Influence of H-bond on the Supramolecular and Helical Discotic Liquid-crystalline Hexabenzocoronenes Studied by Powder X-ray Diffraction

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In this context, two supramolecular systems were included, whereby synchrotron X-ray diffraction measurements were utilized for the elucidation of intermolecular packing patterns. The two systems, xerogels[1] and molecular swirl liquid crystals, form lamellar and columnar suprastructures respectively.

The xerogels obtained from four different gelators were subjected to study by powder X-ray diffraction (XRD). All four gelators show a characteristic broad reflection peak in the wide-angle region at ~4.0 Å, which corresponds to a typical p-p stacking distance (see Fig. 1). The sharp peak at small angle region indicated that all four gelators have a lamellar structure. The spacing of the lamella is 33.3, 23.6, 26.5, and 33.0 Å for CH_2Cl_2 gels of the four gelators, respectively. Gels prepared from other solvents gave similar XRD patterns and *d* values, suggesting that the molecular packing in aggregates of these gels do not depend on the nature of the solvent. The spacing of the lamella correlates nicely with the calculated width of the molecules with extended side chains. The xerogels appeared to form by lamellar-type packing through hydrogen bonding, π-π stacking, and van der Waals interactions, as shown in Fig. 1.

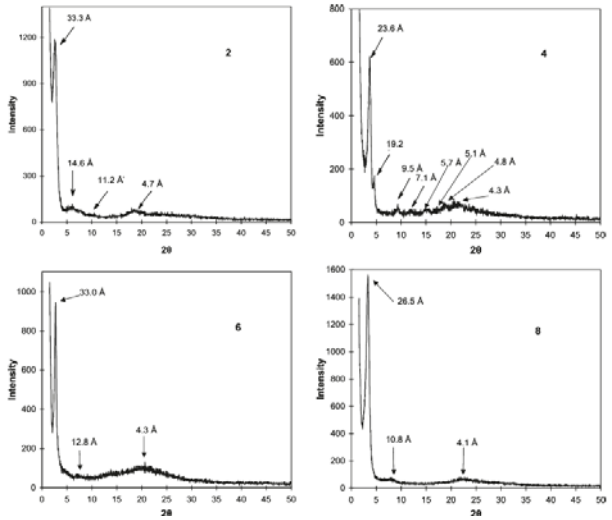

Fig. 1: Powder X-ray diffractograms of xerogels from the four gelators.

The columnar mesophases ofmolecular swirls were probed by X-ray diffraction (XRD) studies and the results are tabulated in Table 1. For all compounds, in addition to the alkoxy halo at ca. 4.5 Å, d_{11} and d_{20} signals were observed, indicative of a rectangular arrangement of columns. The calculated intercolumnar distances, one half of the rectangle diagonal, correspond to in-plane interdisc distances with full inter-digitation of chains. Herein, enhanced intercolumnar VDW interactions assisted by swirl gearing increase upon chain lengthening to maintain full chain inter-digitation. The inter-columnar distances of C12 analogue, 30.7 Å by XRD and 30 Å by STM, are well correlated, indicating the in-plane disc packing patterns in the mesophase to be similar to that in the solid-liquid interface.

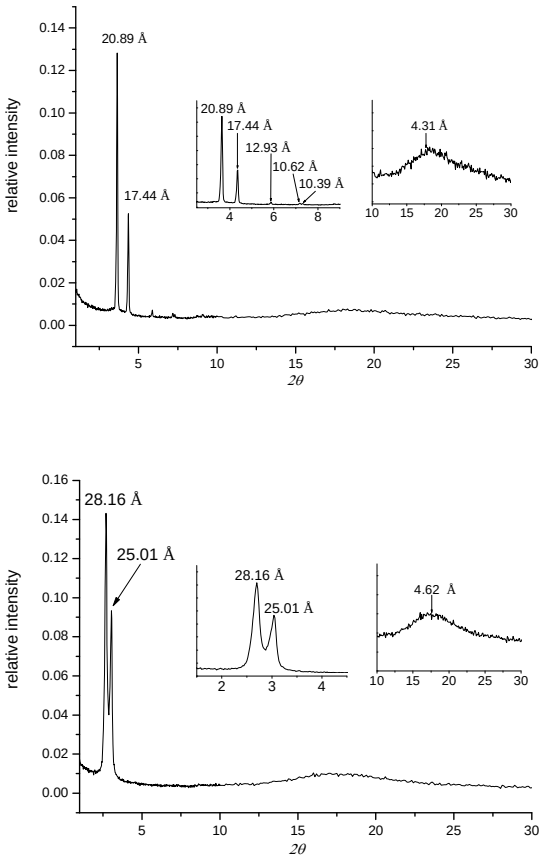

Fig. 2: Powder X-ray diffractograms of molecular swirls with different alkyl chain lengths..

Reference

[1] Y.-T. Shen, C.-H. Li, K.-C. Chang, S.-Y. Chin, H.-A. Lin,Y.-M. Liu, C.-Y. Hung, H.-F. Hsu, and S.-S. Sun, Langmuir **25**, 8714 (2009).