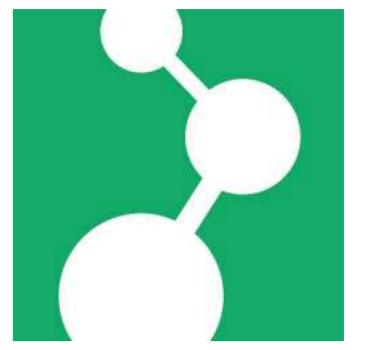




Columnar phases of triphenylenes

or what is better: long legs or a big head?

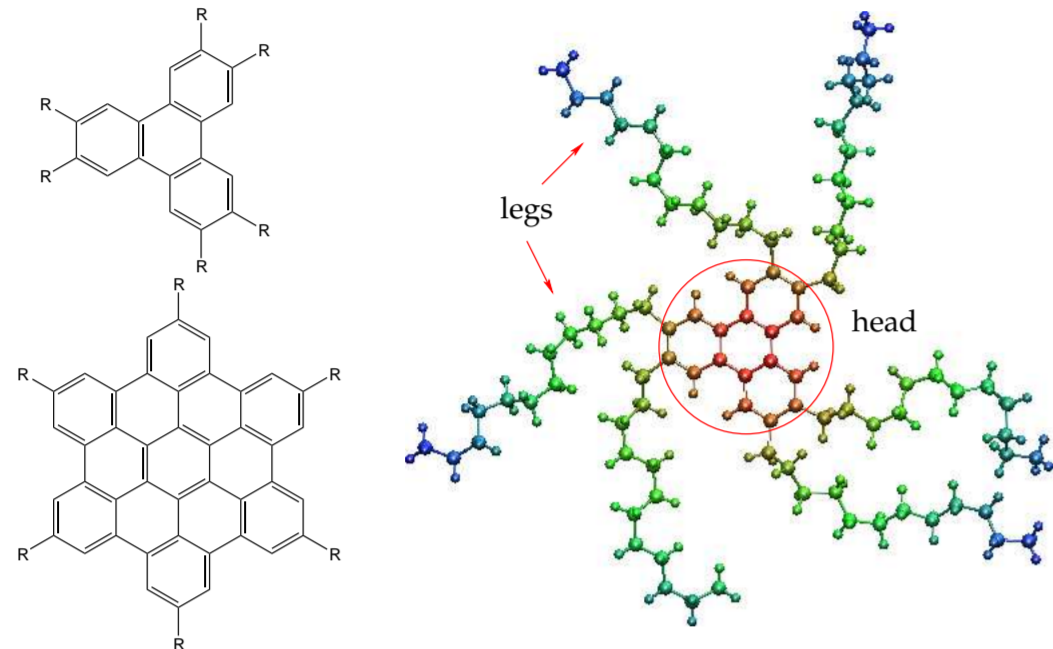


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What?

Columnar phases of discotic liquid crystals (LCs) and their blends. The columnar phase consists of discs stacked on top of each other to form columns arranged in a two-dimensional lattice.



Triphenylene and hexabenzocoronene: typical examples of discotic LCs. $R = C_nH_{2n+1}$. The molecule consists of a triphenylene core (head) linked with six alkyne chains (legs).

Why?

A few reasons:

- They are relatively simple (good test system).
- Good materials: liquid crystallinity at room temperature, good solubility in organic solvents.
- Self-assemble in stacks. This provides the high charge carrier mobility towards the electrodes and helps to avoid charge trapping and recombination.
- See posters of people from Müllen's group as well as Refs. [1, 2, 4].

How?

Atomistic simulations with a simple energy:

$$E = \sum_{\text{angles}} \frac{1}{2} K_{\theta} (\theta - \theta_0)^2 \quad (1)$$

$$+ \sum_{\text{dihedrals}} \left[\frac{V_1}{2} (1 + \cos \phi) + \frac{V_2}{2} (1 - \cos 2\phi) + \frac{V_3}{2} (1 + \cos 3\phi) \right]$$

$$+ \sum_{\text{impropers}} K_d (\psi - \psi_0)^2$$

$$+ \sum_i \sum_{j>i} \left[\frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \right]$$

Parameters of the potentials are taken from the OPLS force field. Only the hydrogen atoms belonging to the aromatic rings of the central core are explicitly considered, whereas the united atom approach is adopted for the alkyl chains. Interactions between pairs of sites belonging to the central aromatic core have been excluded. See Ref. [6] for a similar model.

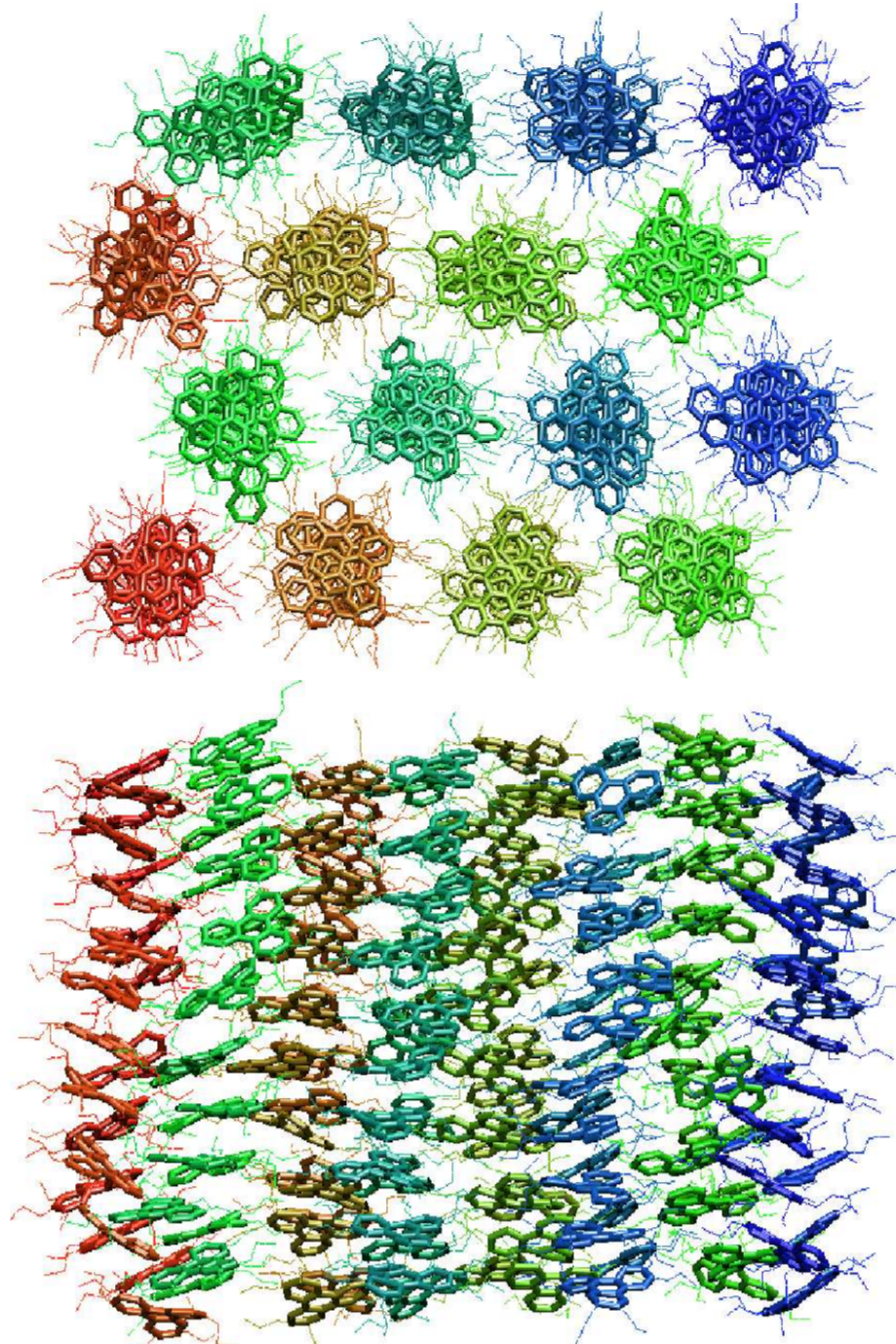
We simulated systems of 160 molecules, arranged in columns of 10 molecules each. The initial configuration was a hexagonal arrangement of the columns. We used Berendsen thermostat with pressure 0.1MPa and a temperature $T = 375K$. The equations of motion have been integrated with a time step of 2 fs. All the bond lengths have been constrained at their equilibrium values.

References

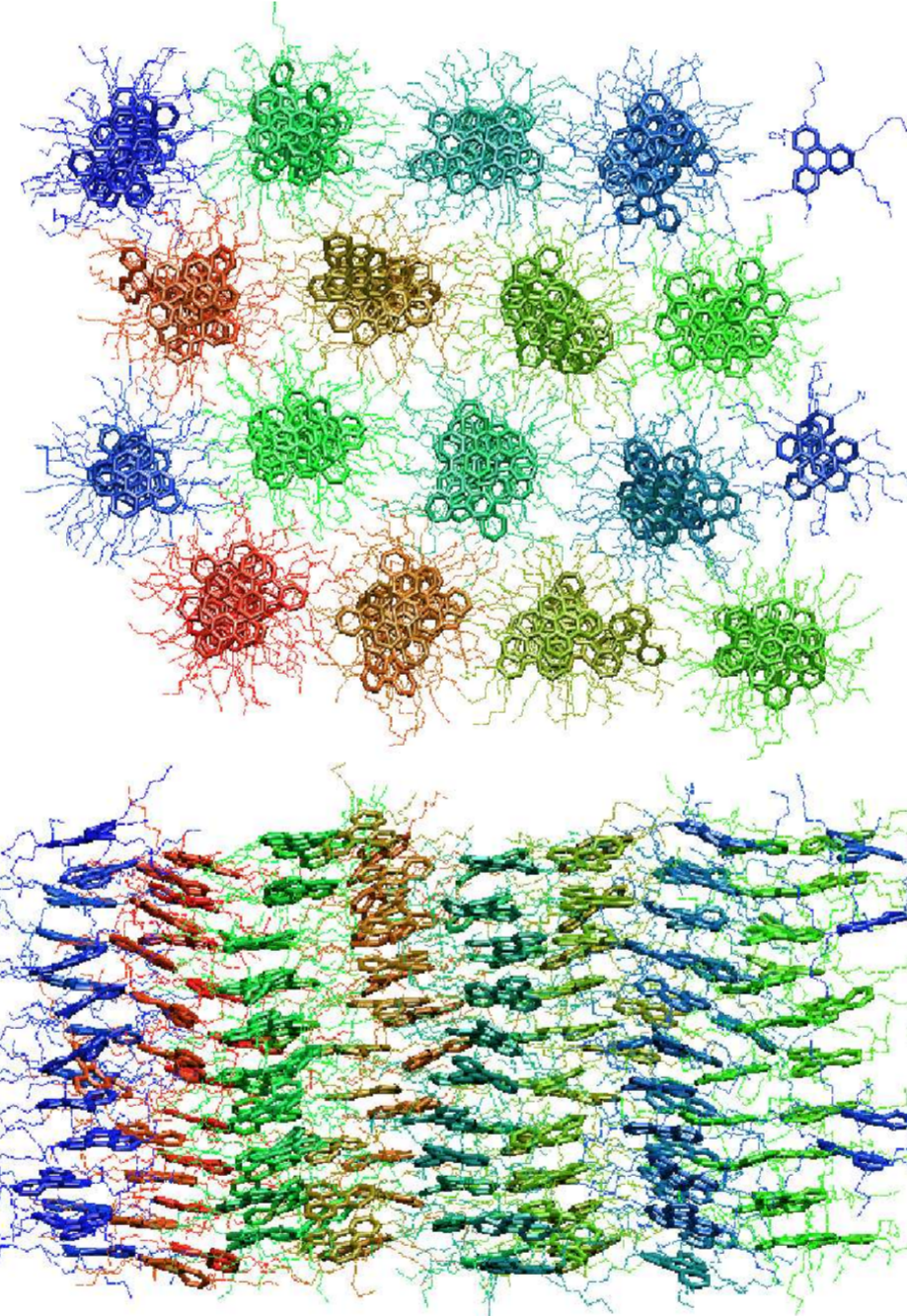
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Results

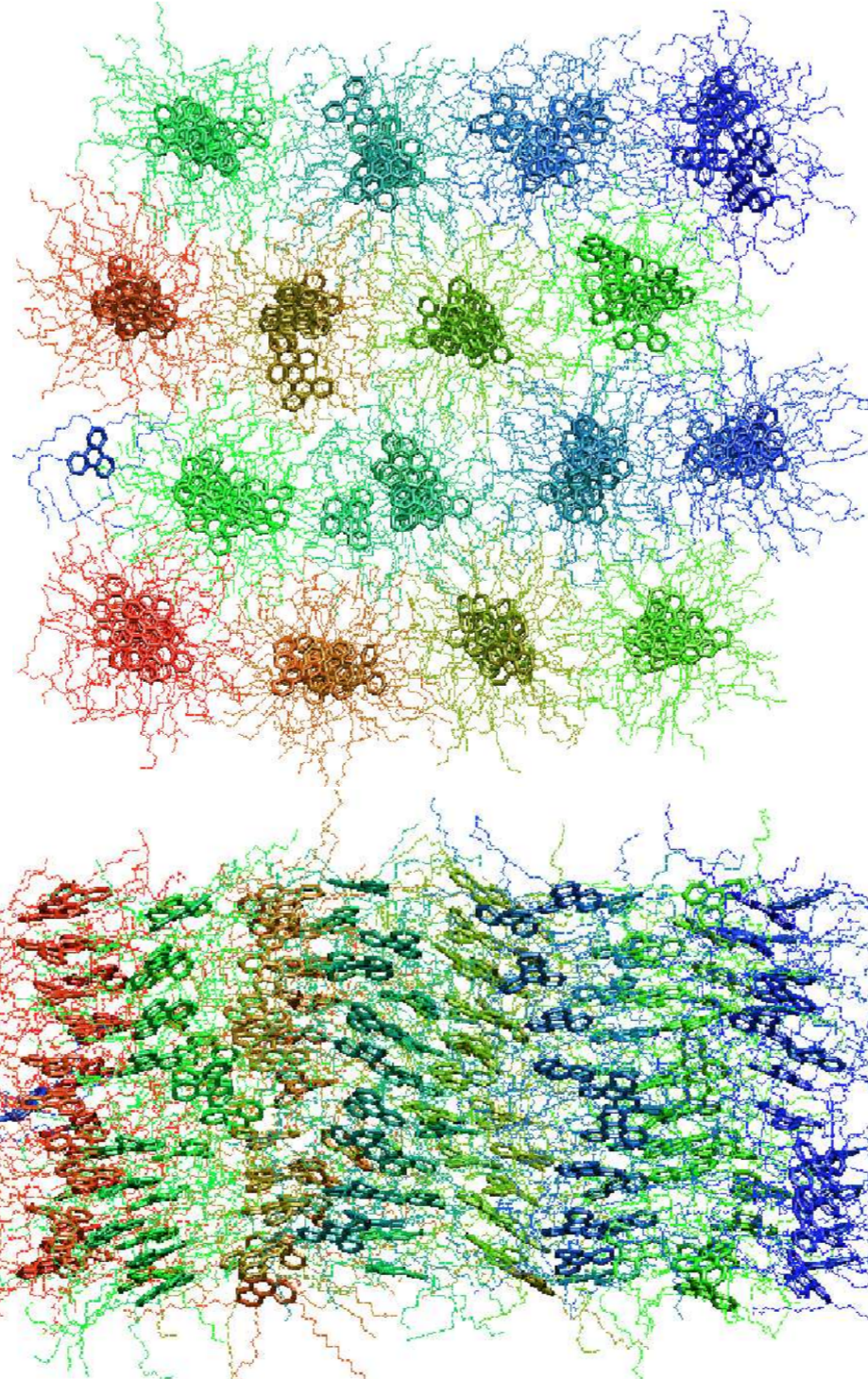
Snapshots of the systems with different lengths of the side chains (top and side views).



Short alkyne chains, $n = 3$.



Slightly longer chains, $n = 6$.



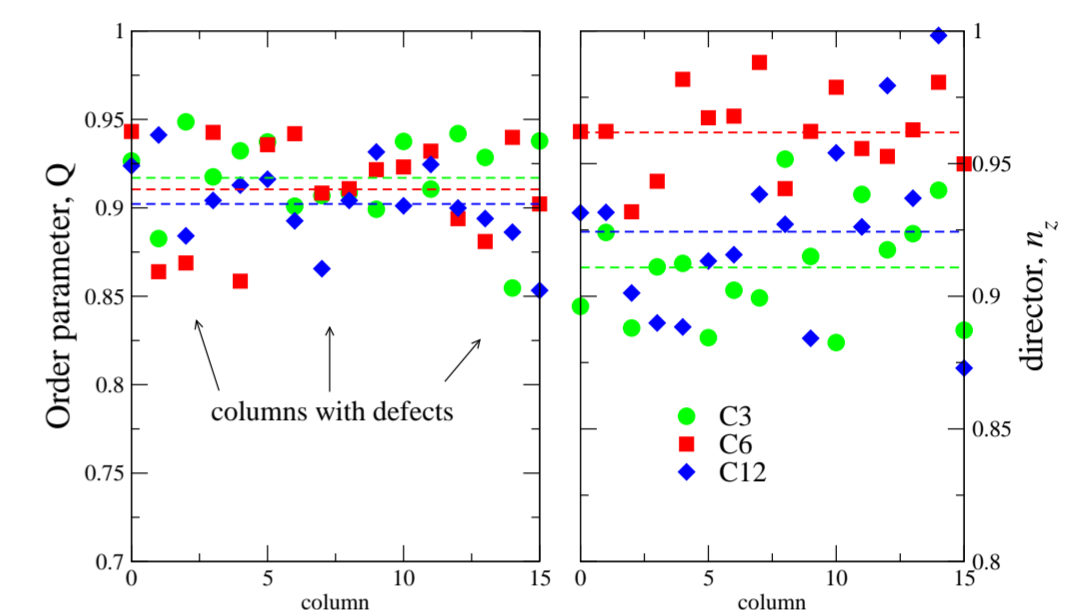
Long chains, $n = 12$.

Orientalional order parameter

For each column, we calculated the orientational order tensor

$$Q_{\alpha\beta} = \frac{1}{N_{\text{col}}} \sum_{\text{col}} \left(\frac{3}{2} n_{\alpha} n_{\beta} - \frac{1}{2} \delta_{\alpha\beta} \right) \quad (2)$$

where \mathbf{n} is a unit vector normal to the central benzene. Diagonalizing this tensor we obtained the order parameter Q of a column (biggest eigenvalue of $Q_{\alpha\beta}$) and the average orientation of the molecules, or director \mathbf{d} (corresponding eigenvector).



Order parameter and the z -component of the director (average tilt in the column).

Positional correlation functions

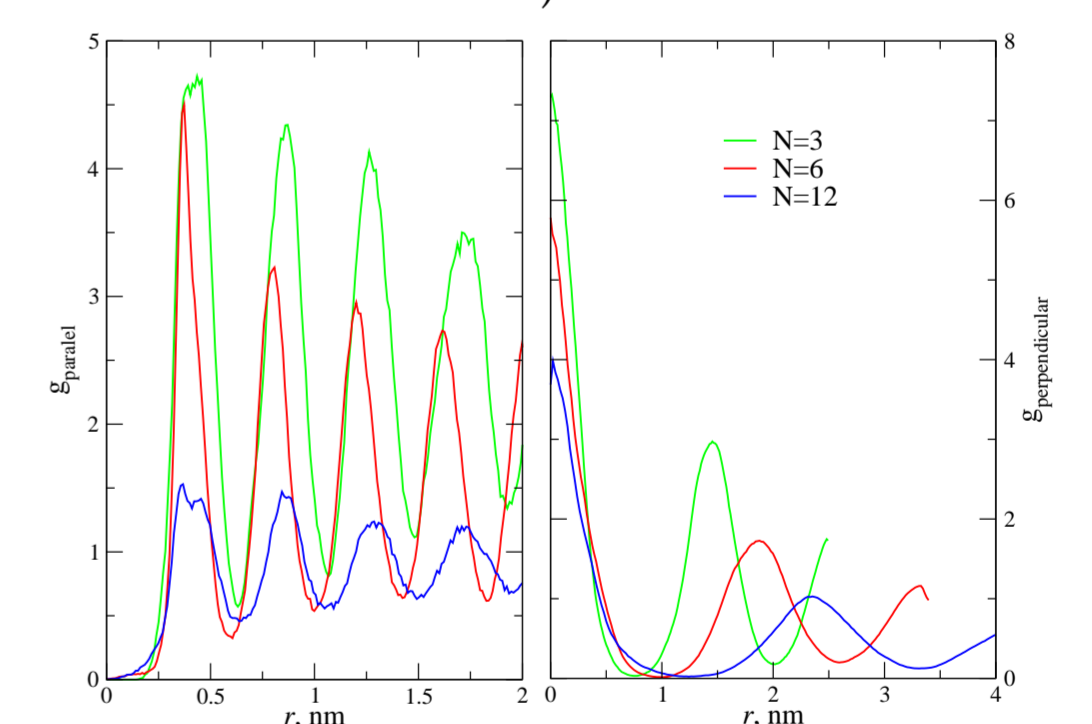
Two types of correlation functions are important for columnar mesophase of discotic liquid crystals

$$g_{\parallel}(r) = \frac{2}{VN} \sum_{\text{columns}} \sum_{i=0}^{N_c} \sum_{j>i}^{N_c} f(\mathbf{r}, \mathbf{n} \cdot \mathbf{r}_{ij}) \quad (3)$$

This is the probability to find a molecule at a distance $\mathbf{n} \cdot \mathbf{r}$ from the reference molecule. The averaging is first performed in a single column, and then over the columns (columns can diffuse with respect to each other).

$$g_{\perp}(r) = \frac{2}{V(r)N} \sum_{i=0}^N \sum_{j>i}^N f(\mathbf{r}, \mathbf{n} \times \mathbf{r}_{ij}) \quad (4)$$

This gives the information about the arrangement of the molecules in the planes perpendicular to the director (in our case - direction of the columns).



Positional correlation functions g_{\parallel} and g_{\perp} .

Preliminary conclusions

- Molecules with short side chains form better (with less defects) columnar phases; systems with long chains have more inter-column molecules and defects.
- The director is tilted in each particular column; its azimuthal orientation changes from column to column.
- The smallest tilt angle, as well as the intermolecular separation we observed for $n = 6$.
- Results are very sensitive to the choice of the initial configuration; coarse-graining is vital to treat larger systems on a longer time scales.

Many thanks to the developers of GROMACS molecular dynamics simulation package, in particular to Berk Hess for his patience and help. This work was supported by the International Association of Spiders.



Spider Lilies