POLAR COLUMNAR PHASES AND SWITCHING CHARACTERISTICS AS STUDIED BY SECOND-HARMONIC GENERATION

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Recently two columnar phases have been reported as polar columnar phases; (1) urea derivatives linearly linked by hydrogen bonding [1] and (2) bent-core polycatenar molecules [2]. Here we report an unambiguous polar switching in the two columnar phases by means of second-harmonic generation (SHG) and its interferometry.

(1) Urea derivatives

The molecule, *N,N*'-bis(3,4,5-trialkoxylphenyl)urea, has a urea unit in the molecular center, forming intermolecular double hydrogen bonding and shows columnar hexagonal (Col_h) and rectangular (Col_r) phases with one-dimensional molecular stacking (Figure 1).

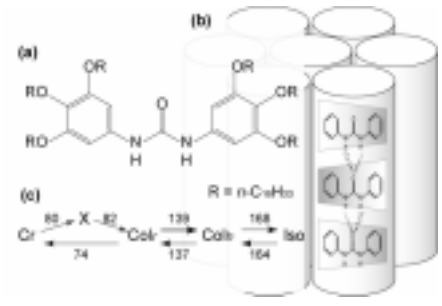

Fig. 1. (a) Chemical structure of a urea derivative, (b) hexagonal structure and (c) phase sequence.

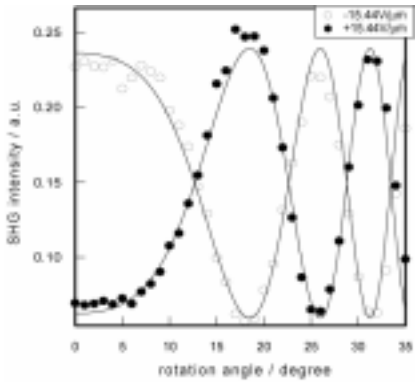

Fig. 2. SHG interferogram under positive and negative electric fields.

These preliminary SHG measurements supply three important informations; (1) a polar order at least of a visible wavelength scale exists only under the application of an electric field, (2) the polar direction is parallel to the columns and (3) fringe structures are clearly observed in the SHG interferometry experiments, and are out of phase under opposite field (Fig. 2), clearly indicating the reversal of the polar direction. Thus, the polar order is formed along the field direction, which coincides with the column axis, by applying an electric field and is reversed when the applied field is reversed. This polar switching brings about a single switching current peak, as reported [1].

(2) Bent-core polycatenars

Another interesting polar column is formed by bent-core polycatenar molecules (Fig. 3) [2]. This molecular system shows Iso-Col_h-Col_{hP}-Col_r phase sequences. A few molecules self-assemble to form an overall disc shape object (Fig. 3). In the Col_h phase the clear dielectric mode suggesting a soft mode was clearly observed [2]. More interestingly, both the Col_h and the Col_{hP} phases are SHG active, under a moderate electric field. The SHG intensity in these phases exhibit a drastic temperature dependence, as shown in Fig. 4, suggesting a soft mode. In the Col_h phase, the disc is more or less of flat shape, showing an umbrella motion. This cooperative motion is the origin of the induced SHG. In the low temperature Col_{hP} phase, SHG activity rapidly decreases with decreasing temperature. This is a consequence of tendency to form a non-polar structure. One of the models is shown in Fig. 3. Alternative model structure(s) will be discussed.

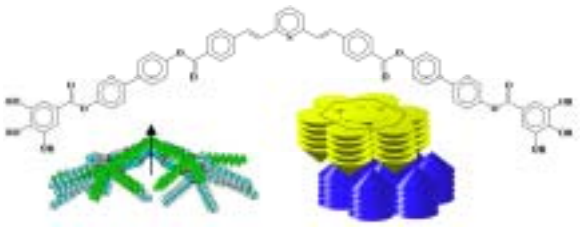

Fig. 3. Chemical structure of a polycatenar molecule, an assembly to form a disc and a model showing non-polar orientation.

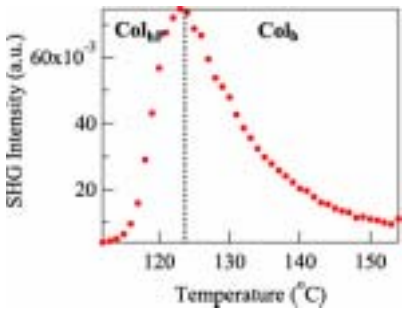

Fig. 4. Temperature dependence of the SHG intensity through the Col_h-Col_{hP} phase transition.

References:

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(2) Gorecka, E.; Pociecha, D.; Mieczkowski, J.; Matraszek, J.; Guillon, D.; Donnio, B. *J. Am. Chem. Soc.* **2004**, *126*, 15946.