± 2
2	270	0.14 ± 0.1	-96 ± 1	16 ± 5
3	270	0.04 ± 0.2	-37 ± 1	21 ± 3
4	270	0.09 ± 0.1	81 ± 1	26 ± 2
5	270	0.24 ± 0.04	145 ± 1	28 ± 2
1	500	0.13 ± 0.05	-125 ± 1	43 ± 7
2	500	0.12 ± 0.01	-108 ± 1	43 ± 9
3	500	0.05 ± 0.01	-38 ± 1	25 ± 3
4	500	0.09 ± 0.03	84 ± 1	31 ± 3
5	500	0.16 ± 0.03	155 ± 1	46 ± 6

T-Shape Calculations

The 2D-maps have been calculated by using a geometrical criterion. For each rotator we computed the angle formed by its molecular vector (***r***, see the definition in Figure S2) with the molecular vectors of the four proximal rotators (one located on the opposite row of the considered rotator, and two rotators, at right and left, belonging the same row). If the angle between the considered vectors is 0^{O} ± 15^{O}, the T-shape is not counted, on the contrary, for an angle 90^{O} ± 15^{O} a T-shape is counted.

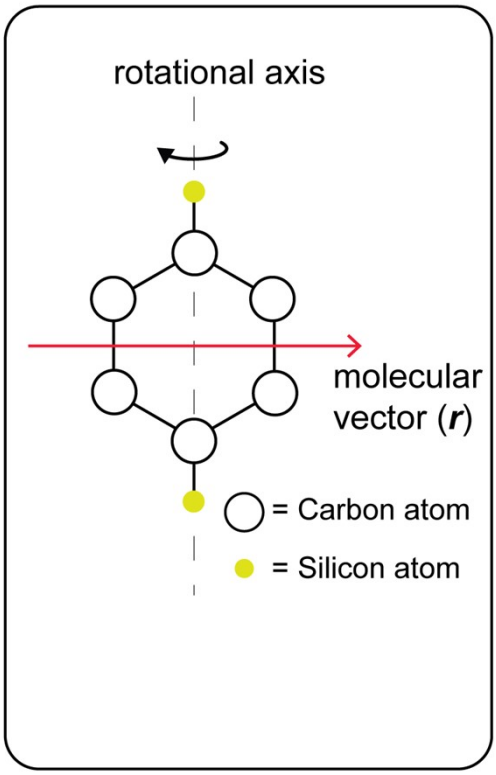


Figure S2. Definition of molecular vector and rotational axis used in the calculation of bidimensional T-Shape maps.

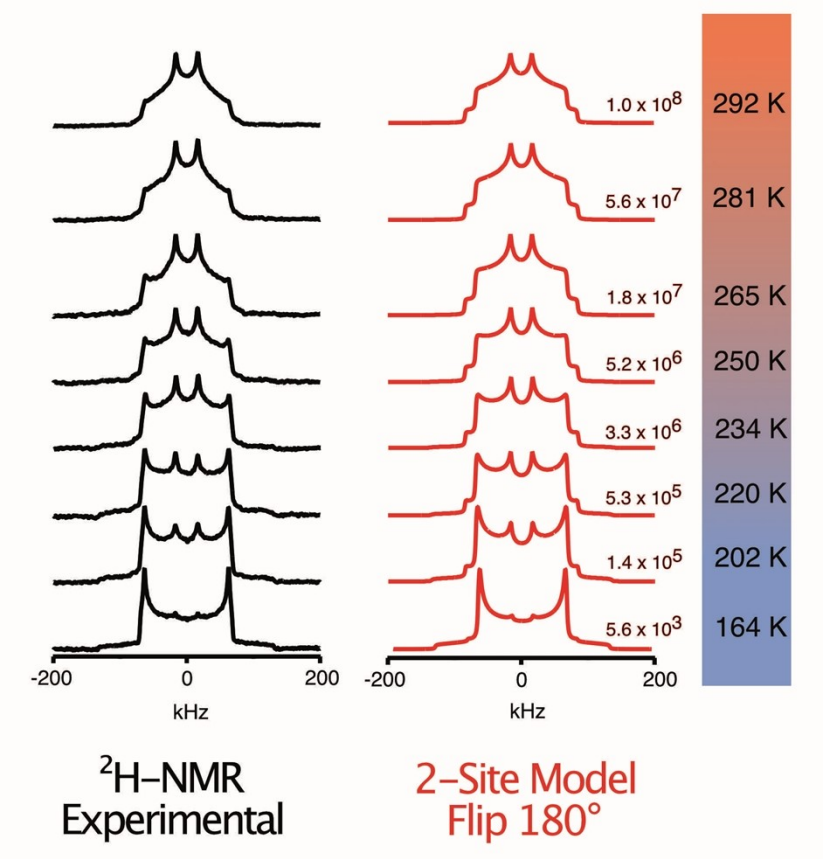


Figure S3. Experimental and simulated ^{2}H-NMR line-shape (with 2-site model) at different temperatures.