Synthesis and dielectric responses of alkylamide-substituted porphyrin derivatives

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【Abstract】Highly photo- and thermostable porphyrin derivatives have been extensively examined from the viewpoints of its unique π-conjugated structure and photoelectric properties, which chemical modifications are relatively easy to achieve. Based on previous studies, the effective intermolecular hydrogen-bonding interactions of –CONHCₙH₂₉+₁ chains can be utilized for the constructions of one-dimensional (1D) π-stacking column to form discotic liquid crystals, 1D nanofibers, and organogels. In liquid crystalline state, the dipole inversion of hydrogen-bonding -CONHCₙH₂₉+₁ chains results in the ferroelectricity. From above point of views, we are aiming to synthesize novel photoelectric and ferroelectric liquid crystalline materials by introducing –CONHC₁₄H₂₉ chains into the porphyrin π-core.

【Introduction】Thermodynamic, optical, and dielectric properties of alkylamide-substituted porphyrin derivative C₁₄TPP are examined, and the liquid crystalline property is observed at the temperature range from 448 to 568 K. In addition, C₁₄TPP shows the fluorescent properties. The temperature-dependent dielectric constants are consistent with the phase transition behavior.

【Experimental】According to the previous methods, TCPP was synthesized, and TPPCOCl was synthesized by using TCPP and SOCl₂ forming acid chloride. The synthesis
of C14TPP was done by the reaction of C14H29NH2 and TPPCOCl in the existence of Et3N in CH2Cl2. The purity of C14TPP was confirmed by NMR and IR spectra. Thermodynamic response, dielectric properties, phase transfer, and molecular assembly structures of C14TPP were evaluated by TG, DSC, and PXRD experiments. Macro cyclic conjugated porphyrin derivatives shows dual fluorescence behavior, which was similar to that of C14TPP. The formation of C14TPP nanofibers was confirmed in the xerogel state by SEM and AFM images. Dielectric response and its loss of C14TPP were examined by the impedance spectroscopy.

【Results and Discussion】The phase transition behavior of C14TPP was reversibly observed at temperature cycle of DSC chart around 448 K for the solid - LC phase transition and 568 K for LC – isotropic liquid one (upper in Fig. 2). The polarized optical microscopy image of C14TPP also indicated the anisotropy of birefringence, which was characteristic to the formation of LC phase (lower in Fig. 2). In the UV-vis spectra of C14TPP, the five absorption peaks were observed in the energy range from 400 to 800 nm, which could be assigned to a Sort- and Q-band, whereas the fluorescent spectra showed the two emission bands at 651 and 717 nm. The temperature-dependent real-part dielectric constants (ε1) are consistent with the phase transition behavior around 448 K, and the low frequency ε1 was much enhanced in contrast with those of high frequencies, suggesting the low frequency slow molecular motions were existed in the LC phase (right in Fig. 3). The electric filed – polarization (P-E) curves at 563 K showed the hysteresis behavior of the ferroelectric state.

![Fig. 2. Liquid crystalline behavior around 448 K. DSC chart (upper) and POM images (below).](image1)

![Fig. 3. Dielectric response of C14TPP. The P-E hystereses behavior at 563 K (left) and temperature-and frequency-dependent real part dielectric constant ε1.](image2)

【References】