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

Supporting Information for:

Designing 2D covalent networks with the lattice Monte Carlo simulations: Precursor self-assembly

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1. Catalog of the tetrasubstituted isomers of naphthalene

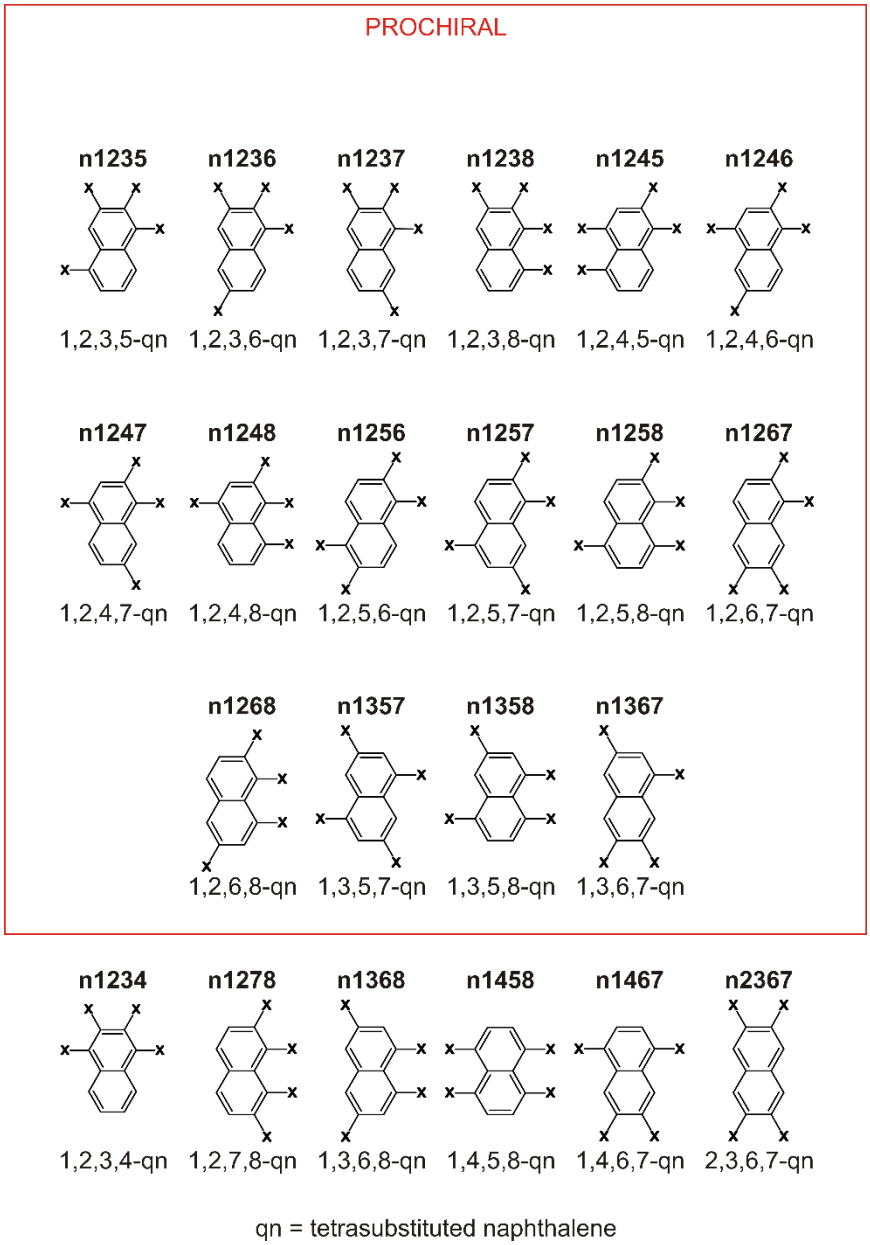


Figure S1. Schematic structures of the 22 possible tetrasubstituted isomers of naphthalene. The sixteen prochiral molecules, able to adopt mirror-image configurations when adsorbed, are grouped inside the red frame. The remaining six achiral molecules are shown below the frame.

2. Different grow paths of the networks comprising n1368 and n2367

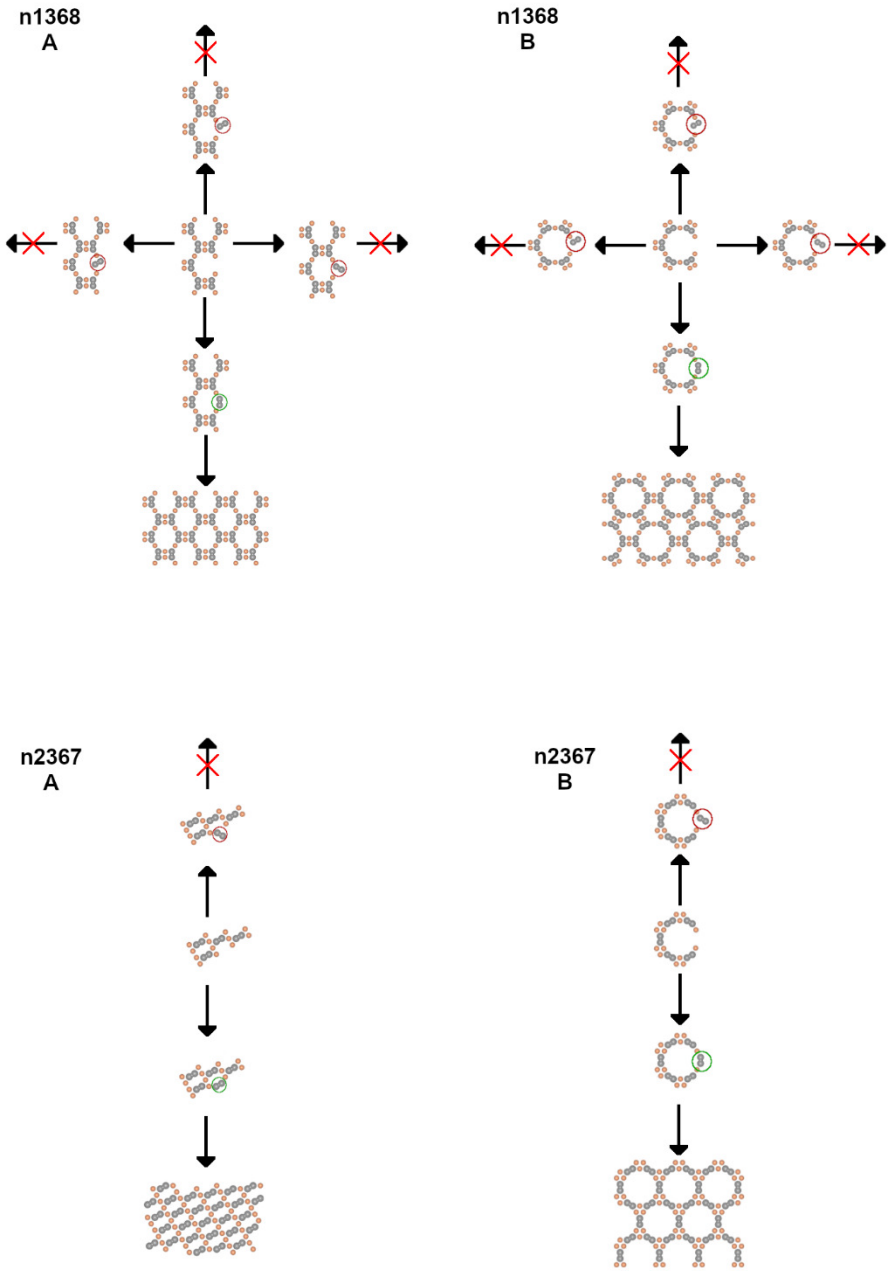


Figure S2. Possible ways in which a molecule of **n1368** and **n2367** can attach to the corresponding polymorphic networks A and B, enabling and disabling defect-free growth of these superstructures. In the example shown here, for the isomer **n1368** there are three erroneous (red) and one correct (green) attachment ways, regardless of the network type (A or B). For **n2367** the corresponding numbers of attachment ways are equal (one correct and one erroneous for A and B).

3. Additional temperature dependencies

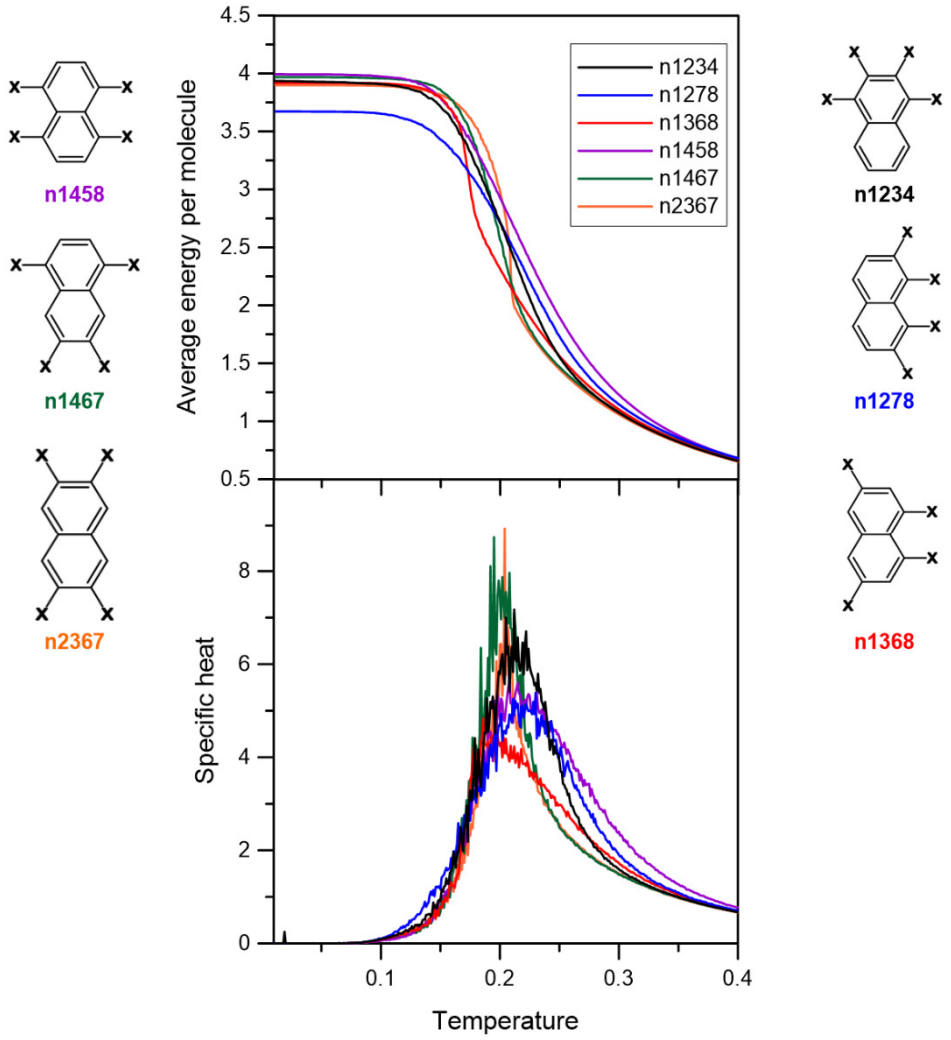


Figure S3. Effect of temperature on the average interaction energy per molecule (top) and specific heat capacity (bottom) calculated for the achiral isomers of **n** shown in the figure. The calculated temperature dependencies are averages over ten independent system replicas, each comprising 800 metal atoms and 400 molecules **n** (L = 200).

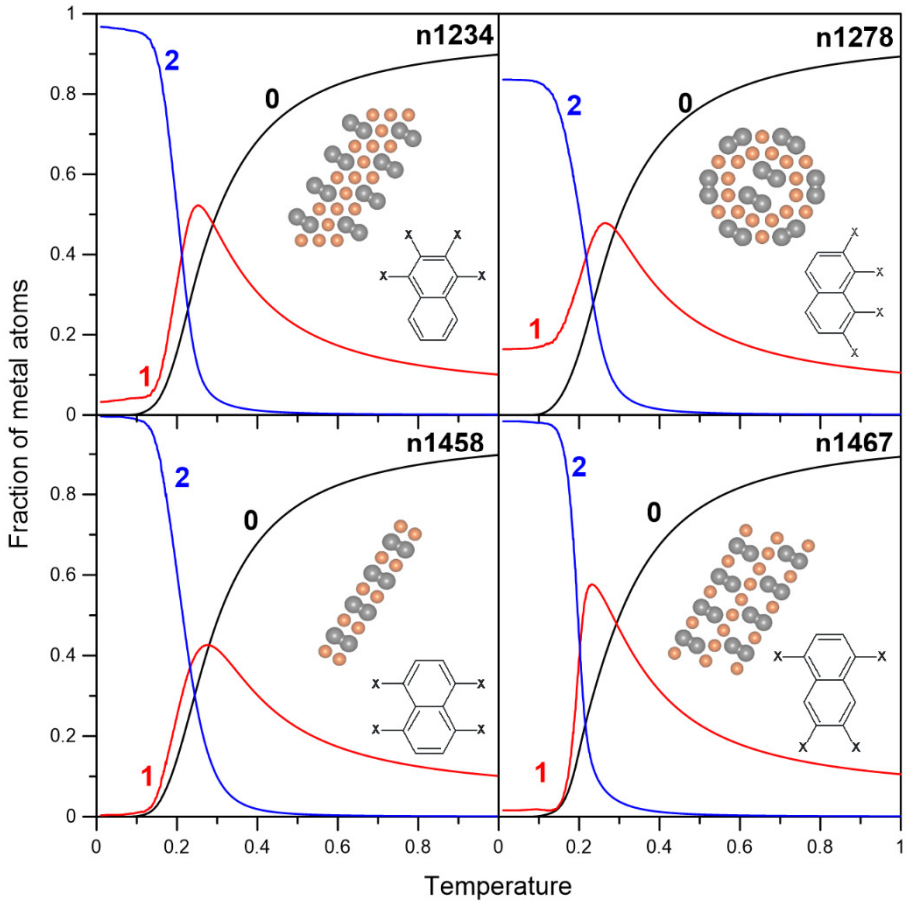


Figure S4. Fractions of metal atoms coordinated to zero, one and two naphthalene linkers as functions of temperature calculated for the achiral isomers **n1234**, **n1278**, **n1458** and **n1467** (N_l = 400, N_m = 800, L = 200).

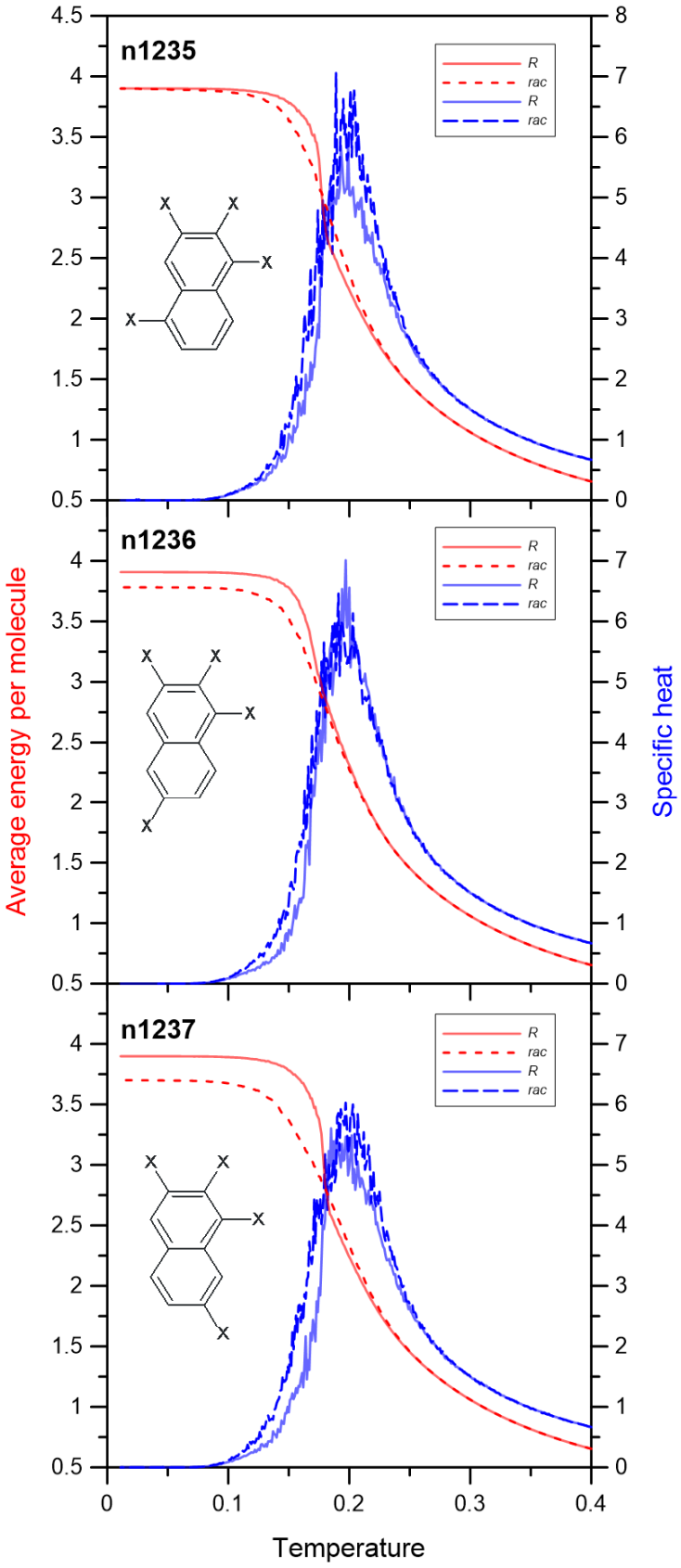


Figure S5. Effect of temperature on the mean molecular energy and specific heat capacity calculated for the enantiopure (*R*) and racemic (*R*+*S*) overlayers comprising the isomers **n1235**, **n1236** and **n1237** (N_l = 400, N_m = 800, L = 200).

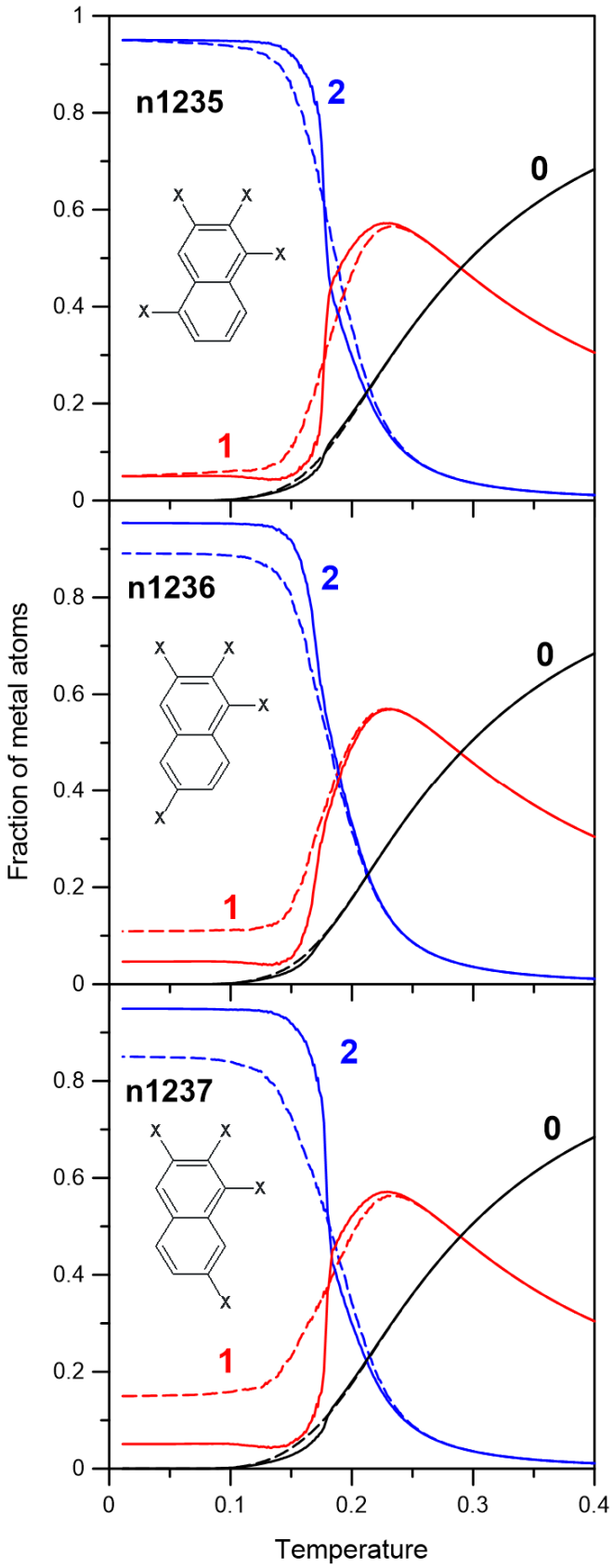


Figure S6. Effect of temperature on the fraction of metal atoms connected to zero, one and two naphthalene linkers, calculated for the enantiopure (*R*, solid lines) and racemic (*R*+*S*, dashed lines) overlayers comprising the isomers **n1235**, **n1236** and **n1237** (N_l = 400, N_m = 800, L = 200).

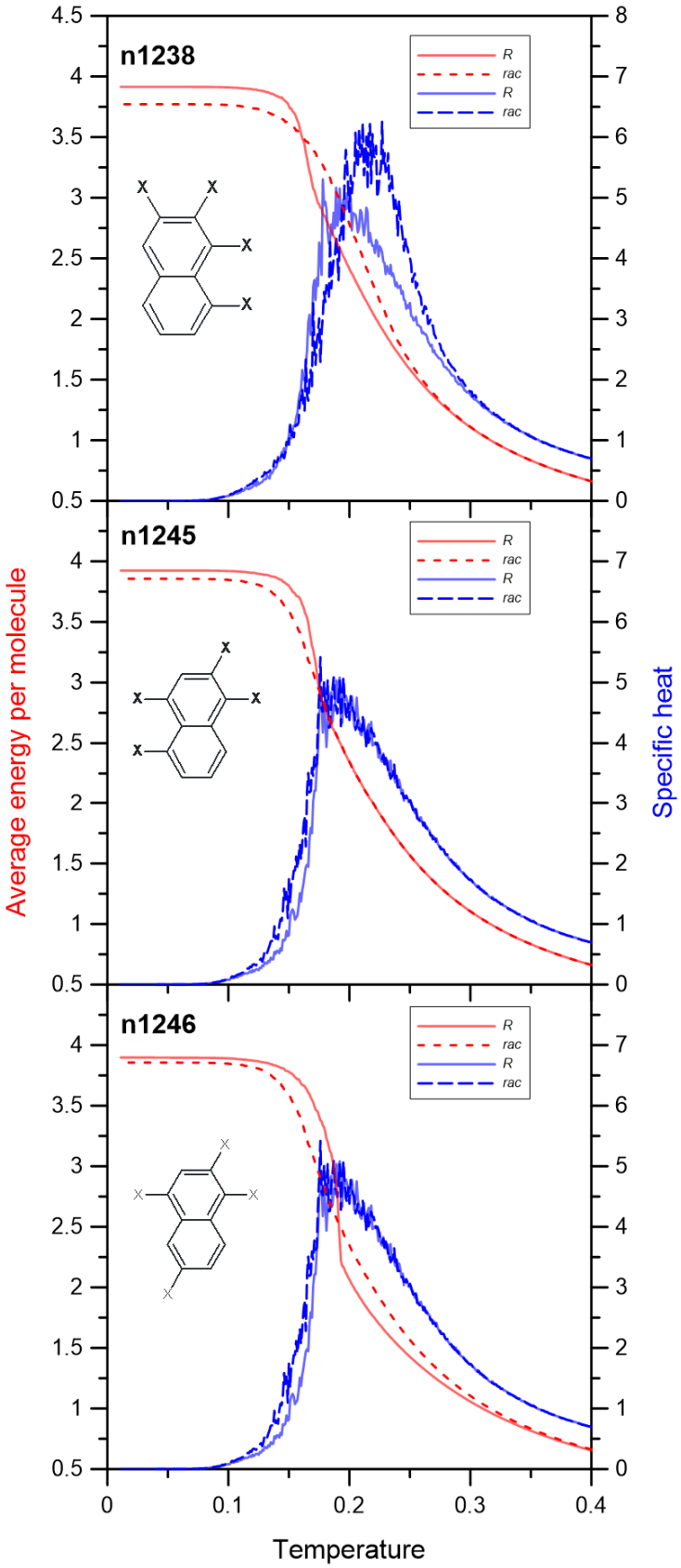


Figure S7. Effect of temperature on the mean molecular energy and specific heat capacity calculated for the enantiopure (*R*) and racemic (*R*+*S*) overlayers comprising the isomers **n1238**, **n1245** and **n1246** (N_l = 400, N_m = 800, L = 200).

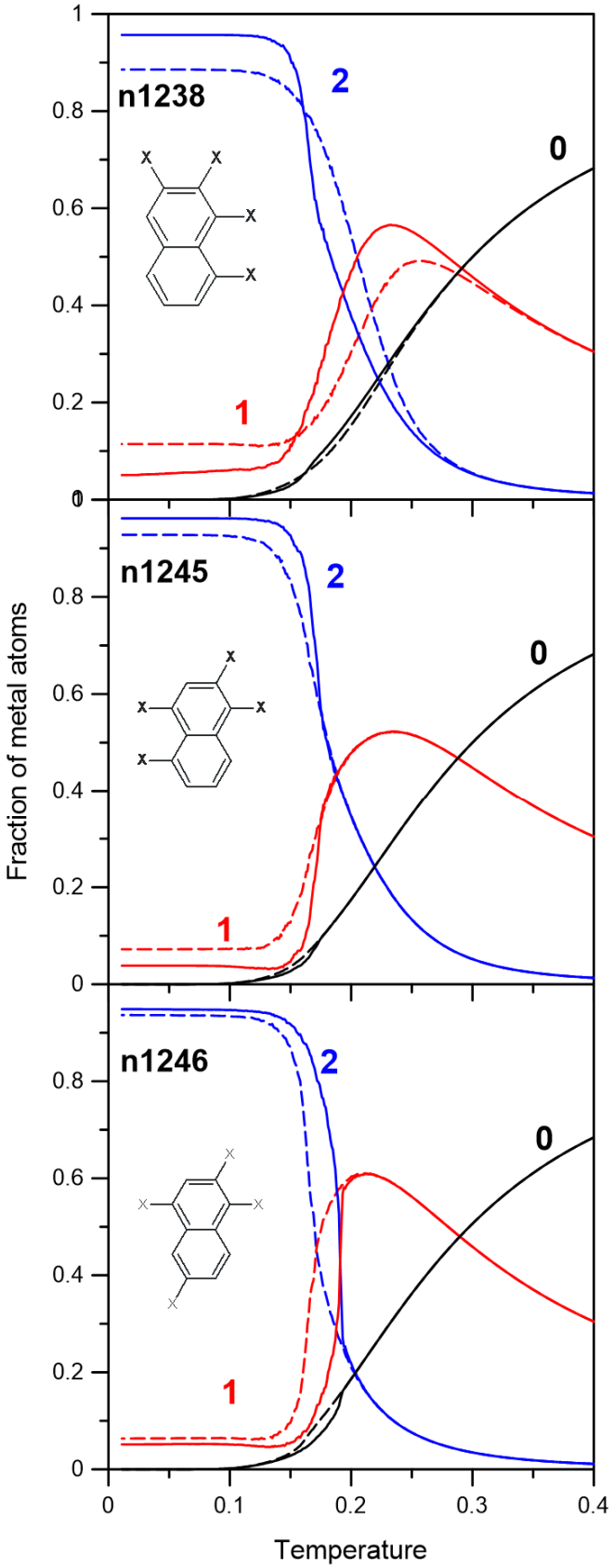


Figure S8. Effect of temperature on the fraction of metal atoms connected to zero, one and two naphthalene linkers, calculated for the enantiopure (*R*, solid lines) and racemic (*R*+*S,* dashed lines) overlayers comprising the isomers **n1238**, **n1245** and **n1246** (N_l = 400, N_m = 800, L = 200).

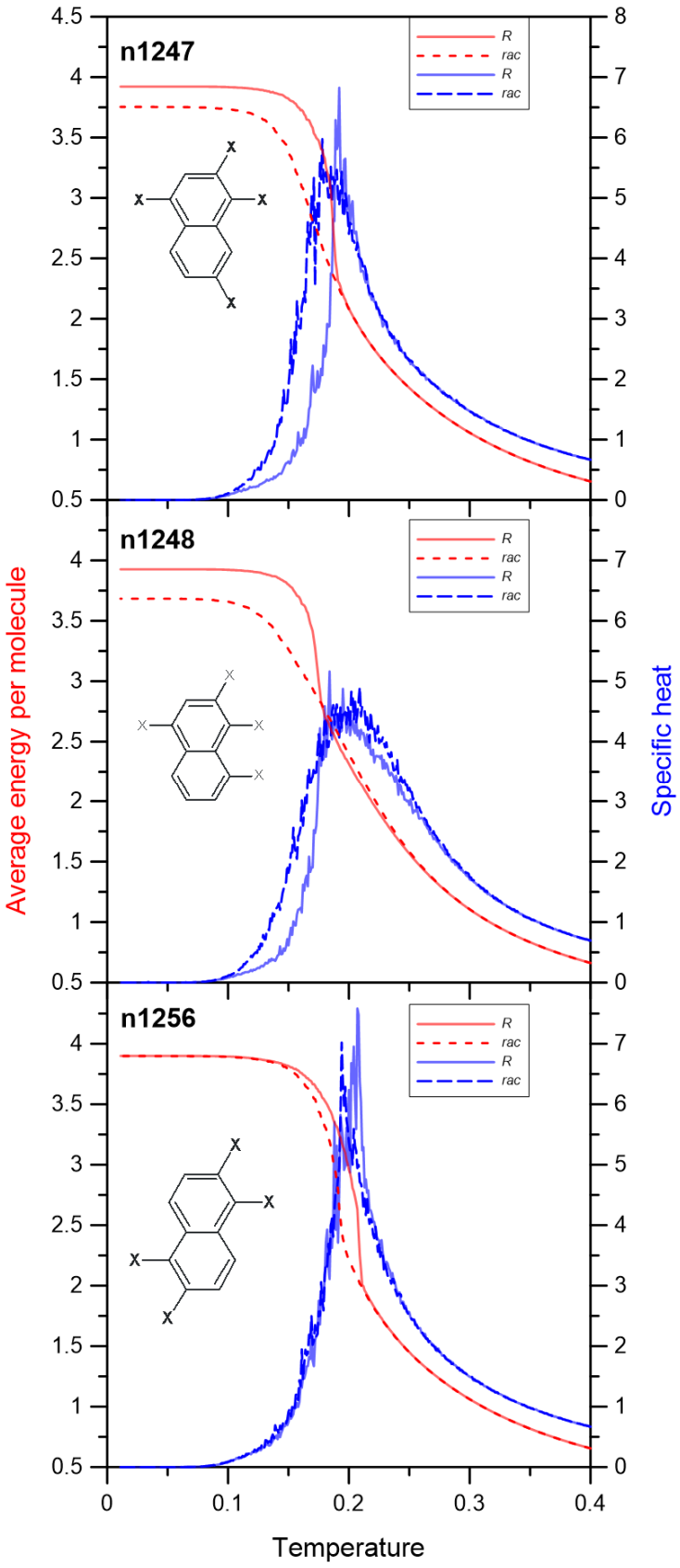


Figure S9. Effect of temperature on the mean molecular energy and specific heat capacity calculated for the enantiopure (*R*) and racemic (*R*+*S*) overlayers comprising the isomers **n1247**, **n1248** and **n1256** (N_l = 400, N_m = 800, L = 200).

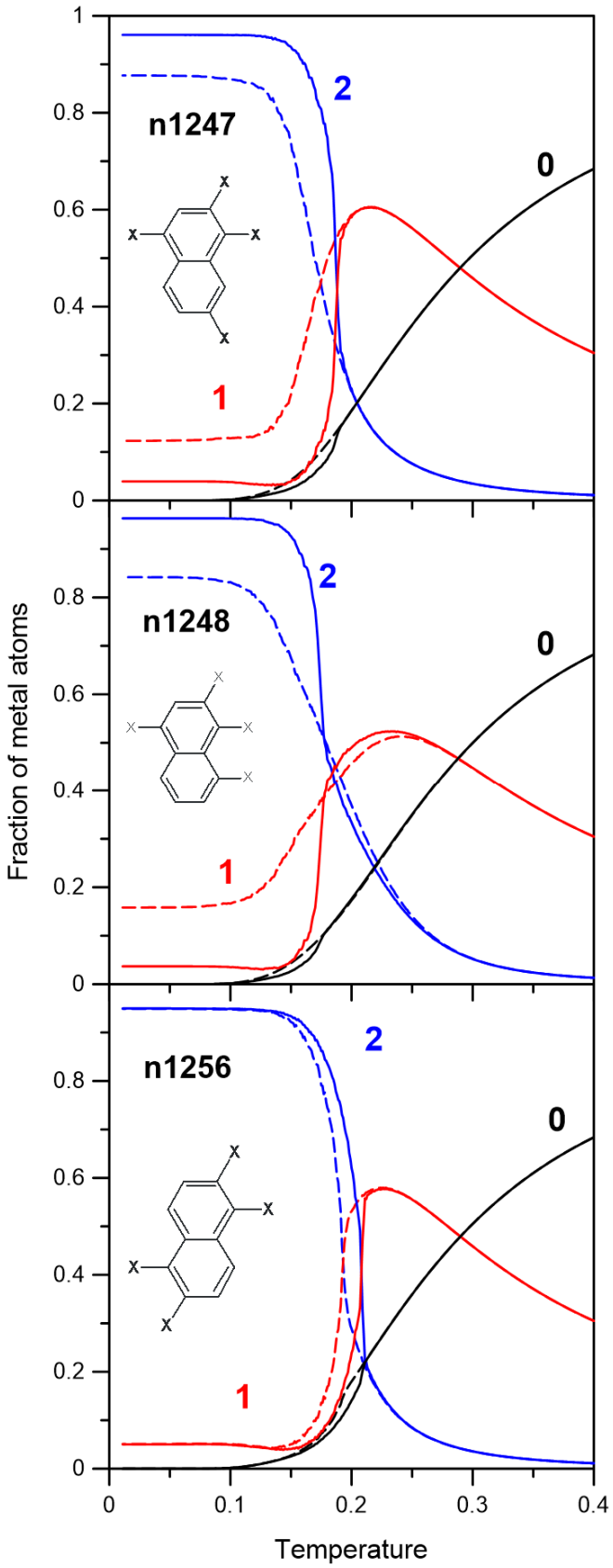


Figure S10. Effect of temperature on the fraction of metal atoms connected to zero, one and two naphthalene linkers, calculated for the enantiopure (*R*, solid lines) and racemic (*R*+*S*, dashed lines) overlayers comprising the isomers **n1247**, **n1248** and **n1256** (N_l = 400, N_m = 800, L = 200).

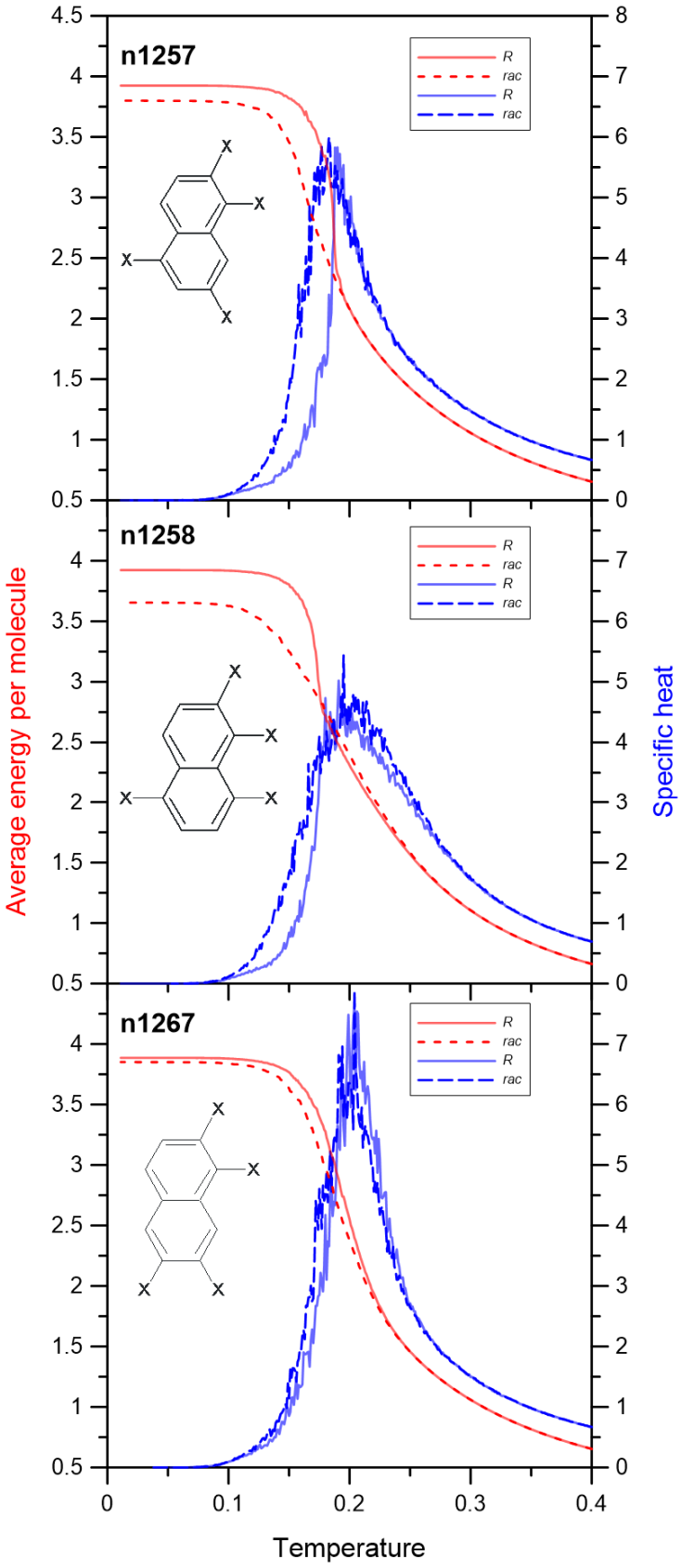


Figure S11. Effect of temperature on the mean molecular energy and specific heat capacity calculated for the enantiopure (*R*) and racemic (*R*+*S*) overlayers comprising the isomers **n1257**, **n1258** and **n1267** (N_l = 400, N_m = 800, L = 200).

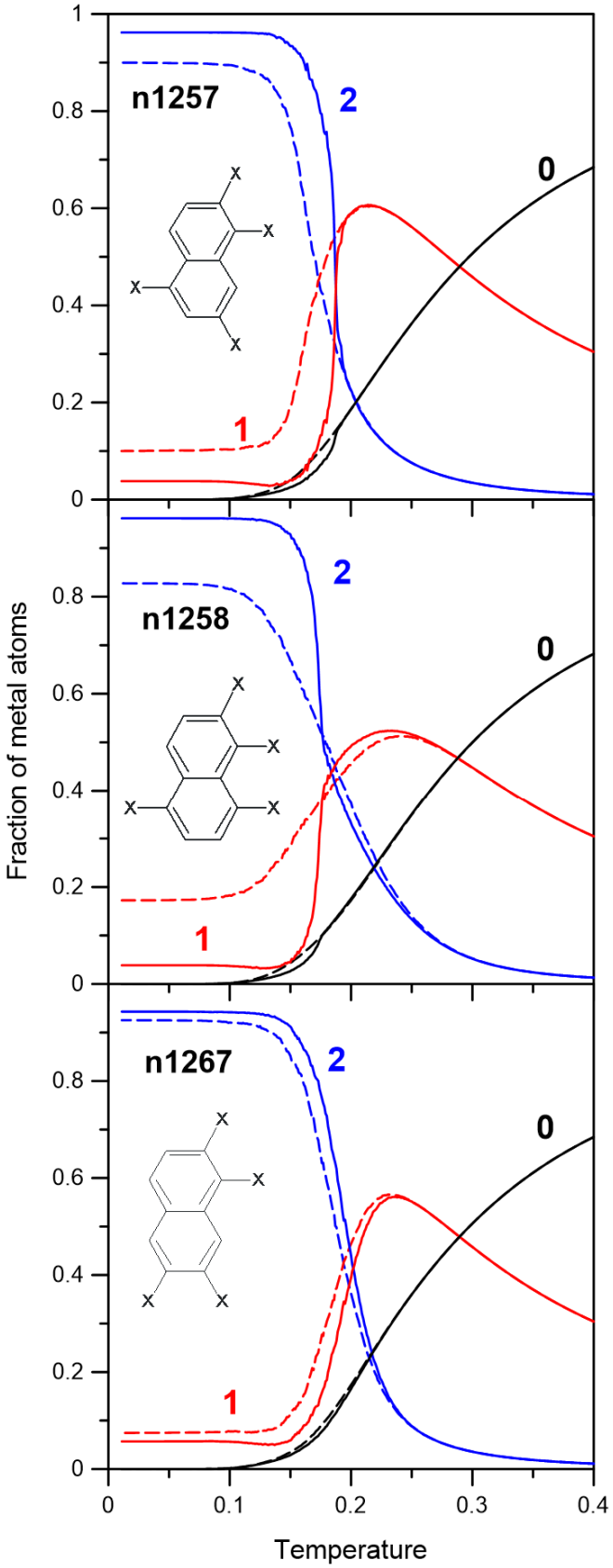


Figure S12. Effect of temperature on the fraction of metal atoms connected to zero, one and two naphthalene linkers, calculated for the enantiopure (*R*, solid lines) and racemic (*R*+*S*, dashed lines) overlayers comprising the isomers **n1257**, **n1258** and **n1267** (N_l = 400, N_m = 800, L = 200).

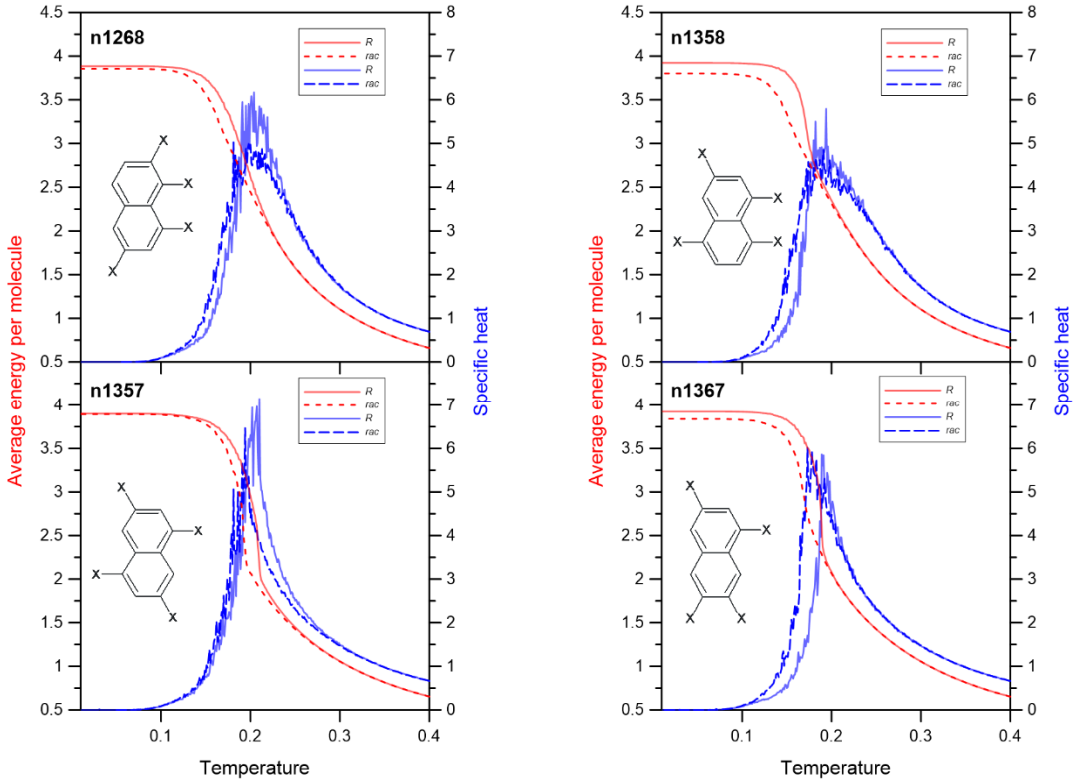


Figure S13. Effect of temperature on the mean molecular energy and specific heat capacity calculated for the enantiopure (*R*) and racemic (*R*+*S*) overlayers comprising the isomers **n1268**, **n1357**, **n1358** and **n1367** (N_l = 400, N_m = 800, L = 200).

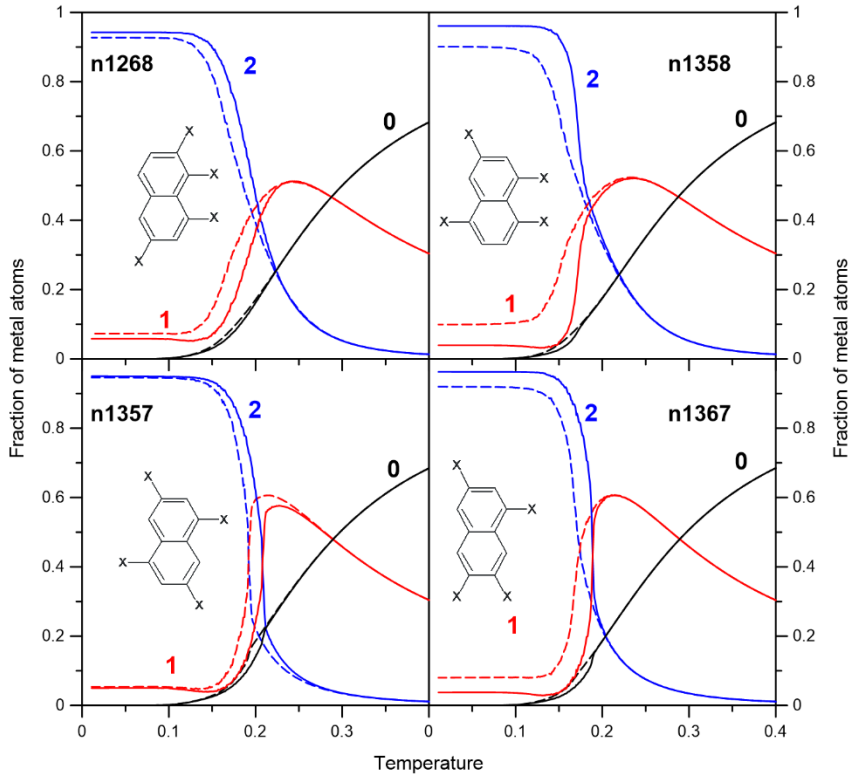


Figure S14. Effect of temperature on the fraction of metal atoms connected to zero, one and two naphthalene linkers, calculated for the enantiopure (*R*, solid lines) and racemic (*R*+*S*, dashed lines) overlayers comprising the isomers **n1268**, **n1357**, **n1358** and **n1367** (N_l = 400, N_m = 800, L = 200).

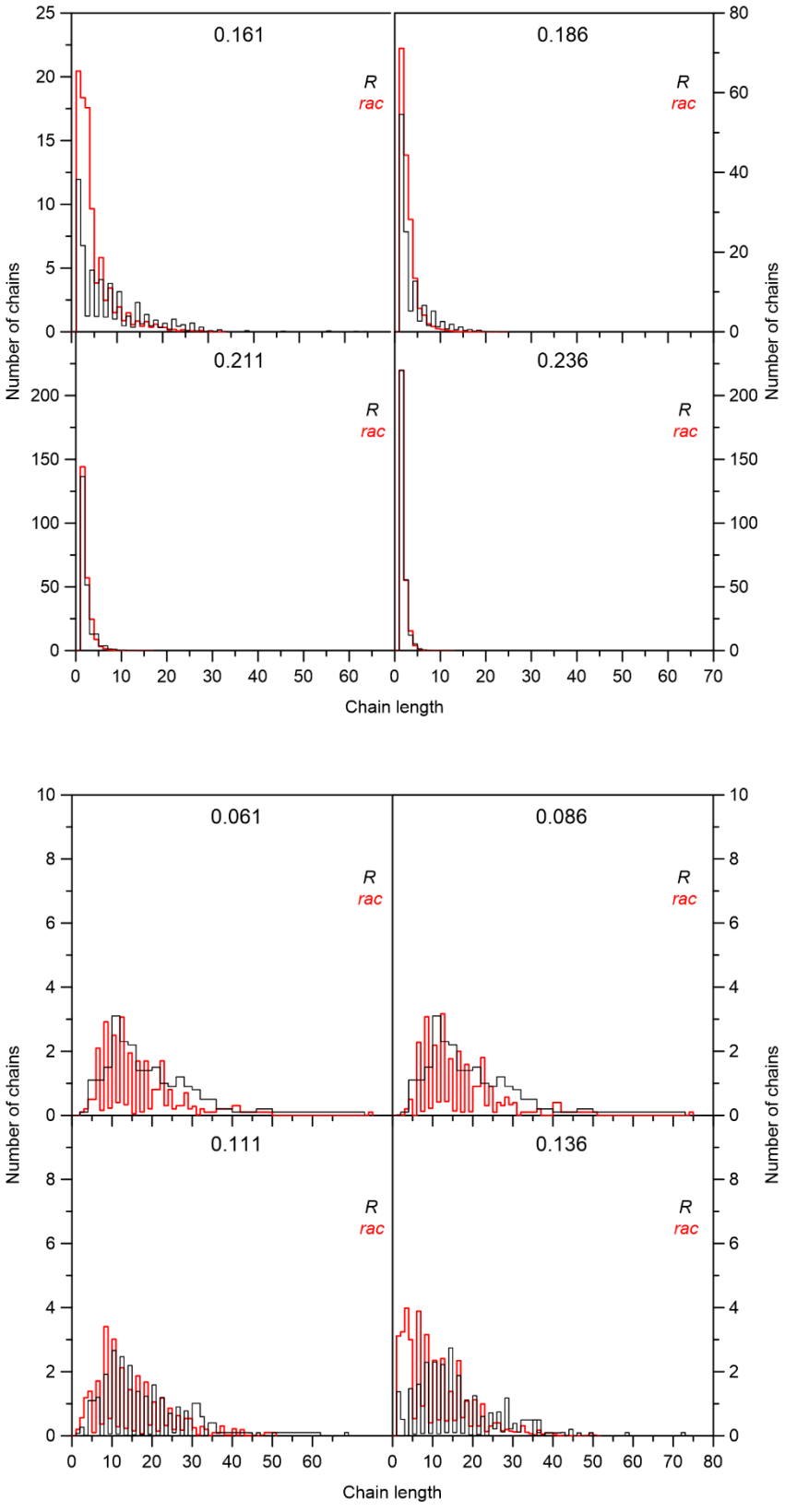


Figure S15. Chain length statistics at different temperatures calculated for the enantiopure (*R*) and racemic self-assembly of the isomer **n1268** (see Fig. 9) (averaged over ten replicas, N_l = 400, N_m = 800, L = 200).

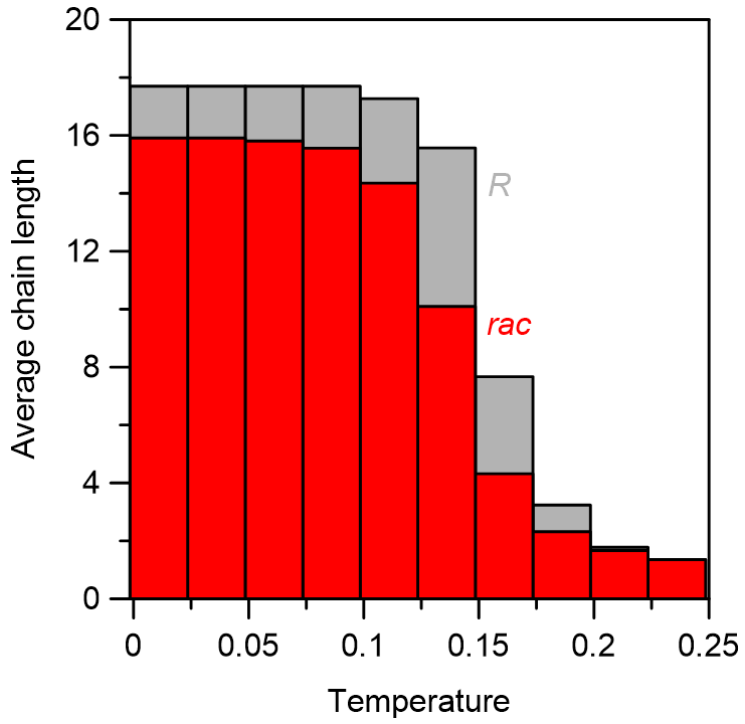
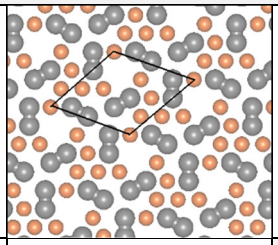
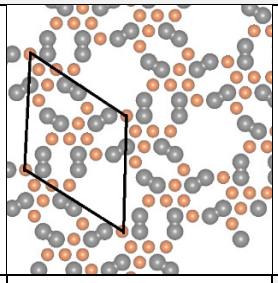
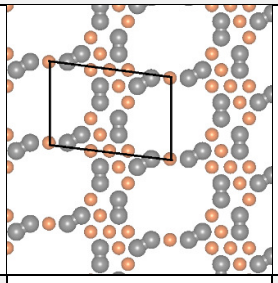
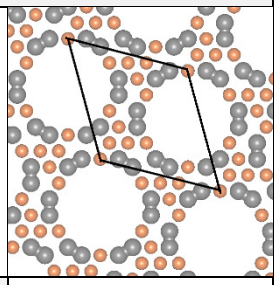
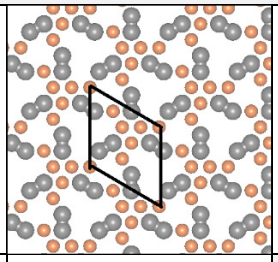


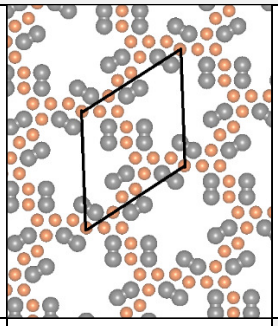
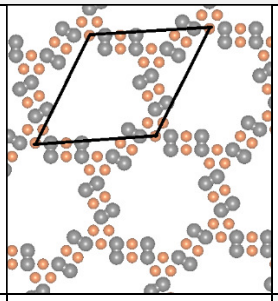
Figure S16. Effect of temperature on the average chain length calculated for the enantiopure (*R*) and racemic self-assembly of the isomer **n1268** (see Fig. 9) (averaged over ten replicas, N_l = 400, N_m = 800, L = 200).

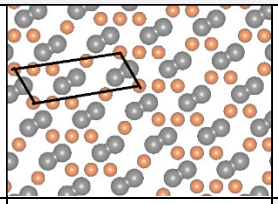
4. Structural parameters of the ordered networks comprising isomers of n

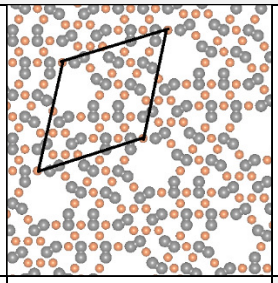
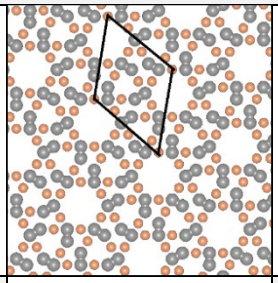
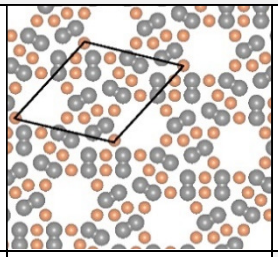
Table S1. Structural parameters of the ordered networks comprising isomers of **n**. The density ρ was defined as the total number of segments per area of the unit cell. The length unit equals to one lattice spacing.

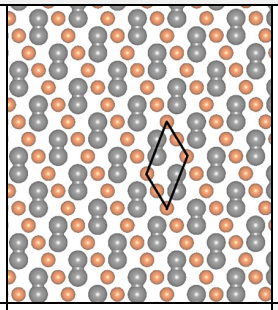
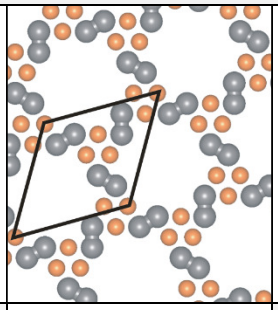
Molecule **n1235**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.220$		-		-
Unit cell parameters	(rhombic) a = $\sqrt{63}$ b = $\sqrt{63}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	6		-		-
Number of metal atoms inside unit cell	6		-		-
Molecule **n1236**					
Phase A		Phase B		Phase C	
Density	$\rho = 0.164$		$\rho = 0.142$		$\rho = 0.153$

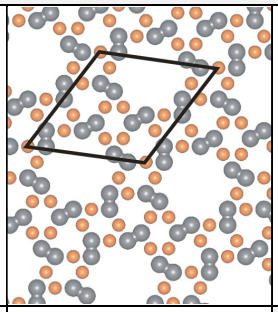
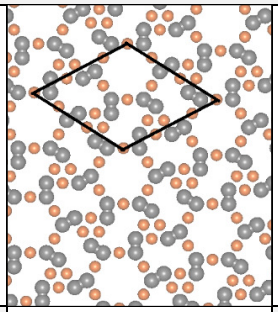
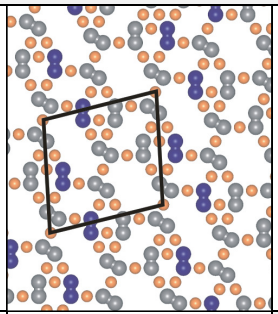
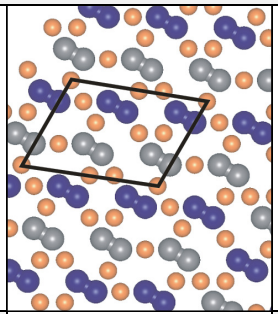
Unit cell parameters	(rhombic) a = 13 b = 13 $\theta_1 = 60°$ $\theta_2 = 120°$		(parallelogram) a = $\sqrt{172}$ b = $\sqrt{75}$ $\theta_1 = 82°$ $\theta_2 = 98°$		(rhombic) a = $\sqrt{181}$ b = $\sqrt{181}$ $\theta_1 = 60°$ $\theta_2 = 120°$
Number of linker segments inside unit cell	12		8		12
Number of metal atoms inside unit cell	12		8		12
Molecule **n1237**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.185$		-		-
Unit cell parameters	(rhombic) a = $\sqrt{75}$ b = $\sqrt{75}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	6		-		-
Number of metal atoms inside unit cell	6		-		-

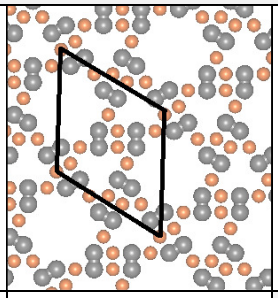
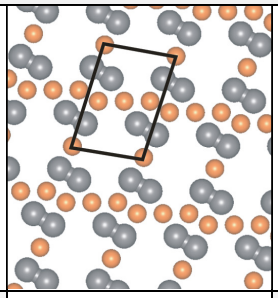
Molecule **n1238**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.164$		-		-
Unit cell parameters	(rhombic) a = 13 b = 13 $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	12		-		-
Number of metal atoms inside unit cell	12		-		-
Molecule **n1245**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.115$		-		-

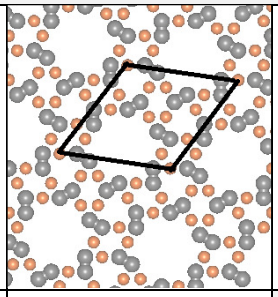
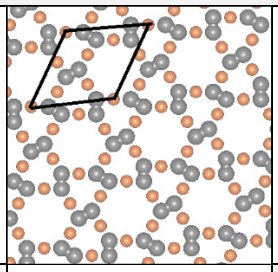
Unit cell parameters	(rhombic) $a = \sqrt{241}$ $b = \sqrt{241}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	12		-		-
Number of metal atoms inside unit cell	12		-		-
Molecule **n1246**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.192$		-		-
Unit cell parameters	(parallelogram) $a = \sqrt{124}$ $b = 4$ $\theta_1 = 69°$ $\theta_2 = 111°$		-		-
Number of linker segments inside unit cell	4		-		-
Number of metal atoms inside unit cell	4		-		-

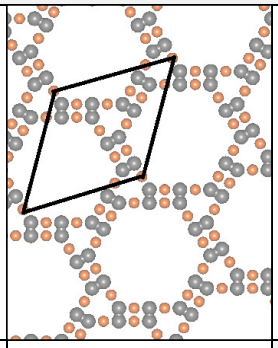
Molecule **n1247**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.175$		$\rho = 0.184$		-
Unit cell parameters	(rhombic) $a = \sqrt{316}$ $b = \sqrt{316}$ $\theta_1 = 60°$ $\theta_2 = 120°$		(rhombic) $a = \sqrt{151}$ $b = \sqrt{151}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-
Number of linker segments inside unit cell	24		12		-
Number of metal atoms inside unit cell	24		12		-
Molecule **n1248**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.199$		-		-
Unit cell parameters	(rhombic) $a = \sqrt{139}$ $b = \sqrt{139}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-

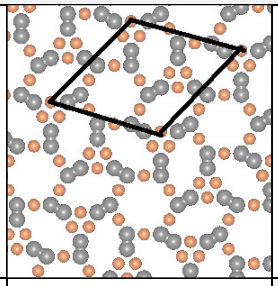
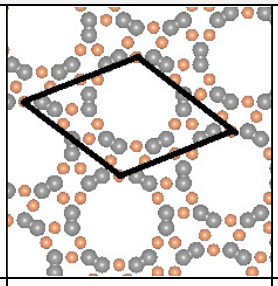
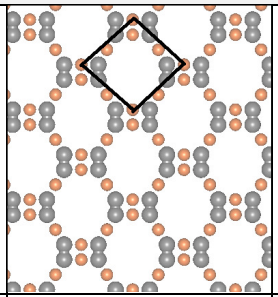
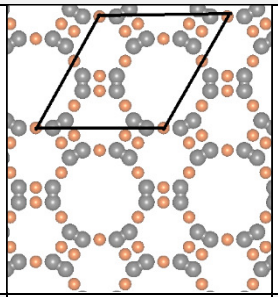
Number of linker segments inside unit cell	12		-		-
Number of metal atoms inside unit cell	12		-		-
Molecule **n1256**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.231$		$\rho = 0.143$		
Unit cell parameters	(parallelogram) a = 4 b = $\sqrt{31}$ $\theta_1 = 51°$ $\theta_2 = 129°$		(rhombic) a = $\sqrt{97}$ b = $\sqrt{97}$ $\theta_1 = 60°$ $\theta_2 = 120°$		
Number of linker segments inside unit cell	2		6		
Number of metal atoms inside unit cell	2		6		

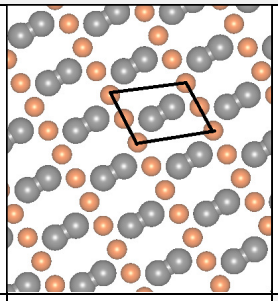
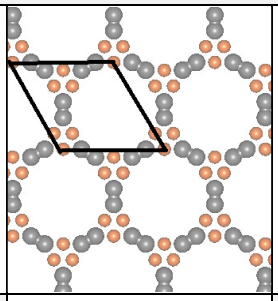
Molecule **n1257**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.161$		$\rho = 0.164$		-
Unit cell parameters	(rhombic) a = $\sqrt{172}$ b = $\sqrt{172}$ $\theta_1 = 60°$ $\theta_2 = 120°$		(rhombic) a = 13 b = 13 $\theta_1 = 60°$ $\theta_2 = 120°$		-
Number of linker segments inside unit cell	12		12		-
Number of metal atoms inside unit cell	12		12		-
Molecule **n1257 rac**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.162$		$\rho = 0.192$		-

Unit cell parameters	(parallelogram) $a = \sqrt{193}$ $b = \sqrt{208}$ $\theta_1 = 80°$ $\theta_2 = 100°$		(parallelogram) $a = 8$ $b = \sqrt{124}$ $\theta_1 = 69°$ $\theta_2 = 111°$		-
Number of linker segments inside unit cell	16		8		-
Number of metal atoms inside unit cell	16		8		-
Molecule **n1258**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.164$		$\rho = 0.178$		-
Unit cell parameters	(rhombic) $a = 13$ $b = 13$ $\theta_1 = 60°$ $\theta_2 = 120°$		(parallelogram) $a = \sqrt{67}$ $b = \sqrt{31}$ $\theta_1 = 81°$ $\theta_2 = 99°$		-
Number of linker segments inside unit cell	12		4		-
Number of metal atoms inside unit cell	12		4		-

Molecule **n1356**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.161$		-		-
Unit cell parameters	(rhombic) a = $\sqrt{172}$ b = $\sqrt{172}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	12		-		-
Number of metal atoms inside unit cell	12		-		-
Molecule **n1357**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.152$		-		-
Unit cell parameters	(rhombic) a = $\sqrt{91}$ b = $\sqrt{91}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-

Number of linker segments inside unit cell	6		-		-
Number of metal atoms inside unit cell	6		-		-
Molecule **n1358**					
Phase A		Phase B	-	Phase C	-
Density	$\rho = 0.107$		-		-
Unit cell parameters	(rhombic) $a = \sqrt{259}$ $b = \sqrt{259}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-		-
Number of linker segments inside unit cell	12		-		-
Number of metal atoms inside unit cell	12		-		-

Molecule **n1367**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.153$		$\rho = 0.141$		-
Unit cell parameters	(rhombic) a = $\sqrt{181}$ b = $\sqrt{181}$ $\theta_1 = 60°$ $\theta_2 = 120°$		(rhombic) a = $\sqrt{196}$ b = $\sqrt{196}$ $\theta_1 = 60°$ $\theta_2 = 120°$		-
Number of linker segments inside unit cell	12		12		-
Number of metal atoms inside unit cell	12		12		-
Molecule **n1368**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.128$		$\rho = 0.103$		-
Unit cell parameters	(rhombic) a = $\sqrt{63}$ b = $\sqrt{63}$ $\theta_1 = 82°$ $\theta_2 = 98°$		(rhombic) a = 15 b = 15 $\theta_1 = 60°$ $\theta_2 = 120°$		-

Number of linker segments inside unit cell	4		10		-
Number of metal atoms inside unit cell	4		10		-
Molecule **n2367**					
Phase A		Phase B		Phase C	-
Density	$\rho = 0.192$		$\rho = 0.115$		-
Unit cell parameters	(parallelogram) a = $\sqrt{31}$ b = 4 $\theta_1 = 69°$ $\theta_2 = 111°$		(rhombic) a = 11 b = 11 $\theta_1 = 60°$ $\theta_2 = 120°$		-
Number of linker segments inside unit cell	2		6		-
Number of metal atoms inside unit cell	2		6		-