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アルキルアミド置換ポルフィリン誘導体の合成と誘電応答

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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 $–CONHC_nH_{2n+1}$ 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 $-CONHC_nH_{2n+1}$ chains results in the ferroelectricity. From above point of views, we are aiming to synthesize novel photoelectric and ferroelectric liquid crystalline materials by introducing $–CONHC_{14}H_{29}$ 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.

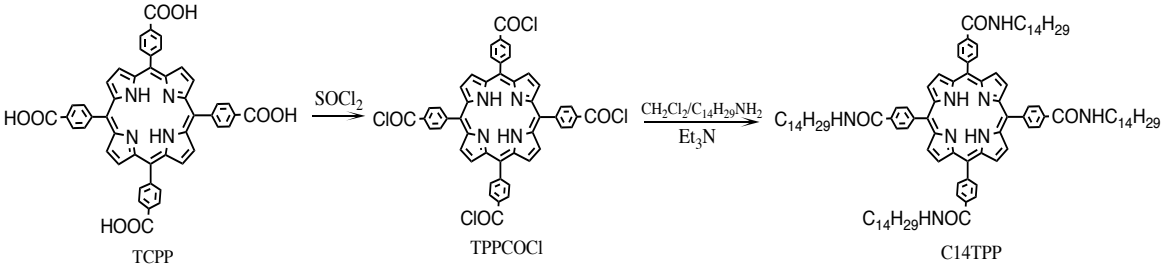

Fig. 1. Synthetic of **C14TPP**

【**Experimental**】According to the previous methods, **TCPP** was synthesized, and **TPPCOCl** was synthesized by using **TCPP** and $SOCl_2$ forming acid chloride. The synthesis

of **C14TPP** was done by the reaction of $C_{14}H_{29}NH_2$ and **TPPCOCl** in the existence of Et_3N in CH_2Cl_2. 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. Macrocyclic 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 (ε_1) are consistent with the phase transition behavior around 448 K, and the low frequency ε_1 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.

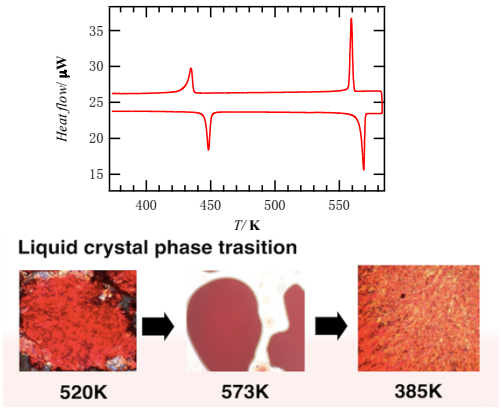

Fig. 2. Liquid crystalline behavior around 448 K. DSC chart (upper) and POM images (below).

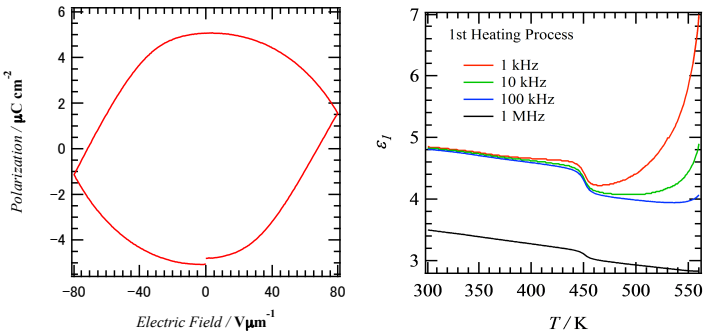

Fig. 3. Dielectric response of **C14TPP**. The *P-E* hystereces behavior at 563 K (left) and temperature- and frequency-dependent real part dielectric constant ε_1.

【References】

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