



HAL
open science

Simulation of SAXS patterns of hexa-n-alkoxy-2,3,6,7,10,11-triphenylene mesophase

Franck Camerel, Olivier Jeannin, F Barriere

► **To cite this version:**

Franck Camerel, Olivier Jeannin, F Barriere. Simulation of SAXS patterns of hexa-n-alkoxy-2,3,6,7,10,11-triphenylene mesophase. *Liquid Crystals*, 2018, 45 (5), pp.698-702. <10.1080/02678292.2017.1376124>. <hal-01771090>

HAL Id: hal-01771090

<https://univ-rennes.hal.science/hal-01771090v1>

Submitted on 27 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Simulation of SAXS patterns of hexa-*n*-alkoxy-2,3,6,7,10,11-triphenylene mesophase

Franck Camerel,* Olivier Jeannin and Frédéric Barrière.

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France.

Corresponding author: franck.camerel@univ-rennes1.fr

Abstract.

Small angle X-ray scattering (SAXS) experiments and molecular dynamic modeling of the mesomorphic organization of hexa-*n*-pentoxy-2,3,6,7,10,11-triphenylene are reported. Simulated SAXS patterns extracted from molecular dynamic simulations account for the fact that, despite a perfect organization of the columns in a 2D hexagonal array, in most case, small SAXS patterns show only the fundamental diffraction peak with a limited number of higher order reflections.

Keywords

Triphenylene, liquid crystal, supramolecular organization, molecular dynamics, SAXS

Introduction.

Discotic liquid crystals (DLCs) formation is due to the self-organization of the disc-shaped molecules with orientational order and potentially positional order.^{1,2,3,4,5} The less ordered mesophase having only orientational order is the nematic (N_D) phase. More ordered columnar (Col) mesophases can be obtained when columns formed by the stacking of the discs self-organize into 2D lattices: hexagonal lattice (Col_h), rectangular lattice (Col_r), and oblique lattice (Col_{ob}). The columnar phase of hexagonal symmetry is certainly the most frequently encountered phase with disc-like molecules. DLCs engineered from disc-shaped molecules are particularly attractive owing to their extraordinary unidirectional electrons and excitons migration property along the column main-axis.^{6,7,8,9} Combined to luminescence properties, this class of liquid crystals is particularly appealing for applications in organic light emitting diodes, photovoltaic solar cells and organic field effect transistors.^{1,10,11}

Among the family of discotic molecules, triphenylene derivatives are archetypical of DLCs since they possess large π -conjugated system with high symmetry, they can be easily functionalized and display excellent photoelectric properties.¹² For example, hexa-alkoxytriphenylene compounds with linear alkyl chains from C4 to C11 are the most studied triphenylene-based discotic liquid crystals and usually form columnar mesophases of hexagonal symmetry (Col_h).¹ This assignment was based on polarized optical microscopy observations and on small angle X-ray scattering (SAXS) experiments. Levelut reported the first diffraction pattern of a single domain of hexa-*n*-pentoxy-2,3,6,7,10,11-triphenylene (HAT) compound with the incident beam parallel to columnar axis.¹³ The diffraction pattern clearly showed both the (10) and the (11) sharp diffraction peaks characteristic of a phase with hexagonal symmetry. The intensity of the higher order peaks was weaker but still visible on the original pattern. However, in many literature reports, the SAXS experiments performed on HAT show one strong diffraction peak in the small angle region with a limited number of very weak higher order reflections.^{14,15,16} To be safely assign as a columnar phase of hexagonal symmetry, the

SAXS pattern should display at least the (11) reflection ($d_{(11)} = d_{(10)}/\sqrt{3}$) in addition to the fundamental (10) reflection. For this compound as for many other purely organic liquid crystals, the higher order reflection peaks are weak and may be difficult or impossible to observe in an informative powder diffraction pattern. Thus, with diffraction patterns displaying only the fundamental diffraction peak, one cannot establish with confidence the symmetry of the mesophase. Molecular dynamics is a powerful tool which has often been used to compute the molecular organization of liquid crystalline phases and in some cases, SAXS patterns have been simulated and compared to the experimental one to further support the proposed molecular model.^{17,18,19}

In the present letter, we show that molecular dynamic calculations can assist the proper assignment the phase symmetry, especially when the SAXS pattern display a limited number of reflection peaks.

Results and discussion.

hexa-*n*-pentoxy-2,3,6,7,10,11-triphenylene was prepared by the direct alkylation of the hexahydroxy-2,3,6,7,10,11-triphenylene with a large excess of bromopentane (10 eq.) in dimethylformamide in presence of K_2CO_3 (12 eq.). After heating at 100 °C for 3 days, the compound was purified by column chromatography on silica gel using a solvent gradient from pure petroleum ether to pure dichloromethane. The purity of the compound was confirmed by 1H NMR spectroscopy (Figure S1), microanalyses (see supporting information) and differential scanning calorimetry (DSC) analyses. The DSC traces of the compound show two transitions on the heating curves centered at 67.4 °C and at 123.1 °C (Figure S2). DSC observation confirmed that the first transition is associated to the melting of the crystalline phase into the liquid crystalline phase and the high temperature transition to the melting of the compound into the isotropic liquid. These two transitions are fully reversible but a strong super-cooling effect is observed on the low temperature transition associated with the crystallization of the compound. The transition temperatures measured by DSC are in good accordance with those reported previously.^{1,20}

The temperature-dependent SAXS patterns of the hexa-*n*-pentoxy-2,3,6,7,10,11-triphenylene compound were recorded using a FR591 Bruker AXS rotating anode X-ray generator operated at 40 kV and 40 mA with monochromatic $Cu\ K\alpha$ radiation ($\lambda = 1.541\text{ \AA}$) and point collimation. The samples were held in Lindemann glass capillaries (1 mm diameter) inserted in a Linkam hot-stage. The X-ray diffraction patterns were collected with a Mar345 image plate detector (Marresearch, Norderstedt, Germany). The SAXS patterns obtained on the liquid crystal phase between 70 and 110 °C on heating display only a strong and sharp peak in the small angle region corresponding to an inter-reticular distance of 17.5 Å ($2\theta = 5.1^\circ$) (Figure 1 and Figure S3) together with a weak reflections at 6.6 Å (13.4°). These two reflections can be indexed as the (10) and (21) ($d_{(21)} = d_{(10)}/\sqrt{7}$) reflections of a 2D array of hexagonal symmetry, as expected. However, the higher order reflection peak is very weak and the (11) and (20) reflections are completely absent. In the wide angle region, a broad halo centered at 4.5 Å ($2\theta \sim 19.5^\circ$), associated to the mean distance between the alkyl chains in a molten state, confirms the liquid crystalline nature of the phase. An additional marked peak centered at 3.6 Å ($2\theta \sim 25.0^\circ$), is also observed and is attributed to the stacking distance between the triphenylene fragments along the column axis. Upon temperature changes, the peak position in the small angle region is little affected. In the isotropic phase, the diffraction patterns display only two broad halos at 16.5 and 4.0 Å whereas in the crystalline phase several sharp peaks are observed in the small and wide angle regions (Figure S3).

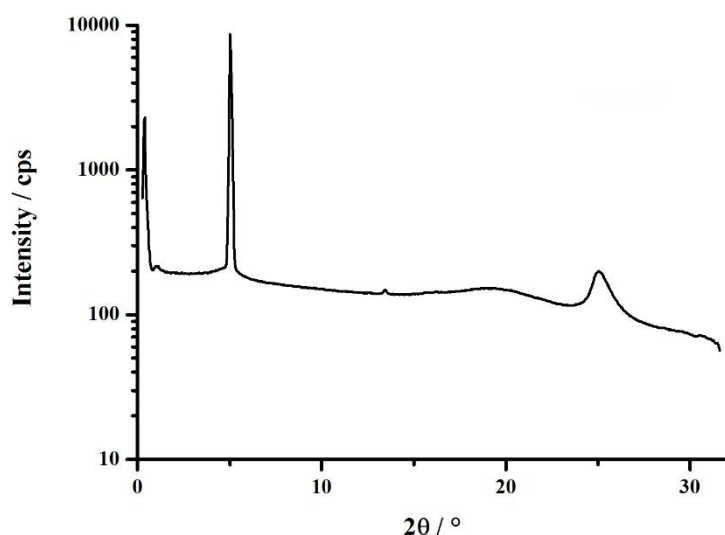


Figure 1. SAXS pattern of hexa-n-pentoxy-2,3,6,7,10,11-triphenylene at 70 °C.

As stated, higher order reflection peaks can easily be absent on the diffraction pattern. With only one peak in the small angle region, the exact nature of the mesophase can hardly be assigned. Thus, in order to gain more insight on the molecular organization at the origin of such a diffraction pattern, molecular dynamic simulations were carried out at 343 K (70 °C). The molecular mechanics studies have been performed on the French supercomputer Occigen using the program suite Materials Studio (Forcite). A starting periodic structure of 96 cells of hexagonal symmetry, each cell containing one molecule, was built according to the cell parameters given by the X-ray measurements ($a_{\text{hex}} = 2d/\sqrt{3} = 20 \text{ \AA}$ and a stacking distance of 3.5 Å, density 1.02). The starting molecular box was built by duplication of an hexagonal unit cell containing one molecule in the three-dimensional space ($ax4, bx4, cx6$). The size of the box is 80x80x21 Å with $\gamma = 120^\circ$ (Figure 2a). The SAXS pattern simulated directly from this starting hexagonal configuration using the Forcite analysis module ($K_\alpha\text{Cu}$, 2θ range = 0.4-32 °, cutoff = 100 Å, radius for the model size correction = 20 Å) displays four strong and sharp peaks in the small angle region at 5.1, 8.85, 10.25, 13.5 ° which can unambiguously be indexed as the (10), (11), (20) and (21) reflections of a 2D hexagonal lattice (Figure 2b). The peak positions are those expected for a columnar phase of hexagonal symmetry with a lattice parameter of 20 Å (inter-column distance). Several less intense sharp peaks are also observed around 25-30 ° arising from the crystalline nature of the starting structure. SAXS pattern were simulated using the Scattering properties on the Forcite analysis dialog. When calculating the scattering intensity, all contributions from pair separations greater than the cutoff value are ignored and the model size correction compensates for scattering resulting from the finite size of the molecule and is especially useful for small nonperiodic structures.

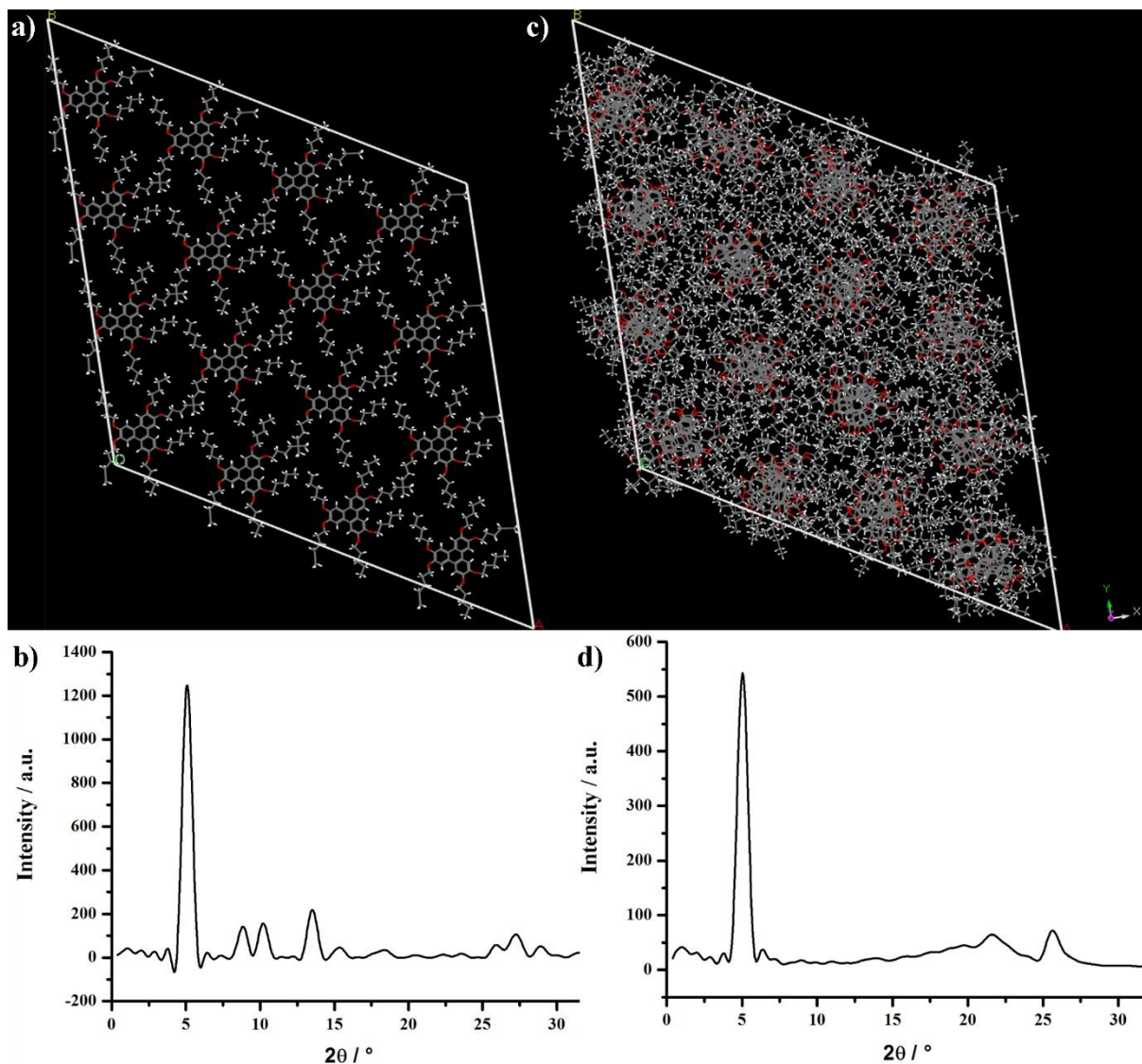


Figure 2. (a) Starting crystalline hexagonal configuration of 96 unit cells ($a = 20 \text{ \AA}$, $b = 20 \text{ \AA}$, $c = 3.5 \text{ \AA}$, $\gamma = 120^\circ$) containing one molecule each; (b) simulated SAXS pattern of the starting configuration; (c) molecular configuration after energy relaxation and 1 ns simulation in NPT ensemble (fixed Number of molecules, Pressure and Temperature); (d) Simulated SAXS pattern obtained after simulation.

After energy relaxation, the simulation consisted of a 1 ns isotherm at 70°C with the universal force field (NPT ensemble, 1 fs time step) under periodic boundary conditions (Figure 2c). Along the simulation, the cell parameters slightly evolved from 80 to 80.49 \AA and from 21 to 21.13 \AA and the density converged from 1.02 to 1.00. As can be seen after simulation, the carbon chains perfectly fill the space around stacks of triphenylene molecules (Figure 2c). The diffraction pattern obtained after the molecular dynamic simulation strongly resembles that obtained by X-ray diffraction at 70°C (Figure 2d). In the small angle region, only one diffraction peak is observed at $2\theta = 5.05^\circ$ ($d = 17.5 \text{ \AA}$), representative of the mean distance between the column. The higher order reflections characteristic of the hexagonal organization originally at 8.85, 10.25, 13.5 $^\circ$ have completely vanished. In the wide angle region, the broad halo associated to the mean distance between the carbon in a molten state is clearly observed at $2\theta = 21.6^\circ$ ($d = 4.6 \text{ \AA}$) as well as the

diffraction peak at 25.65° ($d = 3.5 \text{ \AA}$) associated with the stacking distance of the triphenylene core along the columns.

The width of the simulated 100 reflection peak after molecular dynamic simulations remains almost unchanged (Figs 2b and 2d). The coherence length determined using the Scherrer equation²¹ was found around 115 \AA on the simulated diffraction patterns which is smaller than the coherence length found experimentally around 730 \AA . Sharp peaks imply long range order, while short range order broadens diffraction peaks. Simulations have also been performed on a larger ensemble of $8 \times 8 \times 12$ molecules but the peak width is not affected by the size of the box (Figure S4). After simulation, the higher order reflections have completely vanished. This is due to the melted nature of the tails, which make the electron density profile of a single molecule very smooth, in turn resulting in few higher order Fourier components. On the contrary, the starting artificial hexagonal periodic model, full of holes, presents a rugged electron density function, needing many Fourier terms and hence many reflections. Once subjected to molecular dynamics annealing, the electron density has smeared out, resembling that in a real liquid crystal. The fact that no higher order reflections are observed in the Fourier transform of the simulated structure at the 5% level is consistent with the low intensity of (21) peak in the SAXS pattern (about 1% of the (10) peak intensity). This indicates that the molecular dynamic simulations results correctly simulate the local structure. The concentration profiles along the [100], [010] and [110] directions, showing that the structure become homogenous after simulation, are presented in supporting information (Figure S5-S7).

Similar results have been obtained with NVT ensemble (fixed Number of molecules, Volume and Temperature). The main difference is that the cell parameters and the density remain constant all along the simulation. The simulation also confirmed the stability of the molecular stacking at 3.5 \AA and that the molten chains are in the plane of the central disc as already proposed for *diabolo* like molecules.²⁰ Indeed, the simulation clearly shows that the alkyl chains perfectly fill the space in between the columnar stack of triphenylene cores (density = 1.00 after simulation) in the plane of the central disc. Consequently, the hypothesis of a tubular arrangement of *octopus* molecules²⁰ in which the alkyl chains are perpendicular to the central disc can be ruled out for the hexa-n-pentoxo-2,3,6,7,10,11-triphenylene compound. It can also be noticed that the centroid of the triphenylene cores is not perfectly aligned along the c direction and that the triphenylene fragments can rotate and slightly shift from one another ($\sim 3\text{-}4 \text{ \AA}$) giving rise to undulated columns running along the c axis.

Molecular mechanics studies have also been performed starting from periodic box of 96 cells of square symmetry with a cell parameter of $a = 17.5 \text{ \AA}$ ($ax4, ax4, cx6; \alpha=\beta=\gamma = 90^\circ$) (Figure S8a). After simulation in the NPT ensemble for 1 ns at 70°C , a slight elongation of the unit cell parameter was observed with an increase of the a and b parameters from 17.5 \AA to 18.4 \AA as the density decrease from 1.15 to 0.99 (Figure S8b and S9). The simulated SAXS patterns now displays one diffraction peak at $2\theta = 4.8^\circ$ far away from the one observed experimentally ($2\theta = 5.1^\circ$) and the one simulated for the hexagonal lattice ($2\theta = 5.05^\circ$) (Figure S10). Molecular dynamic simulations thus allow to rule out the formation of a phase of square symmetry and further support the formation of a phase of hexagonal symmetry.

Conclusion.

The molecular dynamic simulations explain the SAXS pattern of HAT, displaying mainly one fundamental reflection peak with higher order reflections being hardly visible. These simulations also support the long range organization of fluctuating columns of stacked HAT molecules in a 2D array of hexagonal symmetry. Such molecular dynamic simulations can be useful for the study of other liquid

crystalline systems, especially when a limited number of reflections detected on the SAXS pattern preclude the unambiguous assignment of the molecular arrangement symmetry in the mesophase.

Acknowledgements

Fredrick Kinloch is gratefully acknowledged for help in the synthesis of the hexa-n-pentoxy-2,3,6,7,10,11-triphenylene compound. The authors thank Dr. Philippe Méléard (Ecole Nationale Supérieure de Chimie de Rennes) for help with the SAXS measurements and Dr. Aziz Ghoufi (Institut de Physique de Rennes) for fruitful discussions. This work was granted access to the high performance computing resources of CINES (Montpellier, France) under allocation 2017-A0020805032 awarded by GENCI.

¹ Wöhrle T, Wurzbach I, Kirres J, Kostidou A, Kapernaum N, Litterscheidt J, Haenle JC, Staffeld P, Baro A, Giesselmann F, Laschat S. *Discotic Liquid Crystals*. *Chem Rev*. 2016;116:1139–1241.

² Kumar S, *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers*. CRC Press, Boca Raton, USA, 2011.

³ Setia S, Sidiq S, De J, Pani I, Pal SK. Applications of liquid crystals in biosensing and organic light-emitting devices: future aspects. *Liq Cryst*. 2016;43(13-15):2009-2050.

⁴ Gupta RK, Manjuladevi V, Karthik C, Choudhary K. Thin films of discotic liquid crystals and their applications. *Liq Cryst*. 2016;43(13-15):2079-2091.

⁵ Said SM, Mahmood MS, Daud MN, Mohd Sabri MF, Sairi NA. Structure–electronics relations of discotic liquid crystals from a molecular modelling perspective. *Liq Cryst*. 2016;43(13-15):2092-2113.

⁶ Adam D, Schuhmacher P, Simmerer J, Häussling L, Siemensmeyer K, Etzbacher KH, Ringsdorf H, Haarer D. Fast Photoconduction in the Highly Ordered Columnar Phase of a Discotic Liquid Crystal. *Nature*. 1994;371:141-143.

⁷ Cornil J, Lemaire V, Calbert J-P, Brédas J-L. Charge Transport in Discotic Liquid Crystals: A Molecular Scale Description. *Adv Mater*. 2002;14:726-729.

⁸ Boden N, Bushby RJ, Clements J, Movaghar B. Device Applications of Charge Transport in Discotic Liquid Crystals. *J Mater Chem*. 1999;9:2081-2086.

⁹ Lemaire V, da Silva Filho DA, Coropceanu V, Lehmann M, Geerts Y, Piris J, Debije MG, van de Craats AM, Senthilkumar K, Siebbeles LDA, Warman JM, Brédas J-L, Cornil J. Charge Transport Properties in Discotic Liquid Crystals: A Quantum-Chemical Insight into Structure–Property Relationships. *J Am Chem Soc*. 2004;126:3271-3279.

¹⁰ O'Neill, M, Kelly SM. Liquid Crystals for Charge Transport, Luminescence, and Photonics. *Adv Mater*. 2003;15:1135-1146.

¹¹ Laschat S, Baro A, Steinke N, Giesselmann F, Hägele C, Scalia G, Judele R, Kapatsina E, Sauer S, Schreivogel A, Tosoni M. Discotic Liquid Crystals: from Tailor-Made Synthesis to Plastic Electronics. *Angew Chem Int Ed*. 2007;46:4832-4887.

¹² Kumar S. Recent Developments in the Chemistry of Triphenylene-Based Discotic Liquid Crystals. *Liq Cryst*. 2004;31:1037–1059.

¹³ Levelut AM. Structure of a Disk-Like Mesophase. *J Physique Lett*. 1979;40:81-84.

¹⁴ Kumar M, Kumar S. Stacking of Ultra-Thin Reduced Graphene Oxide Nanoparticles in Supramolecular Structures for Optoelectronic Applications. *RSC Advances*. 2015;5:14871-14878.

¹⁵ Terasawa N, Monobe H, Kiyohara K. Mesomorphic Phase Transition Behavior of Novel Triphenylene Compounds Possessing Fluoroalkylated Side Chains. *J Fluorine Chem*. 2006;127:954-961.

¹⁶ Wang T, Yan D, Zhou E, Karthaus O, Ringsdorf H. Phase Identification of Triphenylene-Based Discotic Monomer and its Main Chain Polymers. *Polymer*. 1998;39:4509-4513.

¹⁷ *Self-Assembling Systems: Theory and Simulation*, Yan L-T (Ed), John Wiley & Sons: Oxford, UK, 2016

¹⁸ Lehmann M, Gloza S, Roth S. At the Limits of Liquid Crystallinity: Stimuli Responsive 3d Columnar Liquid Crystals and Soft Crystals of Supramolecular Anthracene Mesogens. *Chem Mater*. 2015;27:8181–8184.

¹⁹ Camerel F, Ziessel R, Donnio B, Bourgogne C, Guillon D, Schmutz M, Iacovita C, Bucher J-P. Formation of Gels and Liquid-crystals Induced by Pt...Pt Interactions in Luminescent σ -alkynyl Platinum(II) Terpyridine Complexes. *Angew Chem Int Ed.* 2007;46:2659-2662.

²⁰ Destrade C, Mondon MC, Malthete J. Hexasubstituted Triphenylenes: a New Mesomorphic Order. *J Phys Colloques.* 1979;40:C3-17.

²¹ Scherrer P. *Göttinger Nachrichten Gesell.* 1918;2:98-100.