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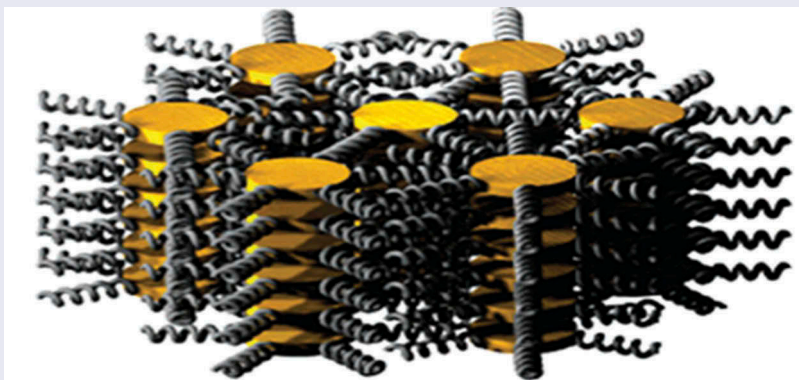
Improving organisation of discotics: annealing, shape, side groups, chirality

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ABSTRACT

Liquid crystals were of premier interest to Zeev Luz. In particular, he studied discotic liquid crystals by NMR spectroscopy in the early 1980s already, very soon after this new class of mesophases was reported in the late 1970s. In these early days, it was hardly imagined that today discotic liquid crystals play a major role in the organisation of columnar systems, which exhibit especially high charge carrier mobility, making them interesting materials for organic electronics. This short commemorative review puts several of Luz' pioneering NMR studies of structure and dynamics of discotic liquid crystals into perspective by relating them to specific current investigations of such supramolecular systems.



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Liquid crystals; discotics; NMR; supramolecular organization; organic electronics

1. Introduction

Zeev Luz clearly was a pioneer in the important field of NMR studies of structure and dynamics of various types of liquid crystals (LCs). At times, where most of the NMR investigations in the field dealt with solutes in liquid crystals [1], he already studied highly viscous smectic LCs in bulk by NMR [2], which was technically much more demanding. In this short commemorative review, I try to honour him by highlighting a few of his landmark papers, whose fundamental results helped us in our research years, or even decades later, in understanding and controlling supramolecular organisation in materials with high charge carrier mobility [3,4], of interest in organic electronics. In our work, NMR spectroscopy also played a central role, because it offers several unique advantages for characterising such systems on the molecular level [5,6], namely,

- Unprecedented site selectivity, via ^1H , ^2H , ^{13}C , ^{15}N NMR due to chemical shifts.
- Structure determination on the molecular level in the range of 0.1–1 nm.
- Elucidation of both, timescale and geometry of rotational motions over a wide range of timescale from ps to 100 s.
- Structure probed by internuclear distances exploiting dipole-dipole couplings.
- Packing probed by additional frequency shifts due to hydrogen bonding or pi-stacking.
- Combination with other techniques, such as scattering, microscopy, dielectric relaxation, quantum chemical calculations.

The corresponding NMR spectra and parameters as well as their analysis have been described in numerous original papers, cited below and in recent reviews [7,8]. Therefore, rather than discussing NMR spectra and parameters here again, we emphasise the findings deduced

from NMR, leaving the details for the interested reader in the original publications and previous reviews.

Also, rather than following the format of an original research paper, the sections of this commemorative review directly follow the topics highlighted in the title, namely annealing, shape of building blocks, side groups, and chirality.

2. Annealing

Columnar systems often exhibit several different phases in the solid with a sequence of phase transitions below the transition temperature to the discotic liquid crystalline phase [9]. Deuteron NMR, combined with X-ray scattering provided important details on the mechanism of these transitions and the molecular order in the discotic mesophase, as shown by Zeev Luz and co-workers [10]. Today, in addition to working with conventional disk-shaped building blocks such as triphenylene and hexabenzocoronene [11], elongated perylene derivatives such as perylene bisdiimide (PBI) units are of interest, because they offer substantial advantages as building blocks being themselves dyes [12]. However, the packing in equilibrium and non-equilibrium phases of such columnar stacks can differ substantially, which can lead to vastly different charge carrier mobility. This was unravelled in detail in PBIs functionalised with dendritic groups [13,14]. As sketched in Figure 1, the dendronised PBIs organise in complex helical columns, composed of tetramers containing two pairs of two molecules each in adjacent strata of the column. Without careful sample preparation, the *intratetramer* (a) and *intertetramer* stacking distances (b) are different, and the charge carrier mobility is only modest. However, by heating above 370 K into the LC phase the packing can be optimised resulting in shorter and more uniform intra – and intertetramer distances leading to much higher charge carrier mobility. This dynamic process was first noticed by NMR

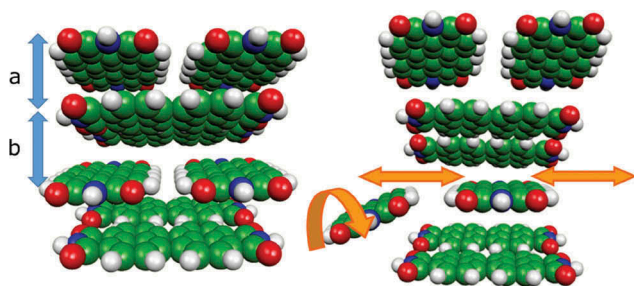


Figure 1. (Colour online) Sketch of the PBI-tetramer packing motif for the supramolecular column (left) and defective stack (right), created by removal of one of the PBI units, which is mandatory for self-healing the stack, Copyright American Chemical Society 2011, reproduced with permission from ref [13].

spectroscopy because it manifests itself in a substantial narrowing of the ^1H NMR lines [13]. Computer simulation showed that this narrowing of the NMR spectra indicates a complex reorganisation mechanism, where the PBI molecules leave the supramolecular column, flip over, and re-enter a column, see Figure 1. Leaving the columns also is a necessary condition for translational diffusion in discotic LCs, which has been elucidated by Zeev Luz and co-workers decades ago [15]. In the PBI systems, this remarkable mobility of the building blocks in the discotic mesophase provides a route to achieve thermodynamic rather than kinetic control of the supramolecular organisation. However, the efficiency of the dynamics in reorganising the columns is rather low, and reorganisation might take as long as hours.

3. Shape of building blocks

In a ground-breaking article [16], Zeev Luz and co-workers showed that columnar mesophases can not only be built from flat units but from rigid pyramidal central cores as well. Hence, they called the resulting columnar LC phase *pyramidic*. The special packing of such non-planar building blocks in columnar stacks can have important consequences for their electronic behaviour. Indeed, dendronised PBI exhibits a particularly interesting aspect of such columnar organisation, namely that a *decrease* in molecular symmetry can result in an *increase* of the columnar stacking order, see Figure 2 [17]. If the flexible linker between the PBI and the dendritic group is missing, the packing of the flat PBI molecules is rather poor, with intermolecular packing distances, as long as 0.48 nm. By introducing halogens at the bay positions of the PBI, the molecule becomes twisted, yet the intracolumnar packing significantly improves as the intermolecular packing distance reduces to 0.42 nm. The improved packing manifests itself in a much higher resolution of ^1H - ^1H double-quantum NMR spectra of the chlorinated species in the solid state [17]. More importantly, the high packing results in increased electron acceptor ability of PBI and extended lifetimes of charge carriers [12].

3. Side groups

The side groups attached to the building blocks of discotic LC phases provide the motional freedom and flexibility needed in organising the columnar stacks. Structural disorder in the side groups, e.g., through an ester linkage in triphenylene discotic suppresses crystallisation and creates a glass forming system [18], in which the cooperativity of axial motion of the discs at the glass transition could be studied by two-dimensional ^2H NMR [19]. From a systematic ^2H NMR study of

enantiomers, self-sorting of the enantiomers was observed, see [Figure 4](#).

Again, the mechanism of this rather slow process is of particular interest. In another fundamental paper, Zeev Luz and colleagues have shown that in solution the pyramidal CVT moieties can also exist in an intermediate saddle form, which introduces flexibility into the CVT moiety and provides a route to racemisation [24]. Indeed, solid-state type NMR of these systems in the bulk columnar phase revealed fluctuations of the flexible crown between ‘up’ and ‘down’ conformations as depicted in [Figure 5](#). Thus, on average, the crown can be imagined to behave like a disc, allowing rotation around the column axis and exchange between columns by translational motion as known from discotic liquid crystals [15]. Again, the remarkable possibilities of NMR spectroscopy

enable elucidation of complex dynamics of building blocks in discotic LCs, offering better organisation of the columns.

As well known from natural compounds particularly high order suitable for advanced organic electronics [25] can be achieved, if homochiral building blocks are used. This makes the synthesis of such materials demanding and expensive. In a recent study of PDI with chiral side groups, it was discovered, however, that a double helices being made of a random mix of left- and right-handed building blocks are more highly ordered than that of DNA, [Figure 6](#) [26]. This opens the door for highly crystalline materials, particularly suited for organic electronics, made from a mix of chiral building blocks, which are easy to synthesise and relatively inexpensive. By

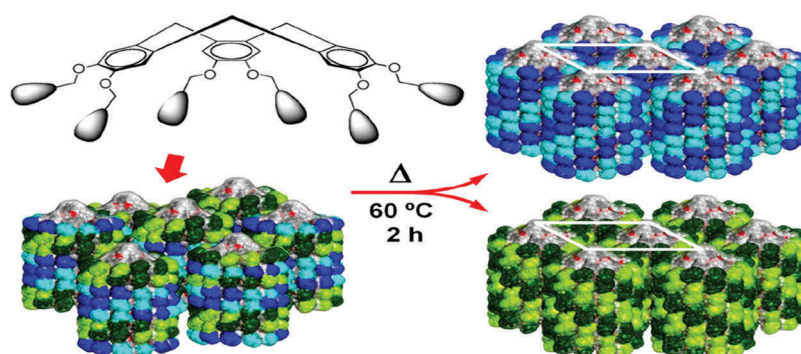


Figure 4. (Colour online) Forming homochiral columns via self-sorting during the supramolecular organisation of hat-shaped molecules. For details see [23]. Copyright 2014 Am. Chem. Soc. reproduced with permission.

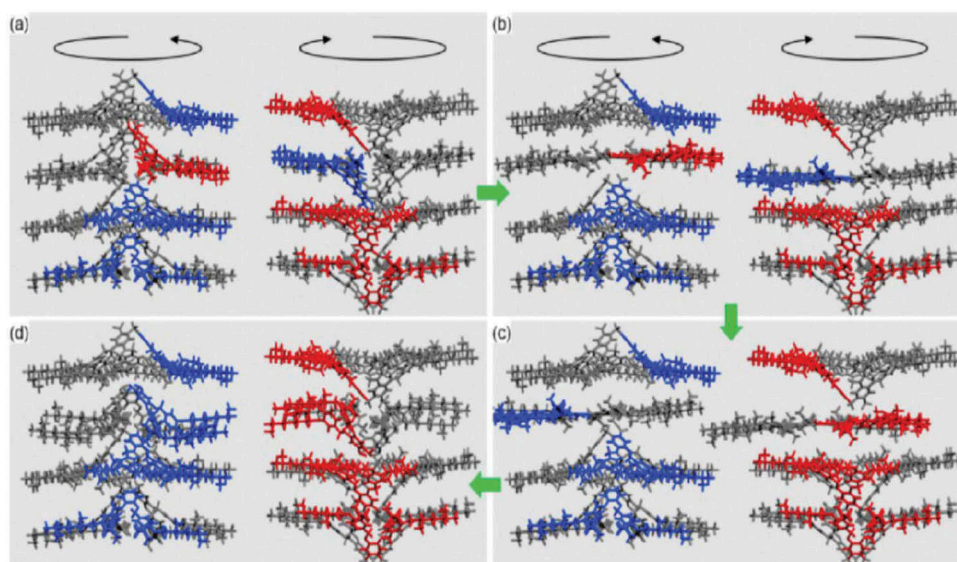


Figure 5. (Colour online) Scheme of self-sorting between enantiomerically different columns of hat-shaped dendronised CTV involving a temporary disc-like conformation through CTV crown inversion [24] allowing translational movement to different columns. Adapted from [23], Copyright American Chemical Society 2014, reproduced with permission.

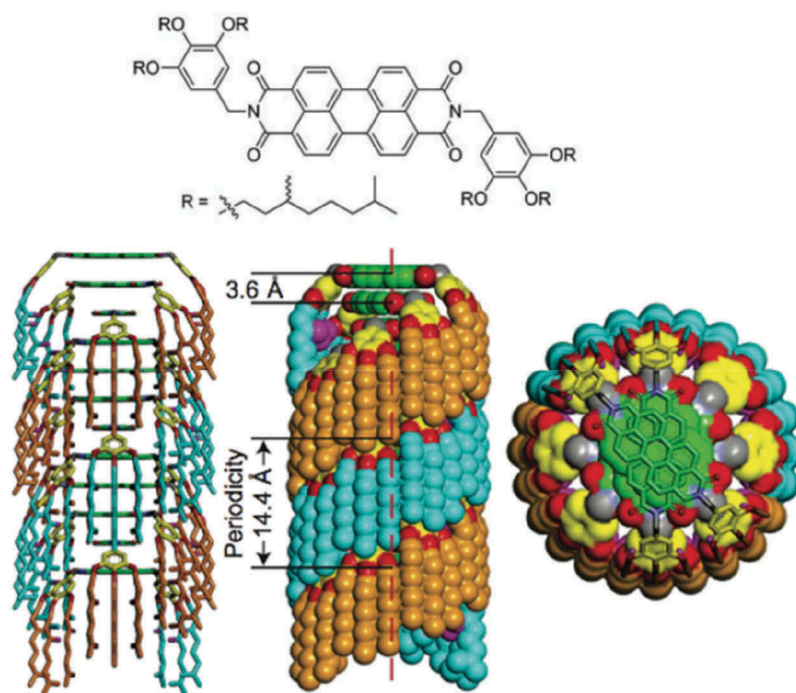


Figure 6. (Colour online) Scheme of supramolecular packing in the highly ordered phase of PDI with chiral side groups in a columnar system, which disregards chirality, adapted from [26], Copyright Nature Publishing Group 2016, reproduced with permission.

solid-state NMR, we were able to show that this high degree of order is facilitated by special conformations of the side groups.

5. Conclusion

The few examples of supramolecular organisation exploiting the columnar order in discotic liquid crystals briefly discussed here demonstrate how important basic studies of structure and dynamics of the building blocks and their phase behaviour are to enable controlled production of materials, of interest in the rapidly growing field of organic electronics [27]. Clearly, Zeev Luz was a pioneer, who developed highly valuable NMR techniques for liquid crystals, being interested in basic science questions, which today prove to be highly valuable in materials science. I feel privileged that I collaborated with him for many years and can call him one of my very close friends in science. Moreover, Zeev was a brilliant teacher and a very modest man, always willing to help young colleagues. His impact was thus even much higher than through his own work alone.

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Disclosure statement

No potential conflict of interest was reported by the author.

References

- [1] Saupe A, Englert G. High-resolution nuclear magnetic resonance spectra of oriented molecules. *Phys Rev Lett.* **1963**;11(10):462–464.
- [2] Luz Z, Meiboom S. NMR studies of smectic liquid crystals. *J Chem Phys.* **1973**;59(1):275–295.
- [3] Schmidt-Mende L, Fechtenkötter A, Mullen K, et al. Self-organized discotic liquid crystals for high-efficiency organic photovoltaics. *Science.* **2001**;293(5532):1119–1122.
- [4] Percec V, Glodde M, Bera TK, et al. Self-organization of supramolecular helical dendrimers into complex electronic materials. *Nature.* **2002**;419:384–387. PubMed PMID: WOS:000178195400042.
- [5] Schmidt-Rohr K, Spiess HW. *Multidimensional solid-state NMR and polymers.* London: Academic Press; **1994**.
- [6] Spiess HW. 50th anniversary perspective: the importance of NMR spectroscopy to macromolecular science. *Macromolecules.* **2017**;50(5):1761–1777. PubMed PMID: WOS:000396639100001.
- [7] Hansen MR, Graf R, Spiess HW. Solid-state NMR in macromolecular systems: insights on how molecular entities move. *Acc Chem Res.* **2013**;46:1996–2007. PubMed PMID: WOS:000330017600010.
- [8] Hansen MR, Graf R, Spiess HW. Interplay of structure and dynamics in functional macromolecular and supramolecular systems as revealed by magnetic resonance

- spectroscopy. *Chem Rev.* **2016**;116:1272–1308. PubMed PMID: WOS:000370216000012.
- [9] Sorai M, Tsuji K, Suga H, et al. Studies of disc-like molecules. 1. Heat-capacity of benzene-hexa-normal-hexanoate from 13-K to 393-K. *Mol Cryst Liq Cryst.* **1980**;59(1–2):33–57.
- [10] Goldfarb D, Luz Z, Zimmermann H. A Deuterium NMR-study of the discotic mesophase of hexa-hexyloxytriphenylene. *J Phys.* **1981**;42(9):1303–1311. PubMed PMID: WOS:A1981MD2780013.
- [11] Herwig P, Kayser CW, Mullen K, et al. Columnar mesophases of alkylated hexa-peri-hexabenzocoronenes with remarkably large phase widths. *Adv Mater.* **1996**;8(6):510–&. PubMed PMID: WOS:A1996UX58600012.
- [12] Wurthner F. Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures. *Chem Comm.* **2004**;14:1564–1579. PubMed PMID: WOS:000223241000003.
- [13] Percec V, Hudson SD, Peterca M, et al. Self-repairing complex helical columns generated via kinetically controlled self-assembly of dendronized perylene bisimides. *J Am Chem Soc.* **2011**;133(45):18479–18494. PubMed PMID: WOS:000297381200073.
- [14] Percec V, Sun HJ, Leowanawat P, et al. Transformation from kinetically into thermodynamically controlled self-organization of complex helical columns with 3d periodicity assembled from dendronized perylene bisimides. *J Am Chem Soc.* **2013**;135(10):4129–4148. PubMed PMID: WOS:000316244200055.
- [15] Dong RY, Goldfarb D, Moseley ME, et al. Translational diffusion in discotic mesophases studied by the NMRE pulsed field gradient-method. *J Phys Chem.* **1984**;88(14):3148–3152. PubMed PMID: WOS:A1984SY47300047.
- [16] Zimmermann H, Poupko R, Luz Z, et al. Pyramidal mesophases. *Z Naturforsch Sect A-J Phys Sci.* **1985**;40(2):149–160. PubMed PMID: WOS:A1985AEA4900008.
- [17] Partridge BE, Leowanawat P, Aqad E, et al. Increasing 3D supramolecular order by decreasing molecular order. a comparative study of helical assemblies of dendronized nonchlorinated and tetrachlorinated perylene bisimides. *J Am Chem Soc.* **2015**;137:5210–5224. PubMed PMID: WOS:000353606700056.
- [18] Werth M, Vallerien SU, Spiess HW. Effect of functionalization on glass-formation by Columnar mesophases of substituted triphenylene mesogens. *Liq Cryst.* **1991**;10(6):759–770. PubMed PMID: WOS:A1991GN99000003.
- [19] Leisen J, Werth M, Boeffel C, et al. Molecular dynamics at the glass-transition - one dimensional and two dimensional NMR studies of a glass-forming discotic liquid crystal. *J Chem Phys.* **1992**;97(5):3749–3759. PubMed PMID: WOS:A1992JL37200095.
- [20] Goldfarb D, Luz Z, Zimmermann H. Deuterium magnetic-resonance in the discotic columnar mesophases of hexaalkoxytriphenylenes - The conformation of the aliphatic side-chains. *J Chem Phys.* **1983**;78(12):7065–7072. PubMed PMID: WOS:A1983QS11000005.
- [21] Pisula W, Kastler M, Wasserfallen D, et al. Relation between supramolecular order and charge carrier mobility of branched alkyl hexa-peri-hexabenzocoronenes. *Chem Mater.* **2006**;18(16):3634–3640. PubMed PMID: WOS:000239396900009.
- [22] Samulski ET, Luz Z. On the blue phase of cholesterogenic liquid-crystals - A deuterium NMR-study. *J Chem Phys.* **1980**;73(1):142–147. PubMed PMID: WOS:A1980KB12700020.
- [23] Roche C, Sun HJ, Prendergast ME, et al. Homochiral columns constructed by chiral self-sorting during supramolecular helical organization of hat-shaped molecules. *J Am Chem Soc.* **2014**;136(19):7169–7185. PubMed PMID: WOS:000336078400062.
- [24] Zimmermann H, Tolstoy P, Limbach HH, et al. The saddle form of cyclotrimeratrylene. *J Phys Chem B.* **2004**;108(48):18772–18778. PubMed PMID: WOS:000225417200052.
- [25] Rowan AE, Nolte RJM. Helical molecular programming. *Angew Chem-Int Ed.* **1998**;37(1–2):63–68. PubMed PMID: WOS:000071925600003.
- [26] Roche C, Sun HJ, Leowanawat P, et al. A supramolecular helix that disregards chirality. *Nat Chem.* **2016**;8:80–89. PubMed PMID: WOS:000366675400016.
- [27] Sergeyev S, Pisula W, Geerts YH. Discotic liquid crystals: A new generation of organic semiconductors. *Chem Soc Rev.* **2007**;36(12):1902–1929. PubMed PMID: WOS:000250701000006.