



Novel class of organic chiral zeolites through molecular self-assembly for applications in separation and heterogeneous catalysis

Experiment number:
MA-4140

Beamline: BM26	Date of experiment: from: 14.06.2018 to: 18.06.2018	Date of report: 30.08.2010
Shifts: 12	Local contact(s): Daniel Hermida Merino	<i>Received at ESRF:</i> Denis Anokhin Kseniia Grafkskaia Dimitri Ivanov

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Report:

We report on new approach for fabrication of organic porous material represented by bicontinuous cubic structure from pyridinium salt of wedge-shaped mesogens. The thermodynamically metastable cubic phase is formed after thermal treatment of thin film in saturated methanol vapors. The found structure is stable in temperature range from 25 to 100C because of local ordering of linear alkyl side groups. Stability of dry cubic phase allows to replace methanol in 3D channels by water during swelling in humid atmosphere. The resulting swollen cubic phase shows formation of water channels with radius of 28 Å and water uptake up to 16. The structural models of the material in dry, partially swollen and fully swollen states were proposed. Below room temperature the cubic phase transforms to thermodynamically stable Lam phase because of ultimate swelling in precipitated water. The proposed mechanism of non-covalent stabilization of metastable bicontinuous phase can help in development of new functional materials built via self-assembly process.

Structural evolution of thin film of C8Na and C8Pyr at different temperatures was addressed by GIWAXS technique. On Figure 1 the phase behavior of C8Na compound upon various conditions is presented. For C8Na at room temperature the columnar monoclinic Col_{mon} ($a_{\text{mon}}=50$ Å, $b_{\text{mon}}=55$ Å, $\gamma = 50$) and columnar hexagonal Col_{hd} ($a_{\text{hex}}=61$ Å) phases coexisted in the sample (Fig.1a). Both structures are well-oriented with columns parallel to the film surface (in-plane orientation). Heating of the film to 100C results in transformation of Col_{hd} to Col_{mon} phase (Fig.1b) During cooling to room temperature only columnar monoclinic phase transforms back to hexagonal one with smaller lattice parameter ($a_{\text{hex}}=51$ Å). After cooling to room temperature the material is represented in “dry” state with minimum content of water in in-plane hydrophilic channels (Fig.1c). The presence of the monoclinic phase in the C8Na film before heating indicates non-equilibrium morphology of as-cast sample. The first heating results in reorganization of side groups and evaporation of water and solvent from the film. It is important to mention that highly-oriented hexagonal structure is unreceptive for water vapors. After 30 minutes at 100% humidity no significant changes in film structure were detected (Fig.1d). We suppose that in columnar phase the hydrophilic channels are isolated from each other that limit diffusion of water inside the film. As the result, material can stay in “dry” hexagonal structure at ambient conditions for long time.

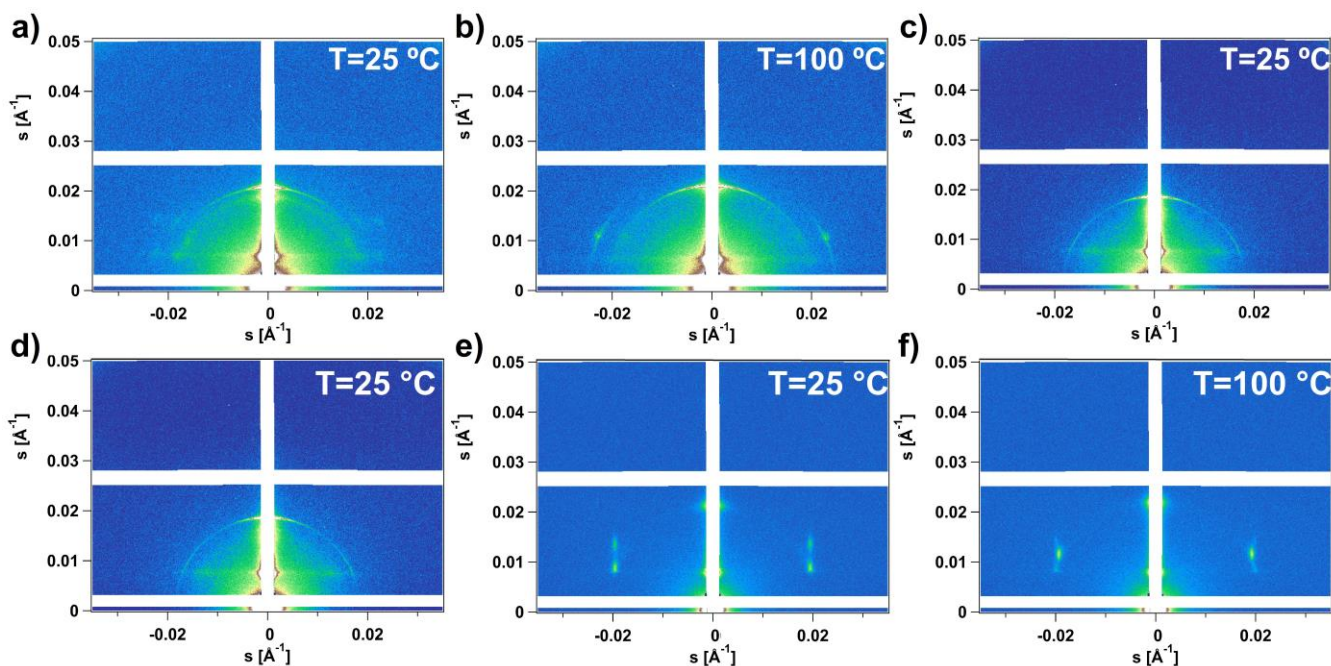


Figure 1. 2D GIWAXS patterns of the C8Na in ambient atmosphere at 25 °C (a), at 100 °C (b), after cooling to 25 °C (c), after swelling under saturated vapors of water at 25 °C (d), methanol at 25 °C (e) and at 100 °C (f).

According to our previous papers, counter-ion of the compounds plays an important role in structure formation and stability [1-3]. The substitution of sodium ion by organic pyridinium one results in changes in phase diagram.

At room temperature the structure of as-received C8Pyr sample is also characterized by mixture of columnar hexagonal Col_{hd} ($a_{\text{hex}} = 58 \text{ \AA}$) and columnar monoclinic Col_{mon} ($a_{\text{mon}} = 54 \text{ \AA}$, $b_{\text{mon}} = 47 \text{ \AA}$, $\gamma=60^{\circ}$) phases (Fig.2a). In contrast to C8Na film, during heating, Col_{mon} phase gradually transforms to Col_{hd} with smaller lattice parameter ($a_{\text{hex}} = 54 \text{ \AA}$) (Fig.2b). The hexagonal phase is indicated on the diffractograms up to isotropization. Consequently, for pyridinium salt the stable phase at 100C is hexagonal. After cooling from 120°C to room temperature the broad peaks of Col_{hd} slowly transform to Col_{mon} which is expected to be thermodynamically stable at room temperature in dry state (Fig.2c). As in the case of sodium salt, saturated humid atmosphere do not stimulate any phase changes (Fig.2d).

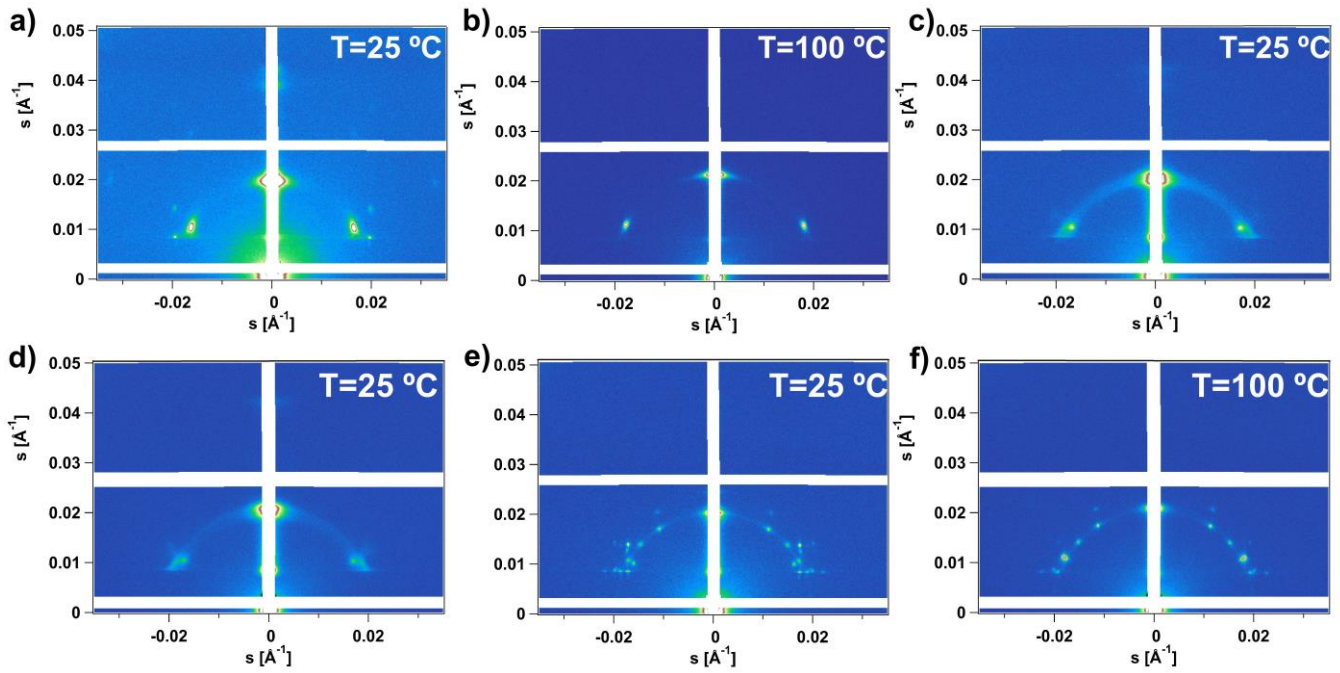


Figure 2. 2D GIWAXS patterns of the C8Pyr in ambient atmosphere at 25 °C (a), at 100 °C (b), after cooling to 25 °C (c), after swelling under saturated vapors of water at 25 °C (d), methanol at 25 °C (e) and at 100 °C (f).

One can see a considerable difference in phase behavior of the studied samples in dry state. Both samples exhibit presence of two columnar phases at room temperature. However, thermal treatment reveals that for sodium and pyridinium salts the thermodynamically stable phases are hexagonal and monoclinic phases, respectively. The difference can be explained by bigger volume of pyridinium ion requiring specific accommodation in hydrophilic channel. Nevertheless, the role of pyridinium counter-ion is not well understood yet and should be investigated further.

As mentioned above, hydrophobic film surface prevents diffusion of water molecules in hydrophilic columnar cores of studied samples. To stimulate swelling, we decrease polarity of solvent that, as expected, can improve affinity of the small molecules to nonpolar alkyl side groups and provide efficient transport of solvent through alkyl-rich regions.

Fig. 2e shows diffractogram of C8Pyr film exposed in saturated methanol vapors in room temperature for 30 minutes. One can observe transition of hexagonal phase to highly-organized Col_{mon} phase ($a_{\text{mon}}=51\text{ \AA}$, $b_{\text{mon}}=57\text{ \AA}$, $\gamma = 56$). The detected phase transition is stimulated by methanol absorbed by the film. The found phase exist in wide temperature range above 100C (Fig.1f). Thus, C8Na film in presence of methanol occurs phase transition from hexagonal to monoclinic phase which earlier was found to stable at high temperature.

If we consider the cubic phase with the smallest lattice parameter $a_{\text{gr}}=12.8\text{ nm}$ as completely dry sample, we can calculate volume fraction of water in swollen cubic phase and estimate diameter of water channel for the films with different thermal history. The volume fraction occupied by water molecules φ_{water} was estimated by the following formula:

$$\varphi_{\text{water}} = \frac{a_{\text{wet}}^3 - a_{\text{dry}}^3}{a_{\text{wet}}^3}$$

where a_{wet} and a_{dry} – lattice parameters of wet and dry samples, respectively. It has been established that φ_{water} accounted for 0.27 for sample exposed in humid atmosphere after cooling from 100C (Fig.3c). According our previous results on wedge-shaped molecules, we assumed that during swelling processes the internal water channels are formed [4-7]. The model of cubic phase presented in Fig. 3 is based on approach which was approved earlier for columnar phases [5]. By this approach, the dry and swollen cubic phase can be considered as two-phase and three-phase systems, respectively. In both cases the interfaces are described

by zero-cavity surfaces according to equation known for gyroid phase. Taking into account the volume fraction of alkyl groups, rigid cores and water, an average water channel radius R_{ch} was found to be 28 Å. This value is slightly bigger of channel radius that we have calculated for Azo-Na compound in Col_{hd} phase - 25 Å [5].

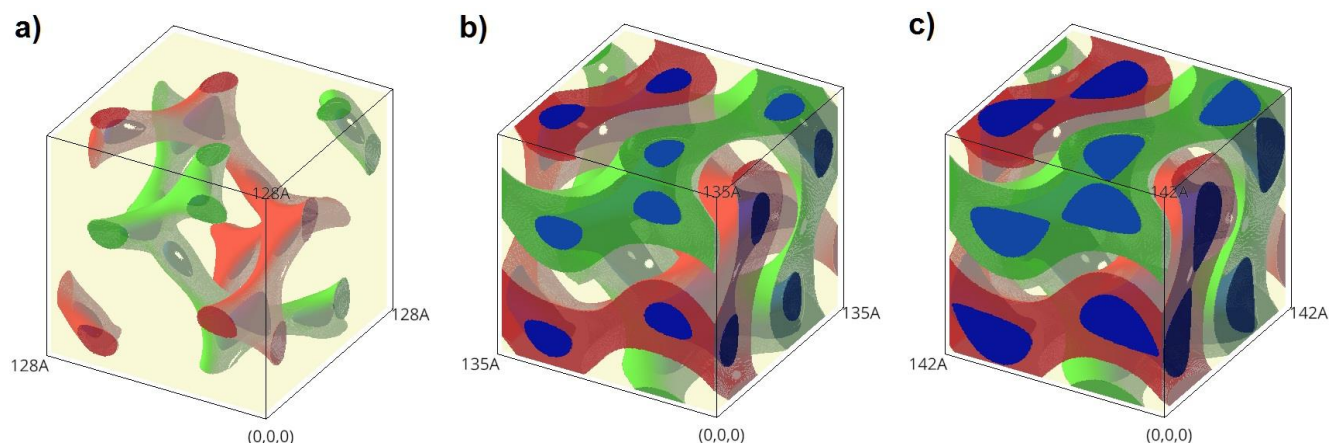


Figure 3. 3D models of hydrophilic channels inside cubic gyroid structure at 25°C: swollen in methanol (a), “dry” state (b) and swollen in water (c). The ion channels are colored in blue, two bicontinuous networks of hydrophilic heads are colored in red and green, respectively. Hydrophobic periphery is colored in yellow.

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