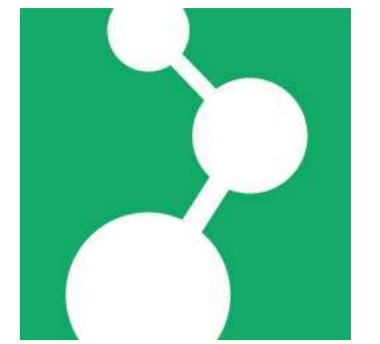




# Structure and dynamics of columnar phases of hexabenzocoronene derivatives

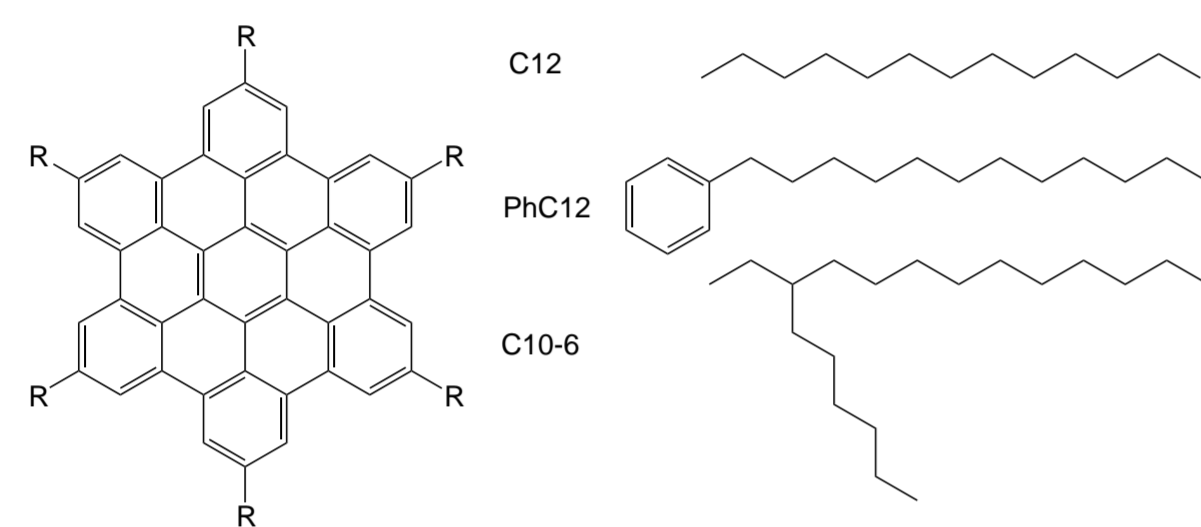


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**Abstract** Using atomistic MD simulations we study the solid columnar discotic and liquid crystalline phases formed by the alkyl-substituted hexabenzocoronene mesogens. Correlations between the molecular structure, packing, and dynamical properties of these materials are established.

## Systems

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.



Hexabenzocoronene (HBC) and its derivatives (R = H, C12, PhC12, C10-6) - typical examples of discotic LCs.

## Motivation

- Good materials: liquid crystallinity at low temperatures, good solubility in organic solvents.
- Self-assemble in stacks. High charge carrier mobility towards the electrodes (along columns). Small charge trapping and recombination.

## Methods

Atomistic simulations:

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

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

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

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

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. [1] for a similar model.

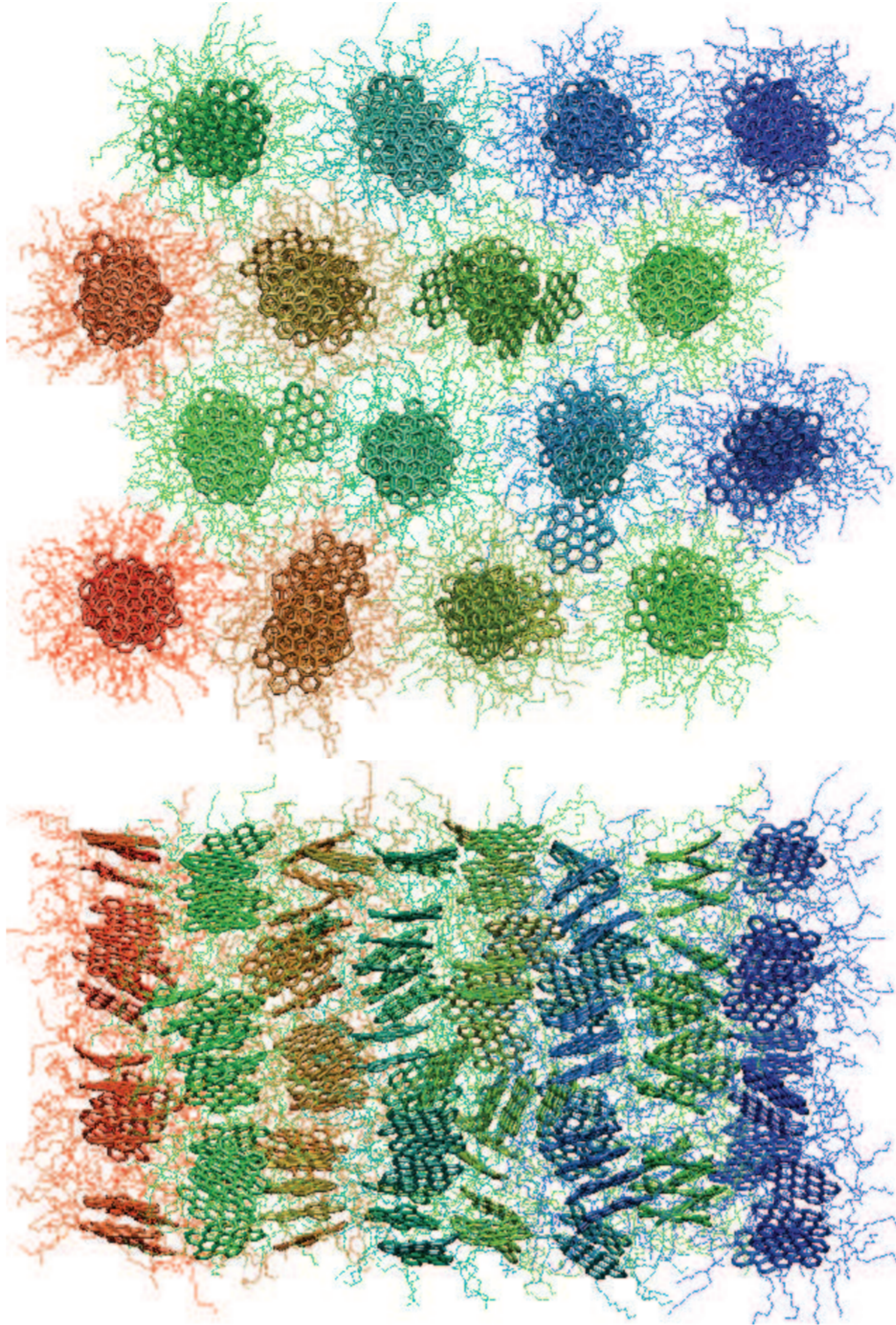
We simulated systems of 160 molecules, arranged in columns of 10 molecules each. The initial configuration was a hexagonal arrangement of the columns. We used Berendsen thermostat with pressure 0.1MPa and a temperature  $T = 375K$ . The equations of motion have been integrated with a time step of 2 fs.

## References

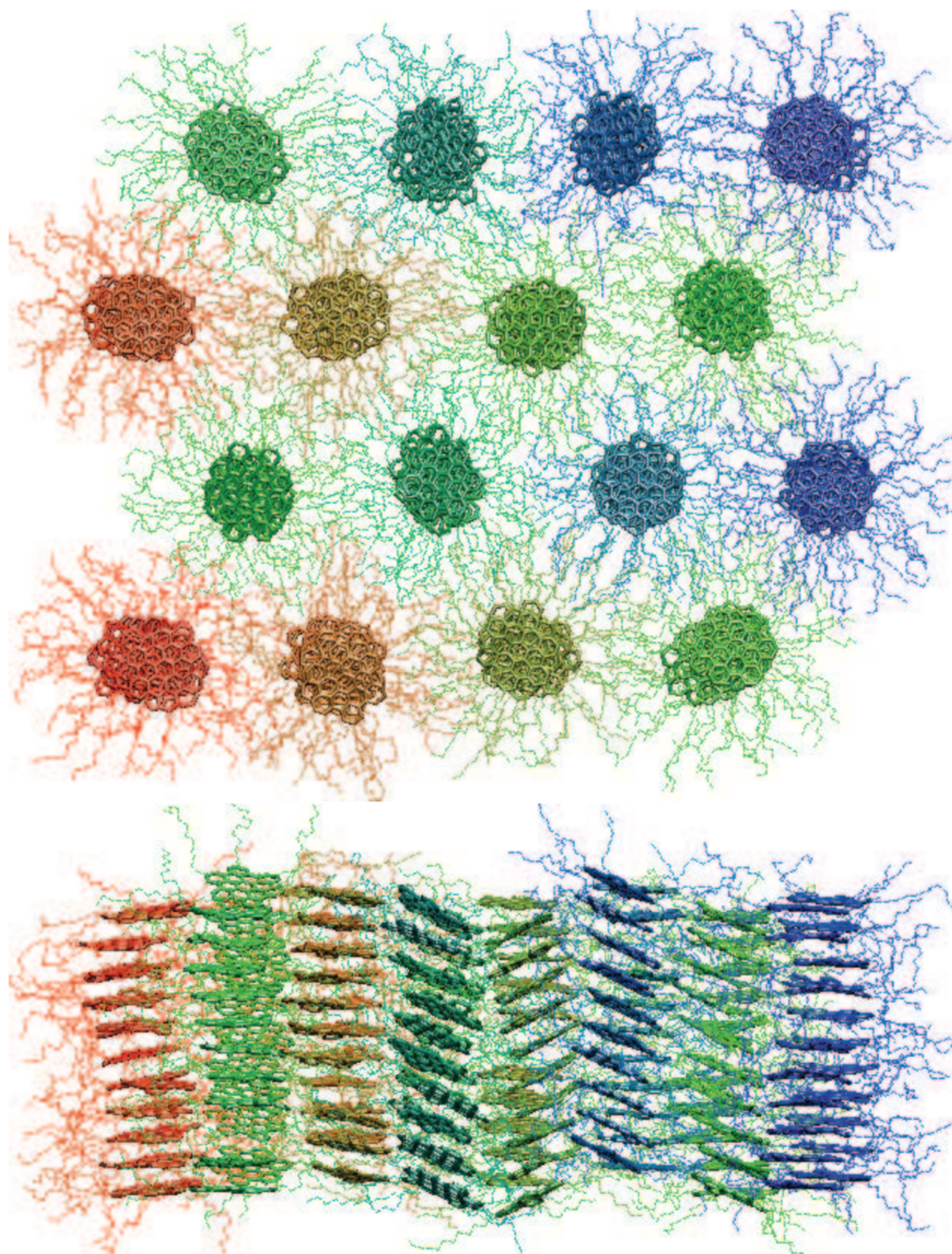
- [1] G. Cinacchi, R. Cole, and A. Tani. Atomistic molecular dynamics simulations of Hexakis(pentyloxy)triphenylene: Structure and translational dynamics of its columnar state *J. Phys. Chem. B* 108, 7969-7977, 2004.
- [2] A. Fechtenkötter, K. Saalwächter, M. A. Harbison, K. Müllen, H. W. Spiess *Angewandte Chemie-International Edition*, 38, 3039, 1999.
- [3] I. Fischbach, T. Pakula, P. Minkin, A. Fechtenkötter, K. Müllen, H. W. Spiess, K. Saalwächter *Journal Of Physical Chemistry B*, 106, 6408, 2002.
- [4] P. Herwig, C. W. Kayser, K. Müllen, H. W. Spiess *Adv. Mater.*, 8, 510, 1996.

## Results

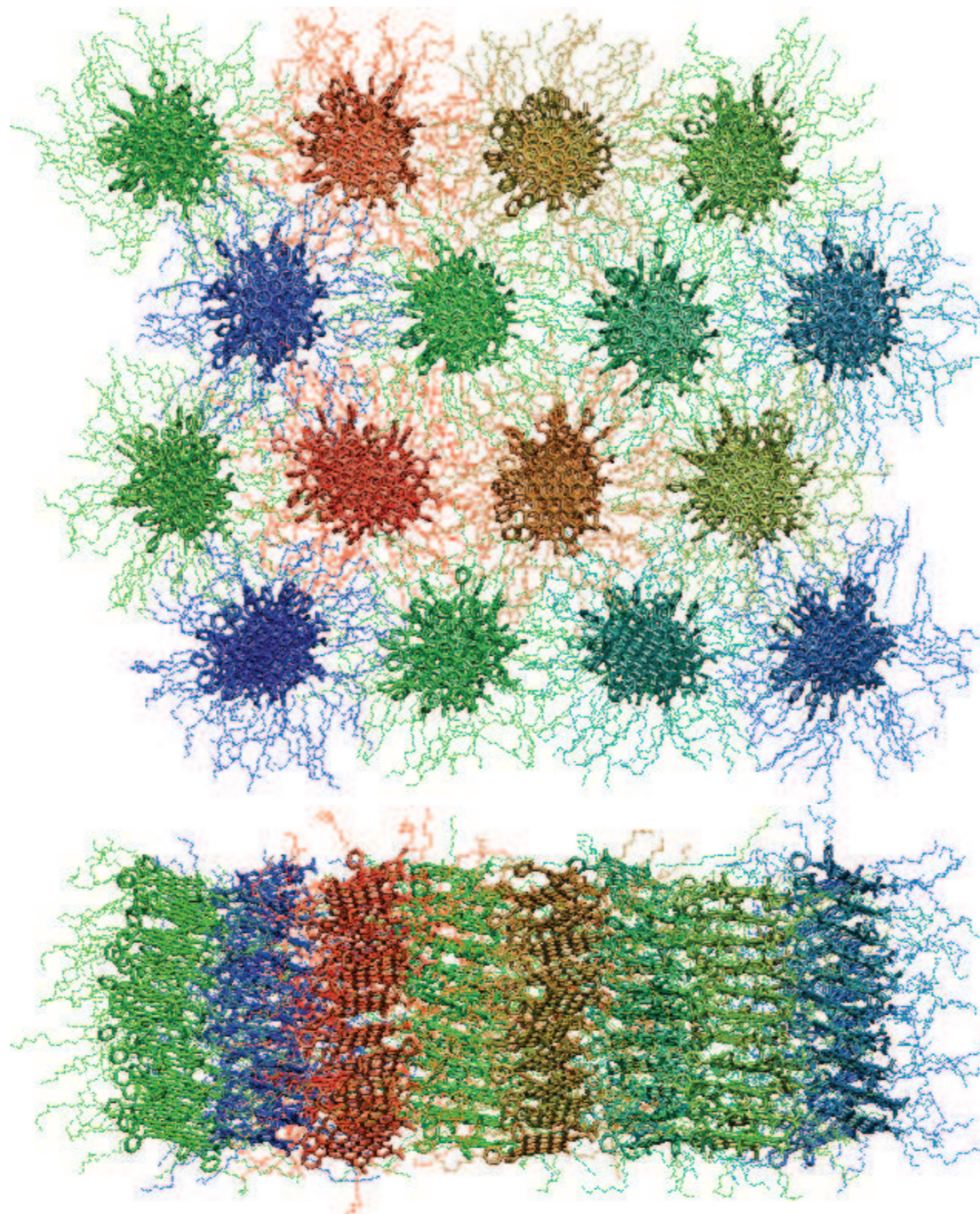
Snapshots of the systems with different lengths of the side chains (top and side views).



R = C10-6.



R = C12.



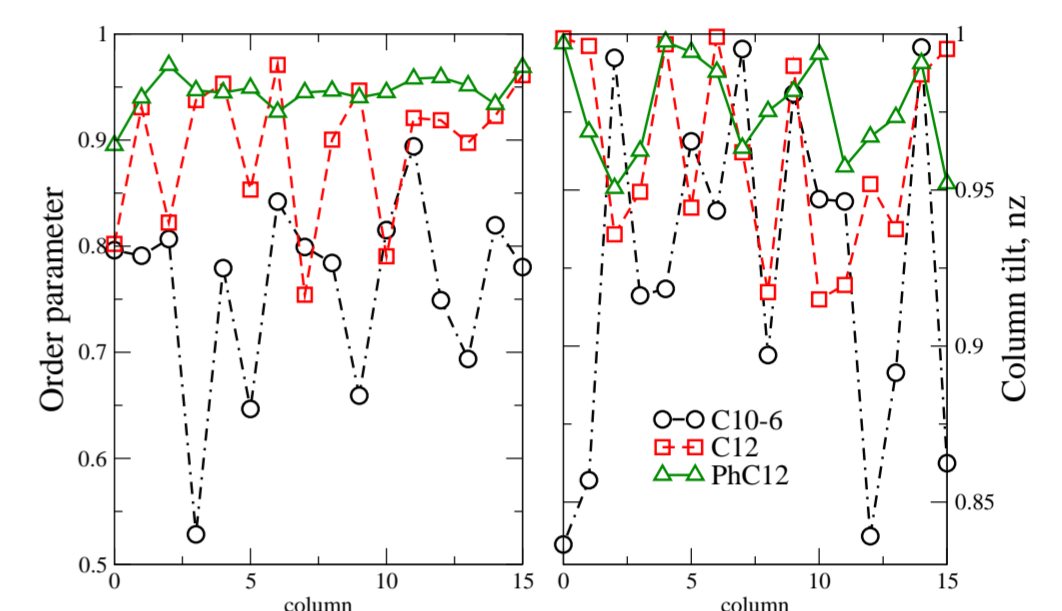
R = PhC12.

## Oriental 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 aromatic core. 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

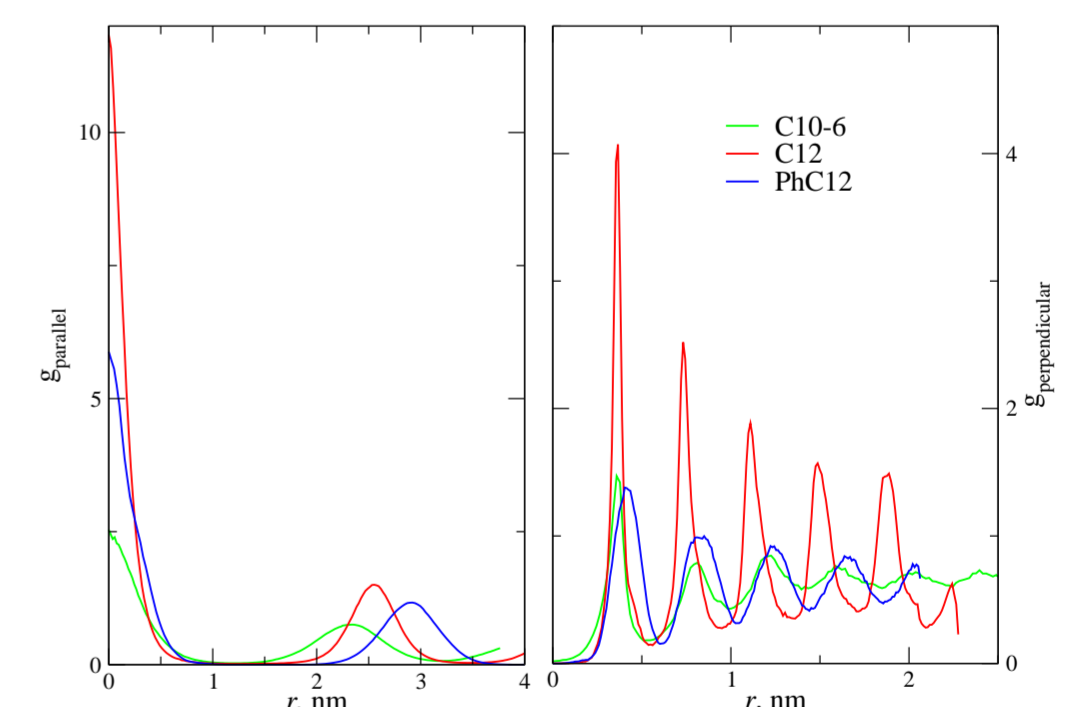
Two types of correlation functions are important for columnar mesophase of discotic liquid crystals

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

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  $g_{\perp}$ .

## Summary

		C10-6	C12	PhC12
$\rho, g \text{ cm}^{-3}$	300K	—	1.06	1.09
	400K	1.00	1.03	1.06
$d, \text{nm}, 400K, C_h$	exp	—	2.52[4] 2.86[3]	3.4[3]
	sym	2.33	2.56	2.91
$d, \text{nm}, 300K, K_1$	exp	—	2.05	—
	sym	—	—	—
$h, \text{nm}, 400K$	exp	—	0.355[2, 4]	0.35[2]
	sym	0.34	0.36	0.41
$S, 400K$	exp	—	0.78 [2] 0.84 [4]	0.93 [2]
	sym	0.76	0.89	0.95

## Acknowledgments

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