Supporting Information for:

On-surface self-assembly of tetratopic molecular building blocks

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1. Analysis of the phase coexistence

To study coexistence of the Kagome (α) and brickwall (β) phase formed by the molecule **A** we used the parallel tempering technique combined with the analysis of the block density distribution functions.[22] To that end the simulations were carried out using 7 system replicas ($L=480$) at evenly spaced temperatures, T ranging from 0.3 to 0.36. Molecular configurations of adjacent replicas (in terms of T) were swapped every 3×10^5 MC steps, using the following conventional acceptance probability:

$$A=\min\left\{1,\exp\left[\left(\frac{1}{kT_i}-\frac{1}{kT_j}\right)(U_i-U_j)\right]\right\} \quad (1)$$

where U is the total potential energy of the adsorbed system and the indices i and j are the numbers of the replicas to be swapped.[54] To determine the relative occurrence probability of the phases (α)**A** and (β)**A** the lattice was divided into 96 by 96 blocks in which local density of the adsorbate, ρ^* was monitored. For the 2D gas phase, when no pattern formation takes place, the relative occurrence probability is a Gaussian-like curve centered at the value which corresponds to a presumed net density of the adsorbate on the surface, ρ. The formation of distinct phases manifests in the associated peaks (phase markers) in the distribution function. For example, the curves shown in the bottom part of Fig. S1 (left) demonstrate the

coexistence of the Kagome phase (black) – spike at $\rho^*=\rho[(\alpha)\mathrm{A}]=0.424$ and 2D gas phase with ρ^* lower than 0.05 (small peak). A similar situation takes place for the brickwall phase for which the maximum of the distribution is located at $\rho^*=\rho[(\beta)\mathrm{A}]=0.462$. To estimate how frequently each of these ordered phases occurs in the system we compared cumulative areas of the phase markers cantered at ρ[(α)**A**] and ρ[(β)**A**]. Figure S1 (bottom-right) presents the obtained results, calculated for $\rho=0.21$, for a few temperatures.

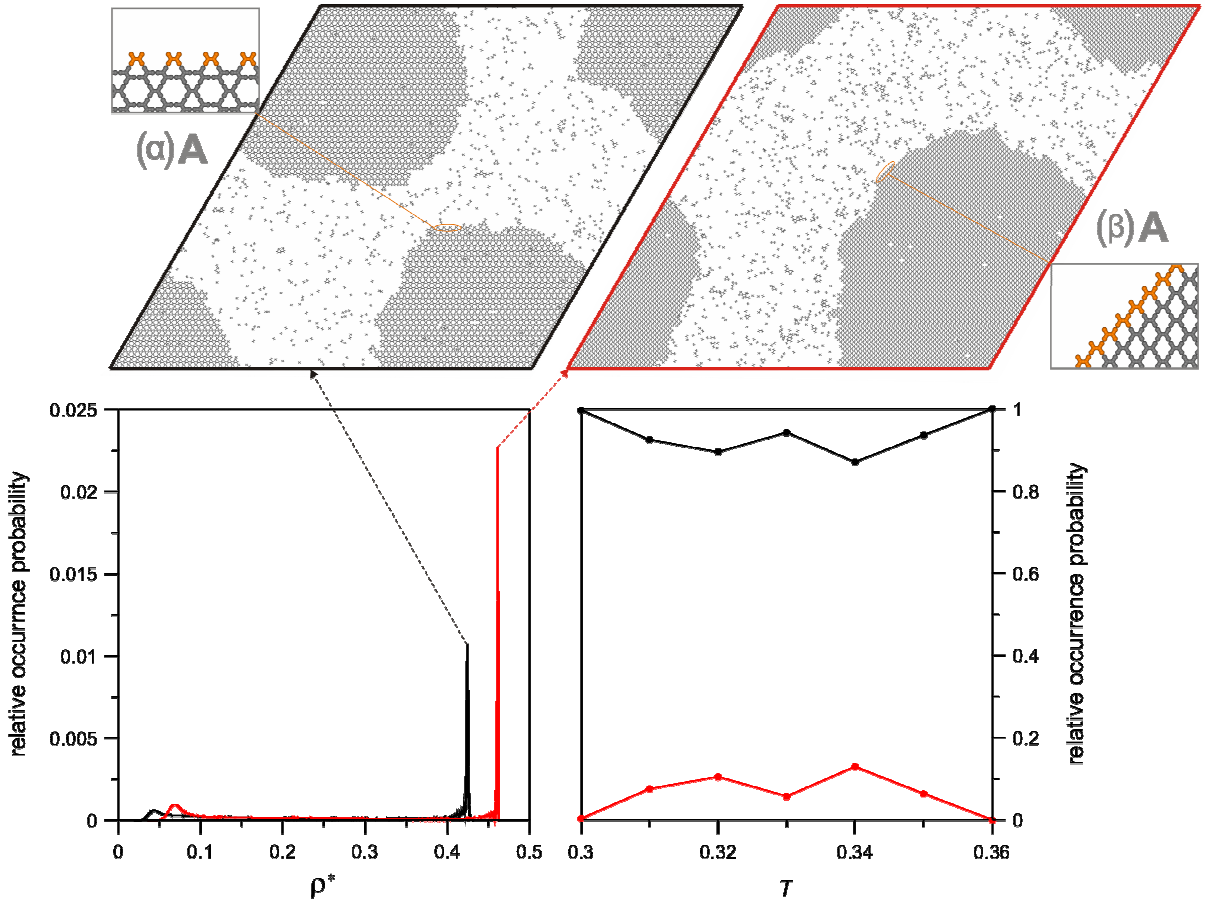


Figure S1. (top) Snapshots of the Kagome (α, left) and brickwall (β, right) phase formed in larger systems comprising 8064 molecules of **A** adsorbed on a 480×480 fragment of the triangular lattice ($\rho=0.21; T=0.30$(α) and $T=0.32$(β)). The insets show peripheral molecules (orange) which make 2 (α) and 3 (β) contacts with neighboring molecules. (bottom) Block density probability distributions calculated for the systems shown in the top part (left). Relative occurrence probability of phases (α)**A** and (β)**B** at the different temperatures calculated for the system with $\rho=0.21$.

2. Additional statistics and snapshots

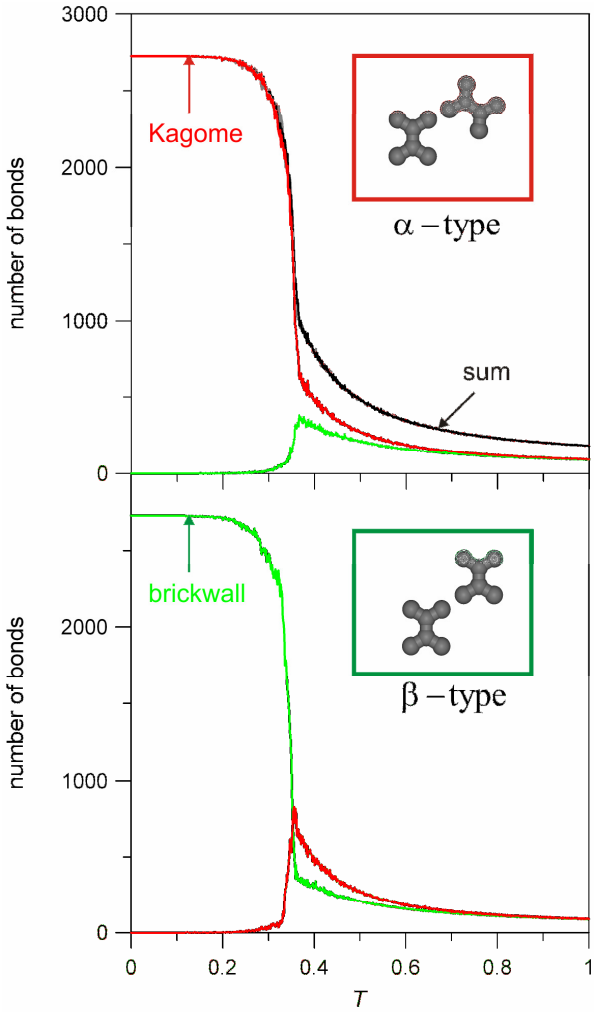


Figure S2. Effect of temperature on the number of bonds of type α and β calculated for two systems comprising 1400 molecules of **A** whose self-assembly resulted in the Kagome (top) and brickwall (bottom) networks ($T \to 0$). The coinciding black and grey lines shown in the top part are the total number of bonds ($\alpha+\beta$) obtained for these two self-assembly scenarios. These curves (shown in Fig. 3) are plotted for comparative purposes.

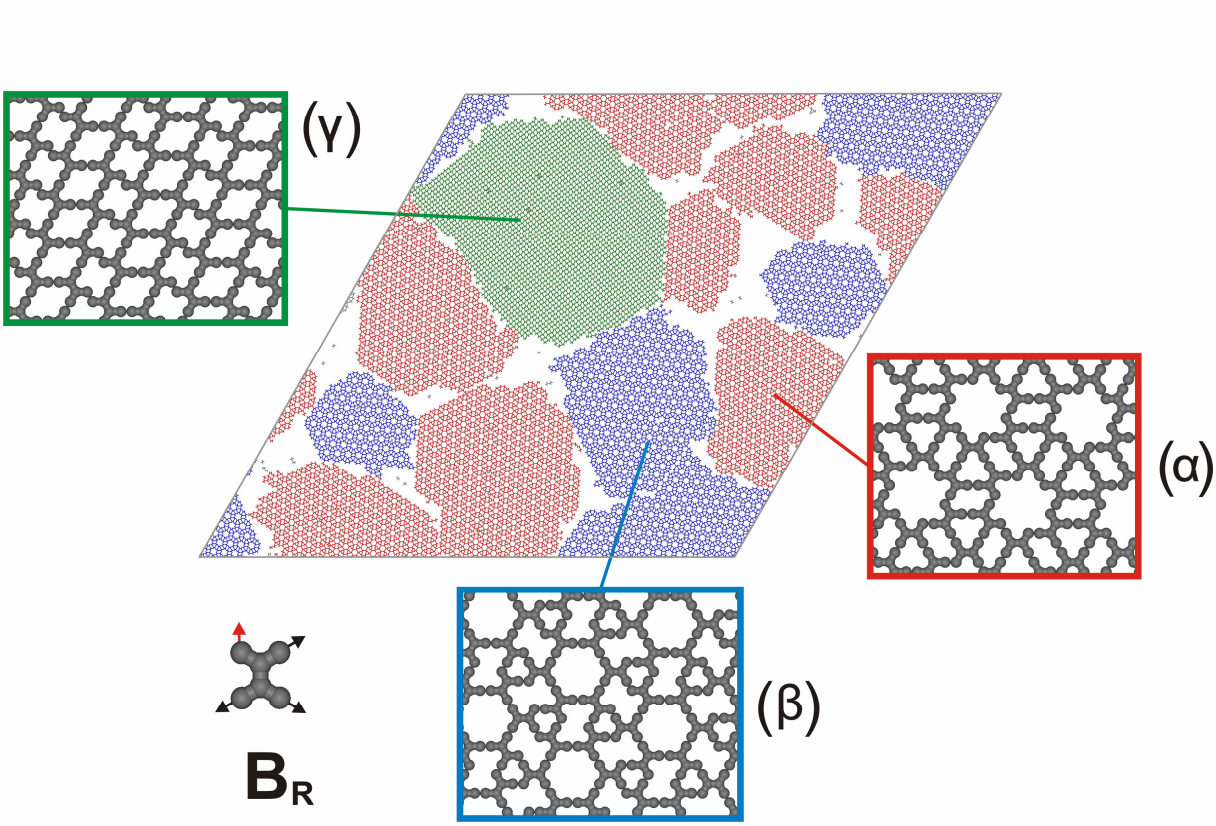


Figure S3. Snapshot of the overalyer comprising 13440 molecules of $\mathbf{B_R}$ adsorbed on a 480×480 triangular lattice (θ=0.35) at T=0.24. The three coexisting porous phases: α, β and γ were colored differently.

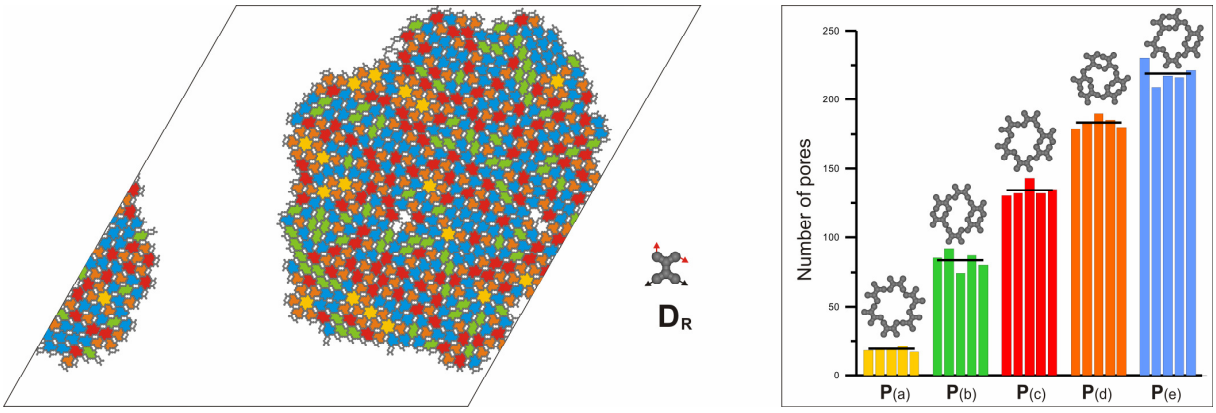


Figure S4. Structural diversity of the aperiodic network from Fig. 5 highlighted by the differently colored pores $P_{(a)}$-$P_{(e)}$ (left). Statistical analysis of the network showing the average number of pores of different types (black horizontal lines) obtained from five independent systems (grouped vertical bars) each comprising 1400 molecules of $\mathbf{D_R}$ at T=0.1 (right).

3. Flory-Schulz distribution of ladder length

The Flory-Schulz (FS) distribution function used in this work has the following form:

$$P(k)=a^2k(1-a)^{k-1} \tag{1}$$

where k is the length of the ladder (chain) expressed in the number of attached molecules and $0<a<1$ is an adjustable parameter. The normalized distribution function $P(k)$ determines the probability of finding a ladder built of k molecules in the entire ladder population. An important parameter of this distribution is the average value of k which has the simple form:

$$\langle k\rangle_{\mathrm{FS}}=\frac{2}{a}-1 \tag{2}$$

To examine the effect of temperature on $P(k)$ one has to know the temperature dependence of the parameter a. This information can be easily obtained by determining $\langle k\rangle_T$ from the simulations performed at selected temperatures, T. The Left panel of Fig.7 presents the required temperature dependence of $\langle k\rangle_T$ from the simulations. Then, assuming $\langle k\rangle_T=\langle k\rangle_{\mathrm{FS}}$ we obtain $a(T)=2/(1+\langle k\rangle_T)$, so that the ladder length distribution can be found at any of the selected temperatures, in our case at 1000 points from the 0.01-1 interval. This method, which we consider to be simpler than fitting of each $P(k)$ curve at a given temperature, was used to determine the FS distribution curves from Fig. 7. The obtained temperature dependence of the parameter a is shown in Fig. S5.

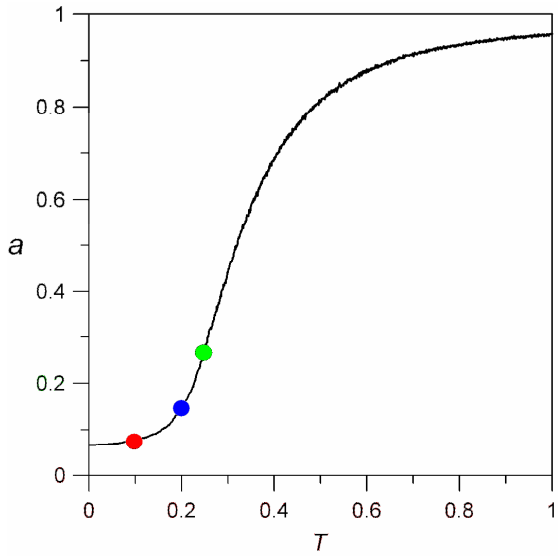


Figure S5. Temperature dependence of the parameter a of the Flory-Schulz distribution (Eqs.1-2) determined from the simulated dependence of the average ladder length, $\langle k \rangle_T$ on temperature (Fig. 7). The colored points correspond to the curves plotted in Fig. 7. The obtained values of a are equal to: 0.278 at $T=0.25$ (green), 0.143 at $T=0.20$ (blue) and 0.076 at $T=0.10$ (red).

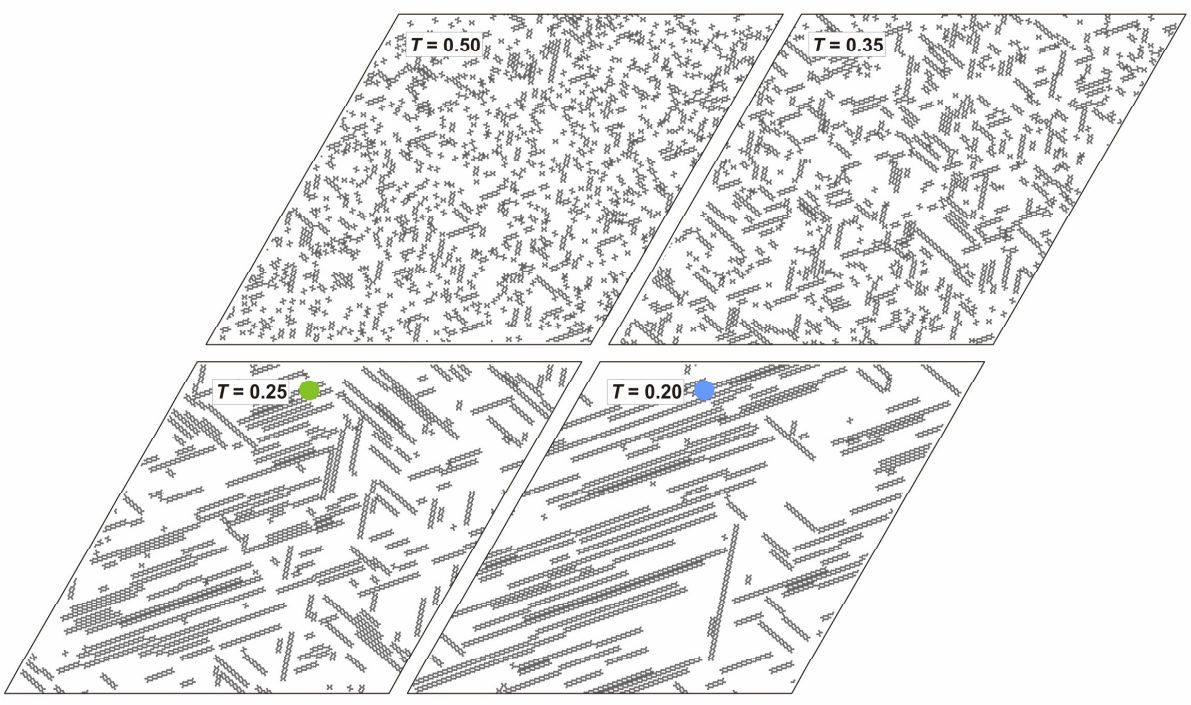


Figure S6. Snapshots of the adsorbed phase comprising 1400 molecules of $\mathbf{F_R}$ ($\theta=0.21$) taken at the different temperatures indicated in the figure. The color codes in the bottom part (circles) are consistent with the scheme used previously for this tecton.

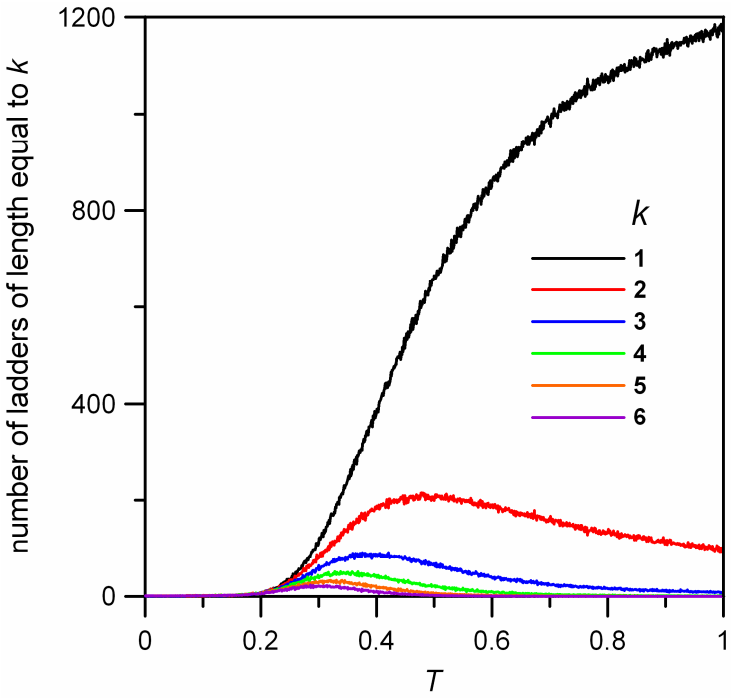
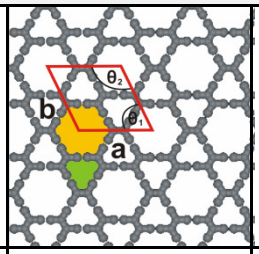
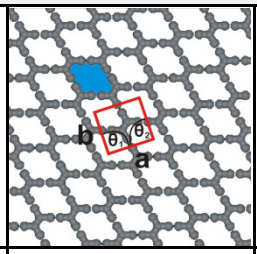
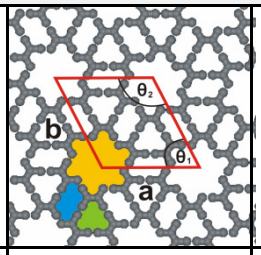
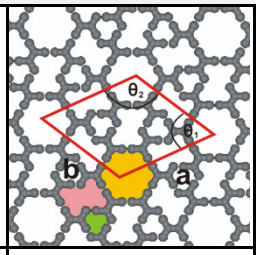
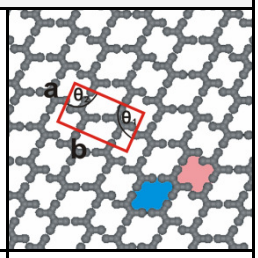
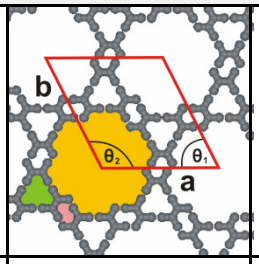
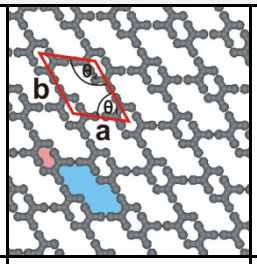
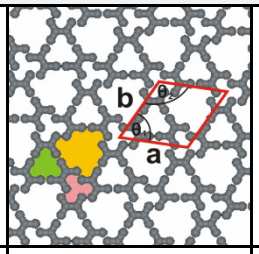


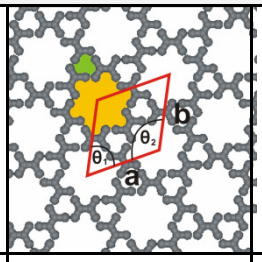
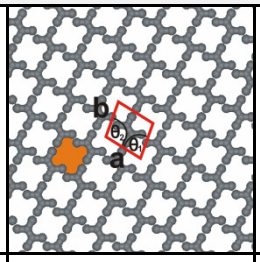
Figure S7. Effect of temperature on the absolute number of ladders with length equal to k (molecules) obtained from the MC simulations of 1400 molecules of $\mathbf{F_R}$ (θ=0.21).

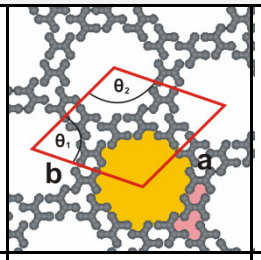
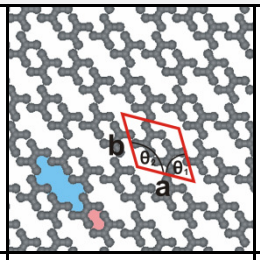
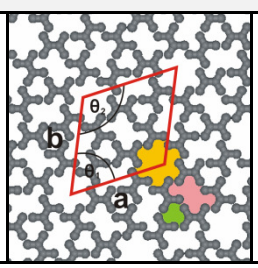
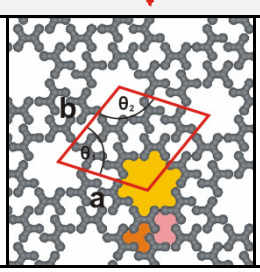
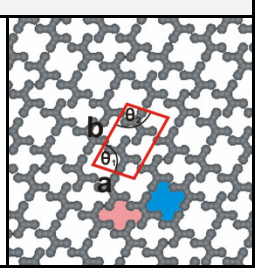
Table S1. Library of the ordered phases formed by the tectons **A**-**J** along with the structural parameters characterizing them.

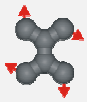
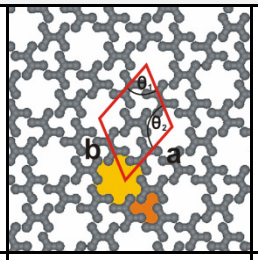
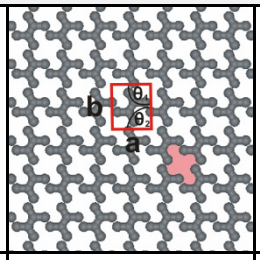
Molecule **A** 					
Phase(α) 		Phase(β) 		Phase(γ)	
Density	ρ=0.424		ρ=0.462		-
Unit cell parameters	(rhombic) a=b=7 θ_1=60° θ_2=120°		(rhombic) a=b=$\sqrt{13}$ θ_1=88° θ_2=92°		-

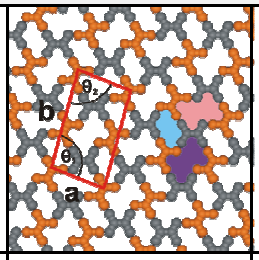
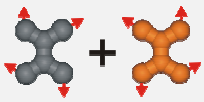
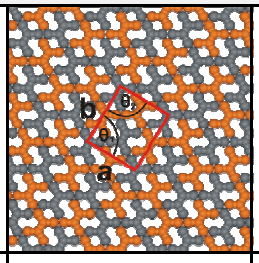
Free adsorption sites inside pores	19		9		-
	6		-		-
Number of molecules inside unit cell	3		1		-
Molecule $\mathbf{B}_R$					
Phase(α)		Phase(β)		Phase(γ)	
Density	$\rho=0.457$		$\rho=0.457$		$\rho=0.478$
Unit cell parameters	(rhombic) $a=b=\sqrt{91}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(rhombic) $a=b=\sqrt{91}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(parallelogram) $a=\sqrt{13}$ $b=7$ $\theta_1=84^\circ$ $\theta_2=96^\circ$
Free adsorption sites inside pores	25		19		9
	6		10		8
	6		3		-
Number of molecules inside unit cell	6		6		2

Molecule $\mathbf{C_R}$					
Phase(α)		Phase(β)		Phase(γ)	-
Density	$\rho=0.313$		$\rho=0.462$		-
Unit cell parameters	(rhombic) $a=b=\sqrt{133}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(parallelogram) $a=5$ $b=6$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		-
Free adsorption sites inside pores	79		16		-
	6		2		-
	2		-		-
Number of molecules inside unit cell	6		2		-
Molecule $\mathbf{E_R}$					
Phase(α)		Phase(β)	-	Phase(γ)	-
Density	$\rho=0.483$		-		-

Unit cell parameters	(rhombic) $a=b=\sqrt{43}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		-		-
Free adsorption sites inside pores	15		-		-
	6		-		-
	4		-		-
Number of molecules inside unit cell	3		-		-
Molecule $\mathbf{G_R}$					
Phase(α)		Phase(β)		Phase(γ)	-
Density	$\rho=0.424$		$\rho=0.495$		-
Unit cell parameters	(rhombic) $a=b=7$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(parallelogram) $a=\sqrt{13}$ $b=\sqrt{12}$ $\theta_1=76^\circ$ $\theta_2=104^\circ$		-
Free adsorption sites inside pores	25		8		-
	3		-		-

Number of molecules inside unit cell	3		1		-
Molecule $\mathbf{H}_R$ 					
Phase(α)		Phase(β)		Phase(γ)	-
Density	$\rho = 0.355$		$\rho = 0.533$		-
Unit cell parameters	(rhombic) $a = b = \sqrt{117}$ $\theta_1 = 60^\circ$ $\theta_2 = 120^\circ$		(parallelogram) $a = \sqrt{31}$ $b = \sqrt{21}$ $\theta_1 = 62^\circ$ $\theta_2 = 118^\circ$		-
Free adsorption sites inside pores	67		12		-
	4		2		-
	2		-		-
Number of molecules inside unit cell	6		2		-
Molecule $\mathbf{I}_R$ 					
Phase(α)		Phase(β)		Phase(γ)	

Density	$\rho=0.526$		$\rho=0.495$		$\rho=0.533$
Unit cell parameters	(rhombic) $a=b=\sqrt{79}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(rhombic) $a=b=\sqrt{84}$ $\theta_1=60^\circ$ $\theta_2=120^\circ$		(parallelogram) $a=\sqrt{12}$ $b=\sqrt{43}$ $\theta_1=82^\circ$ $\theta_2=98^\circ$
Free adsorption sites inside pores	13		25		8
	8		5		6
	3		4		-
Number of molecules inside unit cell	6		6		2
Molecule $\mathbf{J}_R$					
Phase(α)		Phase(β)		Phase(γ)	
Density	$\rho=0.533$		$\rho=0.577$		-
Unit cell parameters	(parallelogram) $a=\sqrt{39}$ $b=\sqrt{21}$ $\theta_1=47^\circ$ $\theta_2=133^\circ$		(rectangular) $a=\sqrt{12}$ $b=3$ $\theta_1=\theta_2=90^\circ$		-
Free adsorption sites inside pores	13		6		-
	4		-		-

Number of molecules inside unit cell	3		1		-
Molecule **B** (racemate) 					
Phase(α)		Phase(β)	-	Phase(γ)	-
Density	$\rho = 0.495$		-		-
Unit cell parameters	(rectangular) $a = \sqrt{165}/2$ $b = \sqrt{29}/2$ $\theta_1 = \theta_2 = 90^\circ$		-		-
Free adsorption sites inside pores	10		-		-
	10		-		-
	6				
Number of molecules inside unit cell	4		-		-
Molecule **I** (racemate) 					
Phase(α)		Phase(β)	-	Phase(γ)	-
Density	$\rho = 0.770$		-		-

Unit cell parameters	(rectangular) $a=\sqrt{27}$ $b=6$ $\theta_1=\theta_2=90^\circ$		-		-
Free adsorption sites inside pores	2		-		-
	1		-		-
Number of molecules inside unit cell	4		-		-