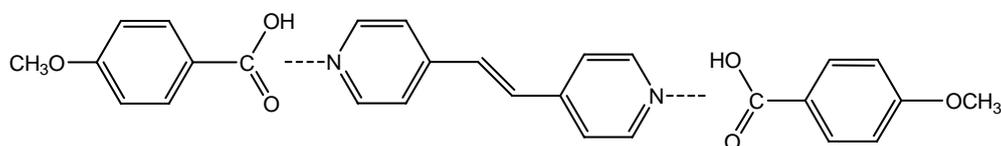


## 4P040

近赤外レーザー分光による水素結合性液晶のフェムト秒ダイナミクス  
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**Introduction** Liquid crystals (LCs) which formed by self-assembling hydrogen-bonds have long been of research interests after the exploitation of Kato *et al.*<sup>1</sup> This kind of non-covalent interaction systems based on benzoic acid-dipyridyl model were synthesized and then their thermal stability was studied.<sup>2</sup> However, their anisotropic optical properties were not reported. Various techniques, such as time-resolved fluorescence, optical-heterodyne-detected optical Kerr effect and anisotropic multiple light scattering, are provided to a detailed view of the dynamics on a fast time scale.<sup>3</sup> The transient absorption spectroscopy have also been widely used to probe molecular dynamics and then the decay of its polarization anisotropy.<sup>4</sup> The overtone transition of hydrogen bond is located in the near IR region. With the electron excitation, the affinitive hydrogen bond and nematic-phase<sup>5</sup> liquid crystal might be influenced by this transition of energy states. In this work, we report studies on the near infrared (IR) steady-state and transient absorption spectra of benzoic acid-dipyridyl liquid crystal and compared with those of the two parental materials.

**Synthesis** 4-Methoxybenzoic Acid (*p*-anisic acid) and 1,2-di(4-pyridyl)ethylene (DPE) (Tokyo Chemical Industry co., LTD) were recrystallized from hot methanol and 3:1 dichloromethane/toluene respectively. Then, 2:1 molar ratio of the above two samples were mixed together and recrystallized in warm methanol as the method in ref. 2. Figure 1 shows the chemical structure of the mixture. The three samples were sealed under vacuum in 2 mm quartz cells separately.

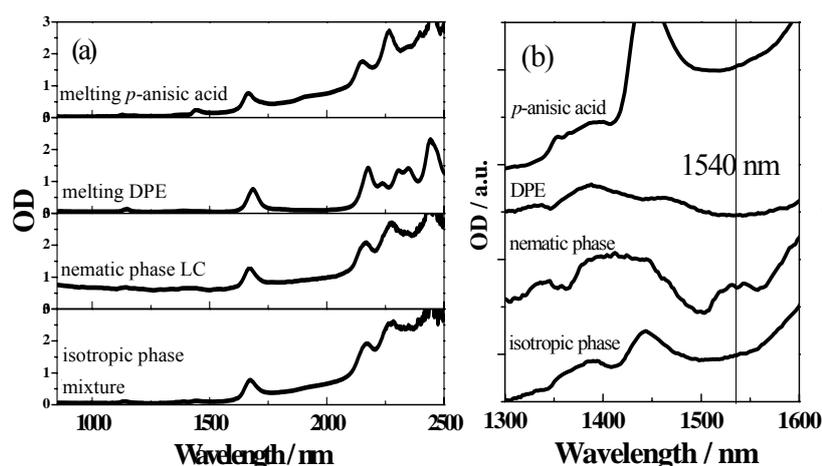


**Figure 1.** Chemical structure of *p*-Methoxybenzoic acid–1,2-di(4-pyridyl)ethylene 2:1 complex

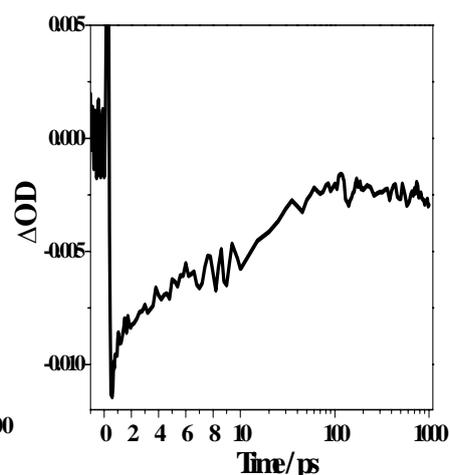
**Measurements** The steady-state absorption spectra were recorded by using an U4100 spectrophotometer (Hitachi). Transient absorption spectra were measured with a conventional pump-probe method. The pump beam was the second or third harmonic generation of the fundamental laser (Spectra-Physics, Spitfire, 1 kHz, 800 nm). The probe beam was the super-continuum white light generated from a 5 mm thick sapphire plate in the near infrared

region (until 1600 nm). The spectra were measured with a home-made heating holder where the temperature was controlled to  $\pm 0.1$  K.

**Results and discussion** Figure 2 shows the absorption spectra of melting *p*-anisic acid, DPE and mixture in nematic and isotropic phases (from top to bottom, the heating temperatures are 180, 150, 170 and 190 °C, respectively) with the detection region of (a) 850 – 2500 nm and (b) 1300 – 1600 nm. A absorption peak around 1540 nm is appeared only in the expanded spectrum of nematic phase LC in figure 2(b), which is due to the overtone transition of hydrogen bond, although it is very weak. Therefore, the subsequent data treatment is important which includes background subtraction, deconvolution, and analysis by multivariate methods. Figure 3 shows the dynamics of nematic phase liquid crystal at the probe wavelength of 1400 nm under the excitation of 400 nm. A fast bleaching recovery within 1 ps was detected and followed with a long lifetime decay component. Moreover, the dynamics should be discussed in terms of electron transfer process and the change of molecular structures.



**Figure 2.** Steady-state absorption spectra of melting *p*-anisic acid, DPE and their mixture with nematic and isotropic phases (from top to bottom) in the regions of (a) 850-2500 nm and (b) 1300-1600 nm.



**Figure 3.** Dynamics of nematic phase liquid crystal at 1400 nm under the excitation of 400 nm.

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