Supporting Information

for

Surface-Confined Metal-Organic Precursors Comprising Naphthalene-Like Derivatives with Differently Distributed Halogen Substituents: A Monte Carlo Model

Jakub Lisiecki and Paweł Szabelski*

Department of Theoretical Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, Pl. M.C. Skłodowskiej 3, 20-031 Lublin, Poland

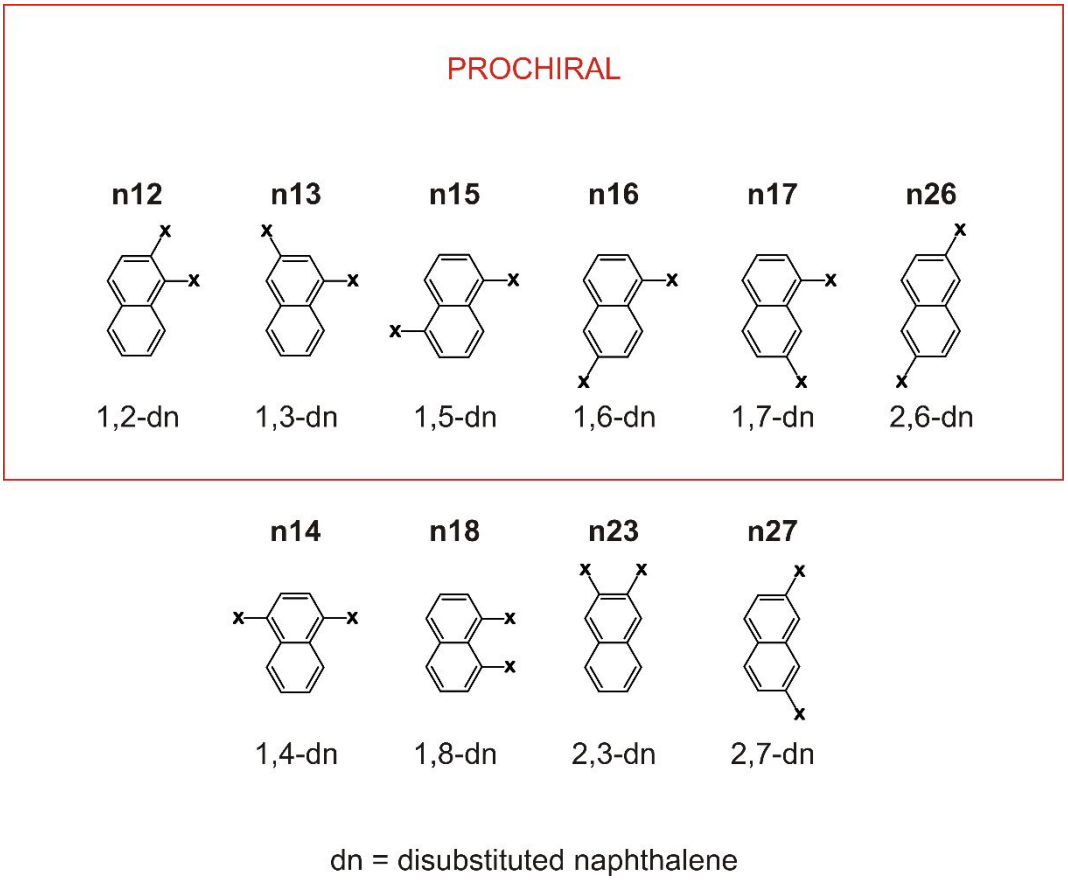

Figure S1. Ten possible disubstituted isomers of naphthalene. The prochiral molecules, able to adopt mirror-image configurations when adsorbed, are grouped inside the red frame.

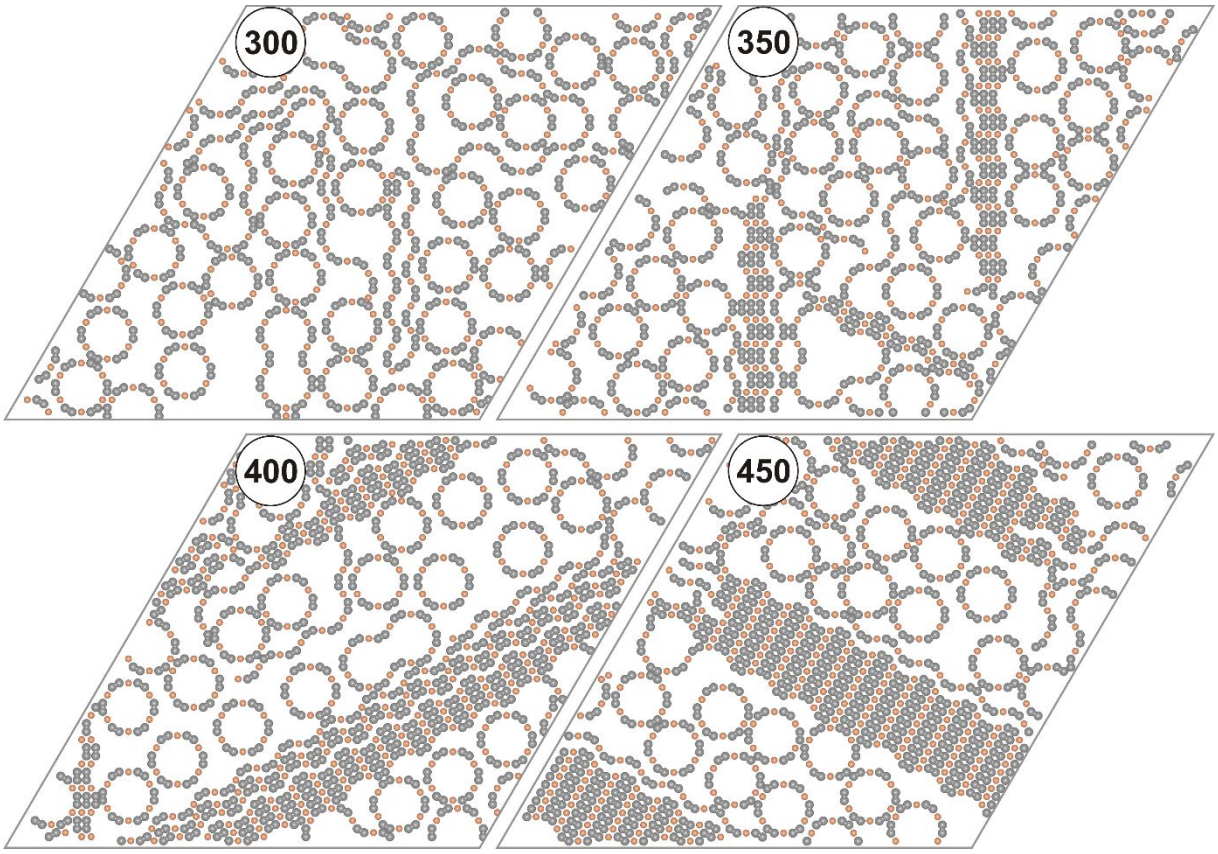

Figure S2. Effect of surface coverage on the morphology of the adsorbed overlayers comprising the distubstituted isomer **n27**. For each snapshot, the number of molecules used in the simulations is shown inside the white circle (normal cooling, $T = 0.01$, $\theta_{300} = 0.09$, $\theta_{350} = 0.105$, $\theta_{400} = 0.12$, $\theta_{450} = 0.135$, $L = 100$).

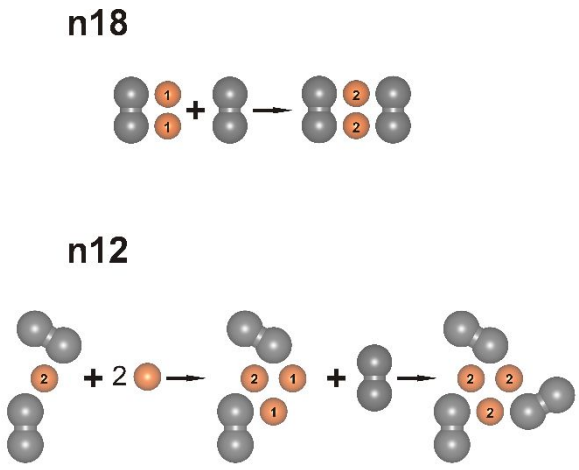

Figure S3. Schematic representation of the most efficient routes to complete metal coordination corresponding to the disubstituted naphthalene derivatives **n18** (top) and **n12** (bottom). For each metal atom its current coordination number is additionally shown.

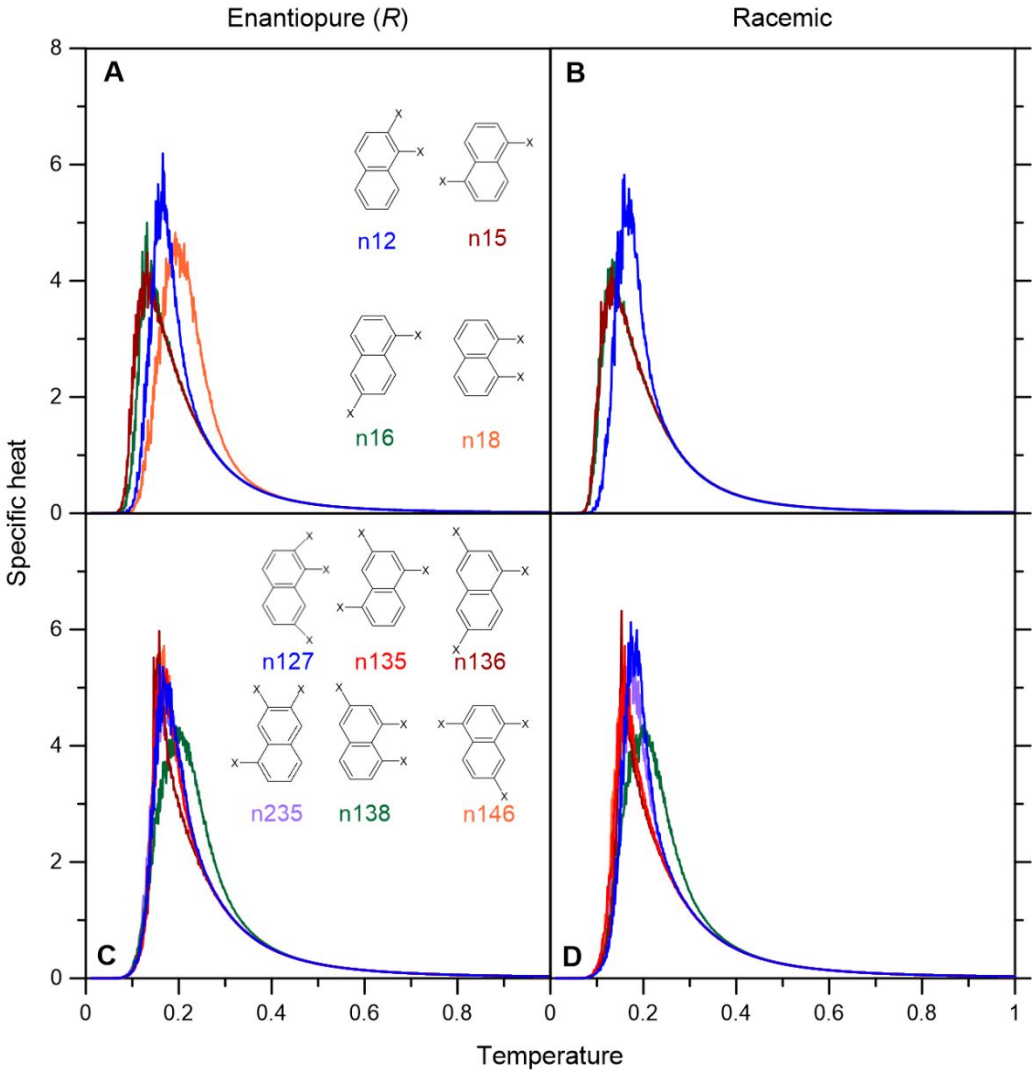

Figure S4. Specific heat curves calculated for the enantiopure (left) and racemic systems (right) comprising differently disubstituted (A,B) and trisubstituted prochiral isomers of **n**. $L = 200$, $N_l = 400$, $N_m = 400$ (for A and B) and 600 (for C and D), $\theta = 0.03$ (A, B) and 0.035 (C, D).

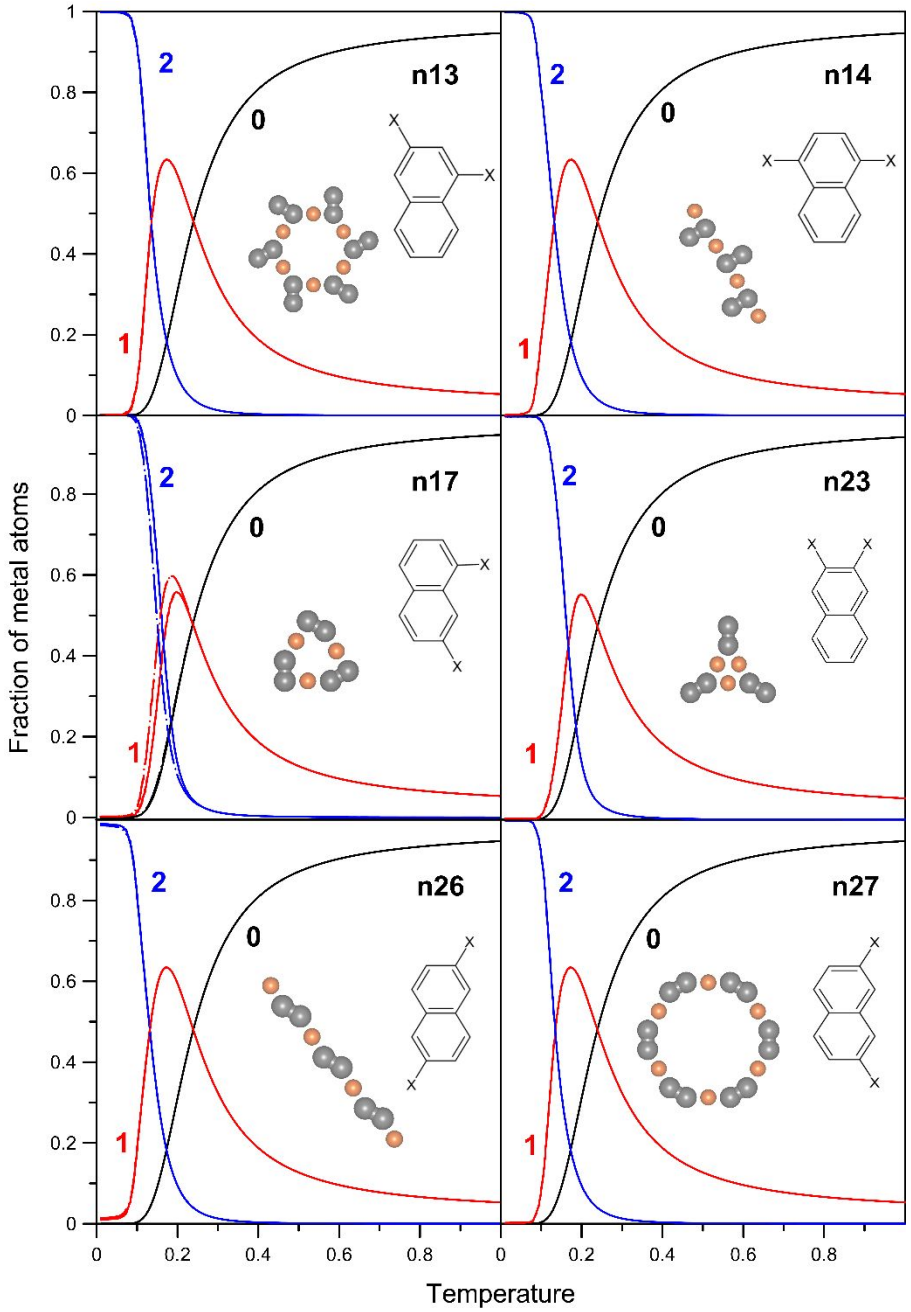

Figure S5. Fraction of metal atoms linked with zero (black), one (red) and two (blue) molecules of **n** (*R* if chiral) as a function of temperature, simulated for the one-monomer type systems. For the prochiral molecules **n13**, **n17** the dashed lines are the results predicted for the corresponding racemic overlayers. Characteristic structural motifs formed in these one-monomer type assemblies are shown in each panel. 400 molecules mixed with 400 metal atoms, $L = 200$.

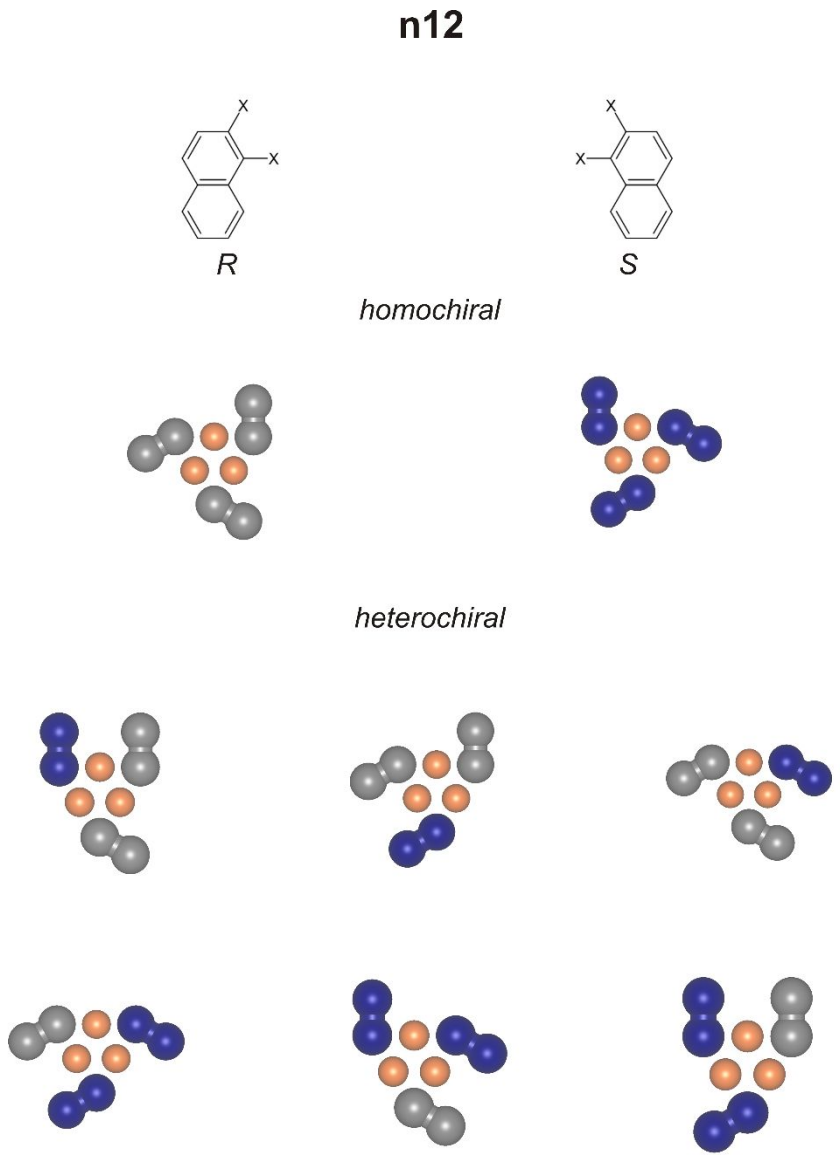

Figure S6. Possible trimeric metalorganic configurations differing in the number of the enantiomers *R* and *S* of the prochiral tecton n12.

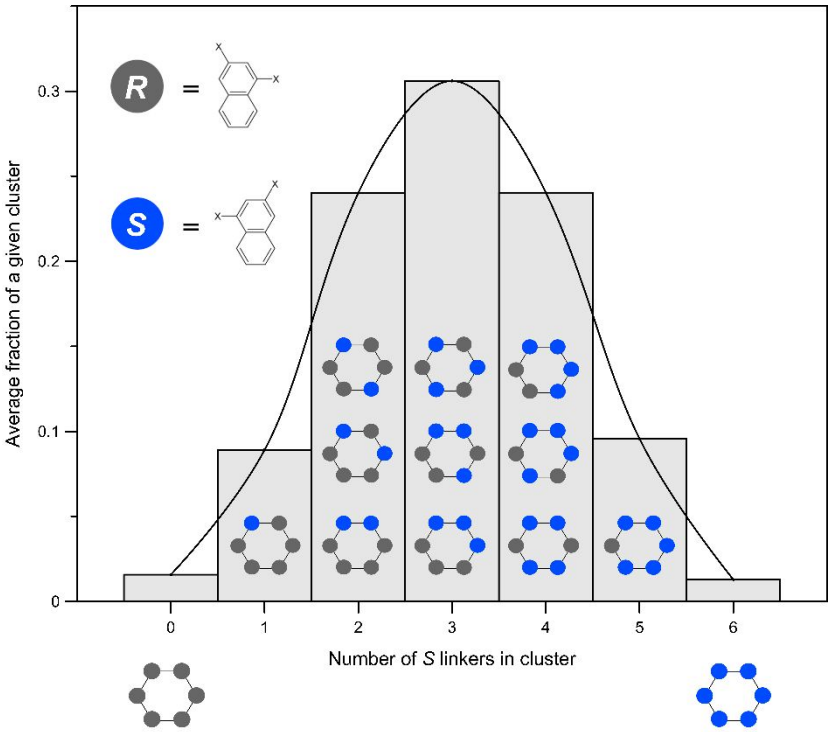

Figure S7. Fraction of hexagonal clusters comprising a given number of the *S*-enantiomer simulated for the racemic overlayer comprising 400 molecules of **n13** and 400 metal atoms. The black solid line is a spline showing normal envelope of the histogram. $L = 200$, $\theta = 0.03$.

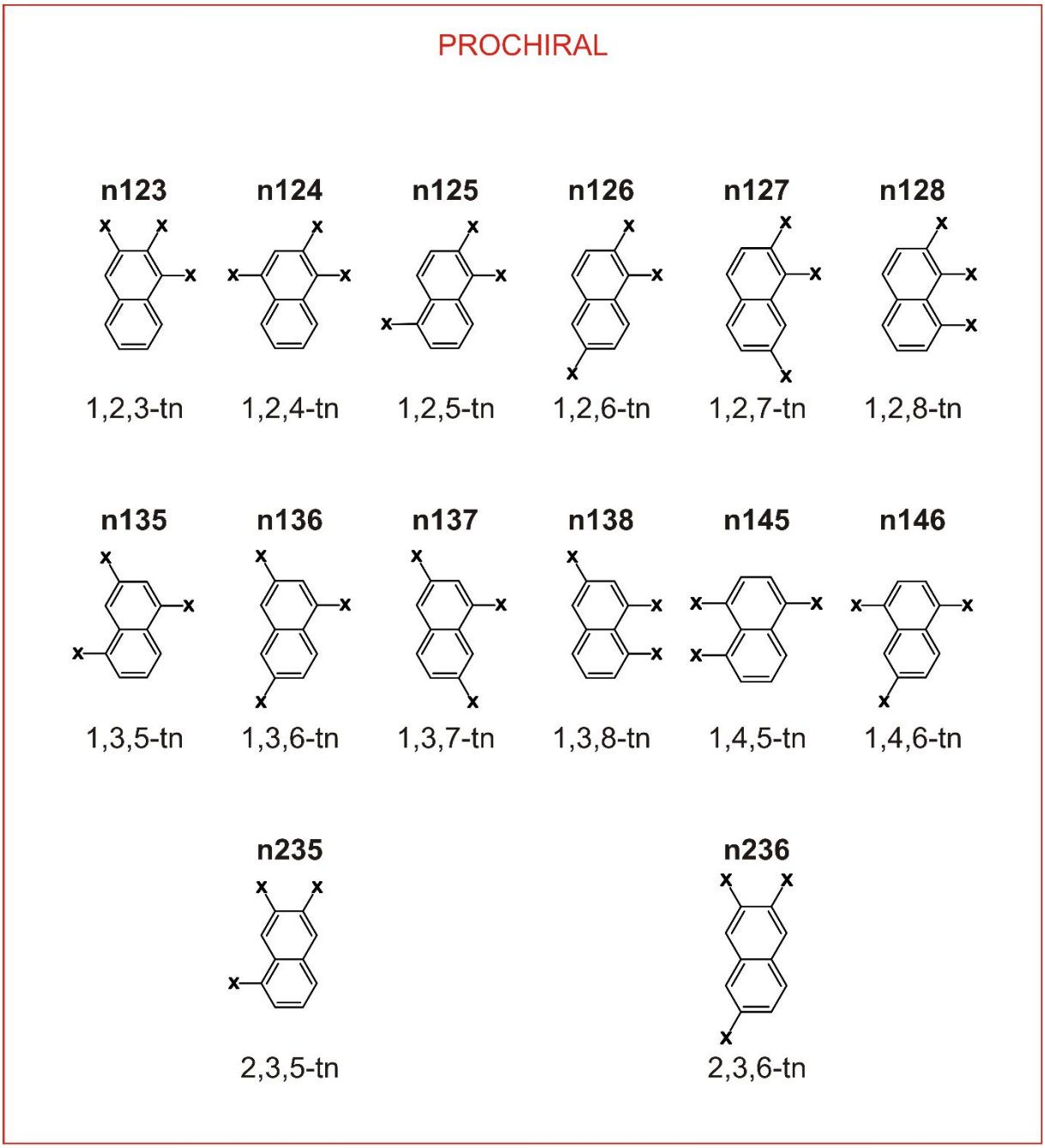

Figure S8. Fourteen trisubstituted isomers of naphthalene. The prochiral molecules, able to adopt mirror-image configurations when adsorbed, are grouped inside the red frame.

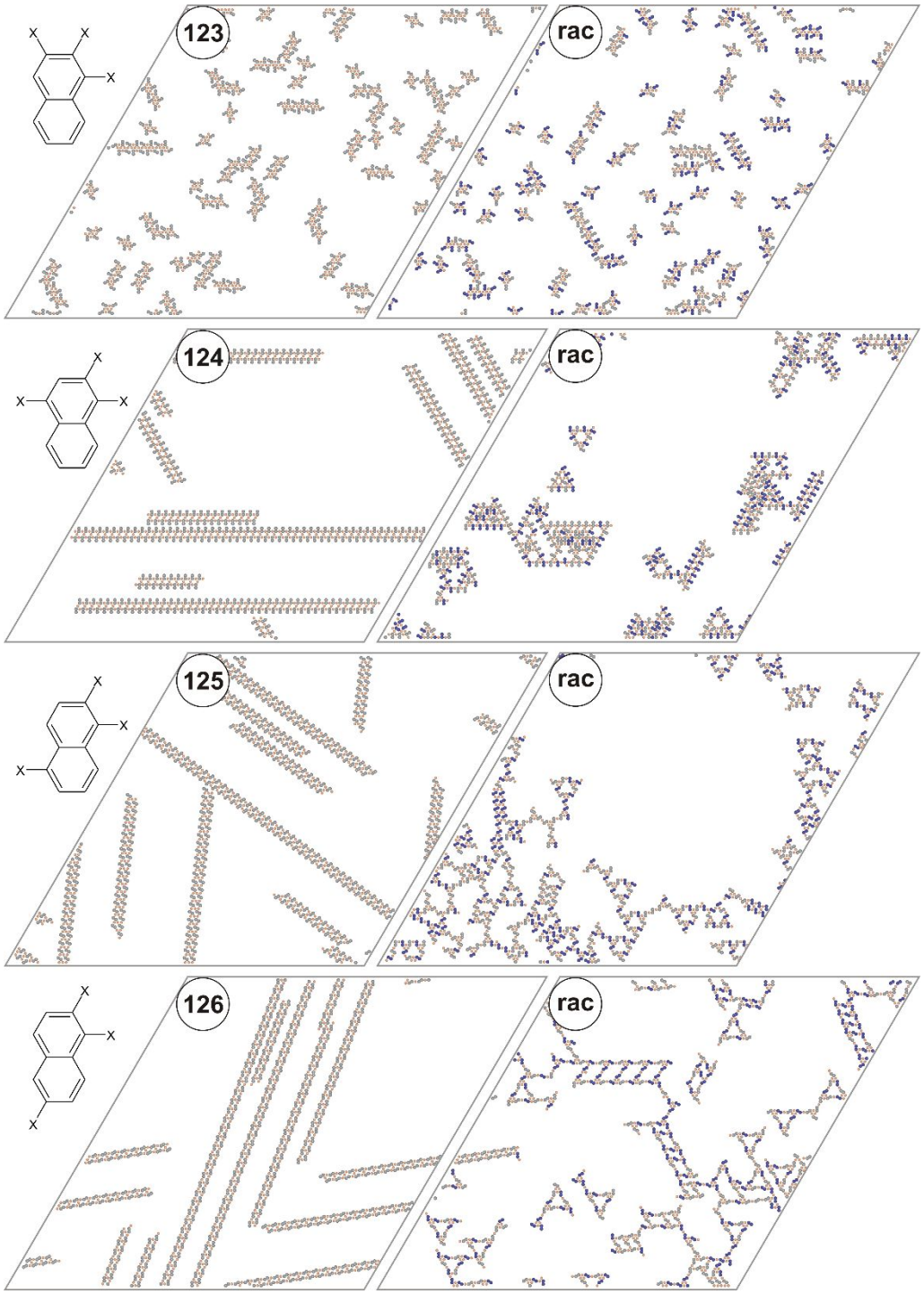

Figure S9. Adsorbed structures formed in the enantiopure (*R*, left) and racemic (right) overlayers comprising 400 molecules of differently trihalogenated naphthalene isomers mixed with 600 metal atoms; the encircled digits denote positions of halogen substituents in the corresponding molecule; $L = 200$, $\theta = 0.035$.

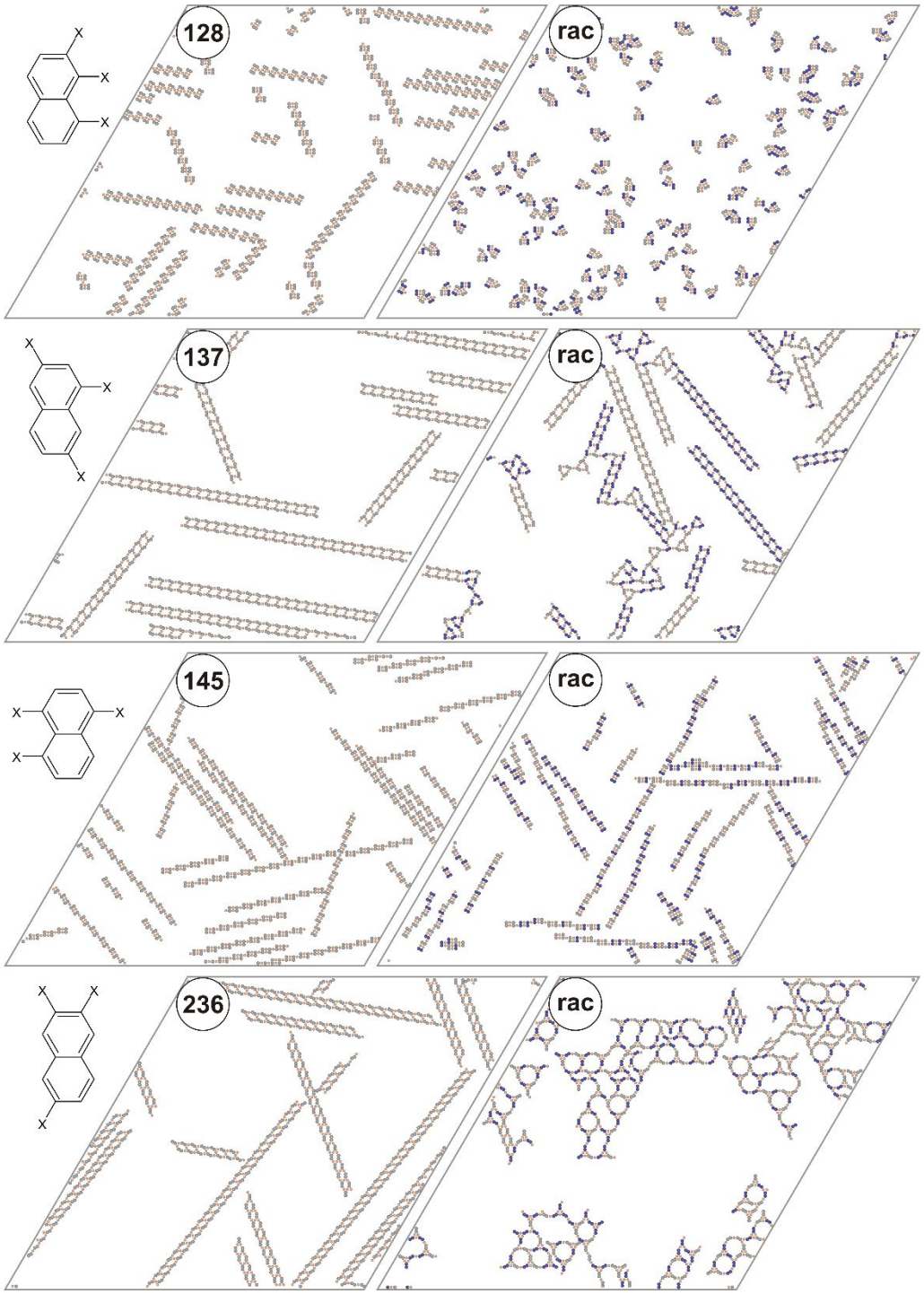

Figure S10. Adsorbed structures formed in the enantiopure (*R*, left) and racemic (right) overlayers comprising 400 molecules of differently trihalogenated naphthalene isomers mixed with 600 metal atoms; the encircled digits denote positions of halogen substituents in the corresponding molecule; $L = 200$, $\theta = 0.035$.

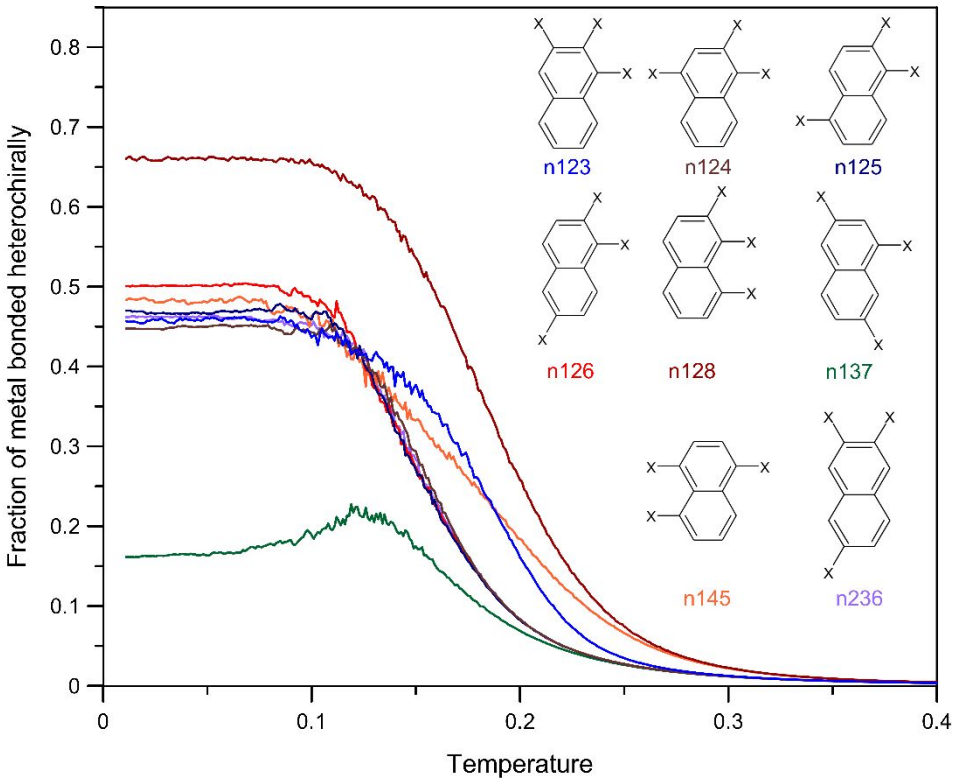

Figure S11. Influence of temperature on the fraction of metal nodes linked with the opposite enantiomers (*R* and *S*) calculated for the remaining trisubstituted isomers of **n**. L = 200, N_l = 400, N_m = 600, θ = 0.035.

Calculation of the radial distribution function

The metal-metal radial distribution function was calculated using the following formula:

$$g(r) = \langle n_r \rangle A / 2\pi r dr N_m$$

where $\langle n_r \rangle$ is the average number of metal atoms in (r, $r + dr$) shell away from any given metal, $2\pi r dr$ is the area of considered shell (dr = 0.2) and A denotes the Cartesian area of the system ($A = L^2 * \sqrt{3}/2$).