

Developing 500 MHz NB ^{19}F - ^{13}C Double Resonance Solid-State NMR Probe for *in-situ* Analysis of Liquid Crystal Display Panels

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The orientational and dynamic behavior of liquid crystal molecules on the alignment layer surfaces of liquid crystal display (LCD) devices is crucial to their performance, but there are only a few methods of experimentally elucidating the interactions between the liquid crystals and the alignment layers. Inspired by the natural and technical similarities between membrane proteins in lipid bilayers and liquid crystals in LCDs, we employed solid-state NMR methodologies originally developed for the study of membrane proteins in lipid bilayers for the *in-situ* analysis of liquid crystal display panels. In this article, we present a home-built 500 MHz narrowbore (NB) ^{19}F - ^{13}C double resonance solid-state NMR probe with a flat-square coil and the first application of this probe for the *in-situ* analysis of LCD panel samples.

Key Words : Home-built, ^{19}F - ^{13}C double resonance, Solid-state NMR probe, Liquid Crystal Display (LCD), LCD panel

Introduction

Liquid crystal display (LCD) panels operate by manipulating the transmission of light through a liquid crystalline medium, which is in turn controlled by the electric field applied across it. The liquid crystal molecules are aligned according to the electric field when the field is turned on, whereas their alignment is governed by their interactions with the polyimide resin surface --- the alignment layer --- when the field is turned off. To obtain a thorough comprehension of the operational characteristics of LCD panels, it is necessary to understand the surface interaction between the liquid crystal molecules and the alignment layer.^{1,2} The determination of the three-dimensional alignment of the liquid crystal molecules would be the crucial first step toward this goal. The crystal rotation method is the current standard method of determining the alignment of liquid crystal directors, but it can only show the average alignment direction by finding the pretilt angle that maximizes the transmission of light and cannot give quantitative information about the proportions of the liquid crystal molecules that are aligned in particular orientations.¹⁻⁴

Solid-state NMR spectroscopy has been widely used to elucidate the structures of membrane proteins, for which neither X-ray diffraction nor liquid-state NMR spectroscopy can give sufficient structural information. The membrane proteins are typically immobilized onto glass plates together with membrane-like lipids, then their static solid-state NMR spectra are taken in a dedicated probehead equipped with a flat-square coil.⁵⁻⁷ The dipole-dipole couplings and chemical shift anisotropies (CSAs) of membrane proteins are the two main parameters used to determine their structures by solid-state NMR experiments. When the protein molecules are

oriented with a specific direction in a membrane-like environment, both the dipole-dipole couplings and CSAs have different values depending on the molecular orientations, and these values can be used to determine the local structures of the protein. For example, the dipole-dipole couplings from the N-H bonds in the protein backbone can give information about the orientation of each N-H bond, and this information can be used to determine the global backbone structure of the proteins.

In this article, we present the first application of flat-square coil probe NMR for the *in-situ* analysis of liquid crystal samples in LCD panels. The liquid crystals in LCD applications contain oligofluorophenyl moieties that can interact with the electric field to effectively control the alignment, so we targeted these fluorine atoms along with their adjacent carbons in solid-state NMR experiments.

Experimental

Preparation of LCD Panel. The LCD panel samples were 10 mm × 15 mm pieces cut from 40-inch LCD panels. One pair of these pieces containing liquid crystals between them was put into the probehead at a time. Although the exact value of the cell gap between the pair of glasses is a trade secret, it is typically around 3 μm. Therefore, approximately 0.5 μL of the liquid crystal was introduced into the probehead. 40-60% (w/w) of the liquid crystal ingredients contain 2,3-difluorophenyl moieties, which align liquid crystal directors perpendicular to the electric field when the field is turned on. The rest of the liquid crystal ingredients contain only carbon, hydrogen, and oxygen, and no fluorine.

***In-situ* Solid-State NMR Probe Design for LCD Panel Samples.** We designed, constructed, and optimized a flat-

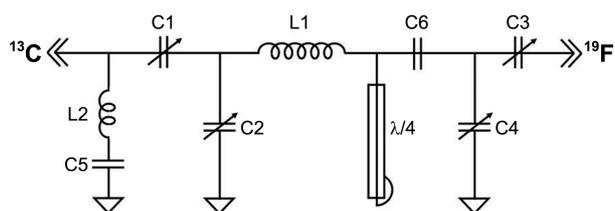


Figure 1. A schematic circuit diagram for home-built 500 MHz NB ^{19}F - ^{13}C double resonance probe. Capacitors C3 and C4 are variable capacitors (1-10 pF) for tuning and matching the ^{19}F channel (470 MHz). Capacitors C1 and C2 are variable capacitors (1-10 pF) for tuning and matching the ^{13}C channel (125 MHz). C5 (= 33 pF) and C6 (= 2 pF) are fixed capacitors. L1 is a five-turn flat-square coil made of gold-plated copper. L2 and C5 constitute the high frequency trap and the length of $\lambda/4$ is about 10.6 cm.

square coil probe with a ^{19}F - ^{13}C double resonance circuit for a 500 MHz narrowbore (NB) magnet to directly observe the LCD panel samples. The optimized circuit is shown in Figure 1.⁸⁻¹⁰ The main coil (L1) was a five-turn, flat-square coil made of gold-plated copper. The overall size of this coil (width = 14 mm, height = 1 mm, length = 16 mm) was designed to incorporate the LCD panel samples cut into 10 mm \times 15 mm pieces as described above. These LCD panel samples were placed normal to the magnetic field.⁷⁻⁹ The ^{19}F channel was tuned and matched with a $\lambda/4$ line and C3, C4 and C6 capacitors. The $\lambda/4$ line was made of coaxial cable, whose length was calculated from the ^{19}F resonance frequency (470.592 MHz on 11.7 T magnet) as shown below.

$$\begin{aligned} \text{Length of } \lambda/4 \text{ line for } ^{19}\text{F} &= \frac{c \cdot \varepsilon}{4 \cdot \nu} \\ &= \frac{3 \times 10^{10} (\text{cm/sec}) \times 0.667}{4 \times 470.592 \times 10^6 (\text{Hz})} \\ &= 10.630 \approx 10.6 \text{ cm} \end{aligned}$$

Capacitors C1-C4 were variable capacitors (1-10 pF, Polyflon USA) for tuning and matching the two channels. Coil L2 and capacitor C5 constituted a high frequency trap that isolated the two channels, so that the high frequency signal could not interfere with the low frequency channel. C5 (33 pF) and C6 (2 pF) were fixed capacitors (ATC, USA). The impedance of the whole probe circuit was matched at 50 Ω and was tuned by a network analyzer (Hewlett Packard 85046A, USA).⁸ We employed fluorine-free materials such as ceramics whenever possible to minimize the probe background signal, as shown in Figure 2.

^{19}F NMR Spectra. The ^{19}F chemical shift was calibrated with the signal of trifluoroethanol (TFE, ACROS; $\delta = -77.03$ ppm) sealed in a glass capillary.

Results and Discussion

Optimization of the Home-Built ^{19}F - ^{13}C Solid-State NMR Probe for the 500 MHz NB Magnet. We optimized the performance of our home-built probe with the ^{19}F signal of TFE as an external standard. We paid particular attention

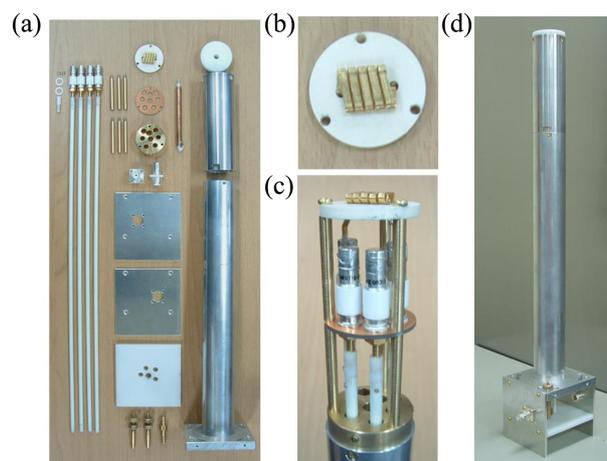


Figure 2. The home-built ^{19}F - ^{13}C double resonance solid-state NMR probe for the 500 MHz NB magnet. (a) The probe parts before assembly. (b) The flat-square coil made of gold-plated copper mounted on a ceramic plate. The choice of ceramics for the plate is to minimize the probe background signal. (c) The optimized circuit of the assembled probehead. (d) The whole probe with the cap on top.

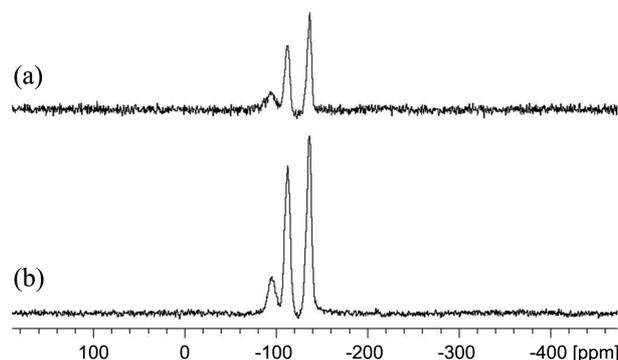


Figure 3. ^{19}F NMR spectra of liquid crystal samples in sealed glass capillaries in a 500 MHz NB magnet spectrometer. (a) In the commercial liquid-state ^1H - ^{19}F double resonance probe with the vertical orientation (S/N = 28.45) and (b) in our home-built solid-state ^{19}F - ^{13}C double resonance probe with the horizontal orientation (S/N = 63.21). The number of transients is 16 and the line broadening is 5 Hz.

to minimize the probe background signal, which arose from the fluorine-based materials in the probe parts, by adjusting the vertical position of the probe inside the magnet bore (data not shown).

Optimization of the Spectra for the LCD Panel Samples. We observed the liquid crystal (LC) sample sealed in a glass capillary in two different orientations; in the vertical orientation with a commercial solution-state NMR probe and in the horizontal orientation with our home-built solid-state NMR probe. The corresponding spectra are shown in Figure 3. The spectra of Figures 3(a) and 3(b) are basically the same, which means that the home-built solid-state NMR probe is well-made and perfectly optimized.

The optimization of the LC spectra for the LCD panel samples was even more difficult, due to their much lower signal-to-noise ratio compared to that in common ^{19}F NMR

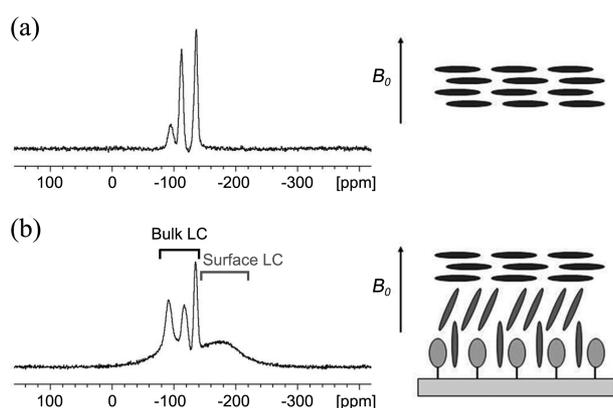


Figure 4. ^{19}F solid-state NMR spectra of liquid crystal sealed (a) in a glass capillary (the number of scans = 16, LB = 0.3 Hz) and (b) in an LCD panel sample (the number of scans = 20 k, LB = 0.3 Hz). The signals of the bulk liquid crystals and surface liquid crystals in the LCD panel can be differentiated in the spectra.

experiments; to achieve a comparable S/N ratio, the LCD panel samples required approximately 1000 times as long as the experimental time of the neat LC samples.^{11,12}

After the optimization of the LCD panel samples, the NMR spectrum of the neat liquid crystal sample in a glass capillary was acquired with this probe. The resulting spectrum is shown in Figure 3(b). The spectrum of the same sample with a commercial 500 MHz ^{19}F - ^1H double resonance solution-state NMR probe was also taken for comparison, and is shown in Figure 3(a). These results showed that our flat-square coil probe exhibited better performance than the commercial solution-state probe in terms of its ^{19}F channel sensitivity. Finally, we could successfully acquire the ^{19}F NMR spectra of the liquid crystal inside the LCD panel samples with the same probe, as intended. The resulting spectra are shown in Figure 4(b).

Analysis of the Spectra of the LCD Panel Samples. We took the ^{19}F NMR spectrum of the neat liquid crystal sealed in a glass capillary by placing the capillary horizontally inside the flat-square coil. After optimizing the probe position, the resulting spectrum clearly showed three sharp peaks without any significant background signal. All of these ^{19}F peaks come from the 2,3-difluorophenyl moieties contained in 40–60% (w/w) of the liquid crystal ingredients and in more than 5 of the 8–15 components in the liquid crystalline mixture.

We also took the ^{19}F NMR spectrum of the liquid crystal in the LCD panel sample by placing the panel sample horizontally inside the flat square coil; that is, with the plane normal parallel to the magnetic field. In addition to the sharp peaks similar to those in the spectrum of the neat liquid crystal, that of the LCD panel also showed a broad hump at 100–150 ppm upfield of the sharp peaks.

The alignment layer of the LCD panel is typically made of a surface-modified polyimide resin, which aligns the liquid crystal molecules in a specific direction by molecular interactions when the electric field is turned off. The LCD panels used in this experiment employed “vertical alignment”

mode, in which the surface functional groups on top of the polyimide resin align the liquid crystals perpendicular to the panel plane. Since we did not apply an electric field across the panel, we can assume that at least the liquid crystal molecules in the alignment layer surface are aligned parallel to the magnetic field, as is the case with actual LCD panels in normal operation. However, in a strong magnetic field (11.7 T in the case of a 500 MHz spectrometer), the behavior of the bulk liquid crystal molecules can be different from that without a magnetic field.

The 2,3-difluorophenyl based liquid crystals have negative values of D_e (dielectric anisotropy), because the electric dipole moments from the two C-F bonds add to each other in the direction perpendicular to the molecular long axis. When the electric field is applied between the pair of glass sheets, the liquid crystal molecules are aligned perpendicular to it. This is why the 2,3-difluorophenyl based liquid crystals are used in “vertical alignment” mode. Although it is not $\Delta\epsilon$ but $\Delta\chi$ (magnetic susceptibility anisotropy) that governs the behavior of the liquid crystal inside the magnetic field, the signs and magnitudes of $\Delta\epsilon$ and $\Delta\chi$ are known to follow similar trends in most liquid crystals. For example, the rotational viscosities of liquid crystals with a very low e are often measured by applying a magnetic field. Based on this argument, if we assume that the $\Delta\chi$ values of the liquid crystals in this experiment are also negative, then the liquid crystals would be expected to be aligned perpendicular to the magnetic field without the surface interaction with the alignment layer.

In the neat liquid crystal sample, there is no surface interaction with the surface modification groups of the alignment layer and the alignment of the liquid crystals is solely governed by the magnetic field. Therefore, the liquid crystals are very likely to be aligned uniformly in a horizontal orientation in this neat liquid crystal sample. In the LCD panel sample, the bulk liquid crystals --- those far from the alignment layer --- are aligned mainly by the magnetic field, so they will also be aligned perpendicular to the magnetic field, provided that our assumption of $\Delta\chi < 0$ is correct. On the other hand, the alignment of the liquid crystals on the alignment layer surface is mainly governed by the surface modification groups, so the liquid crystals will be aligned parallel to the magnetic field. This behavior results in the manifestation of two different domains --- bulk LC and surface LC --- in the LCD panel spectrum. We illustrated the resulting model in Figure 4, along with the data already shown in Figures 3(b).

Conclusion

We obtained the solid-state NMR spectrum of the liquid crystal in the LCD panel sample with the home-built probehead with flat-square coil and differentiated the bulk and surface domains of the liquid crystals from the spectrum. Further application of solid-state NMR techniques will enable the determination of the three-dimensional alignment properties of the liquid crystal molecules in LCD panels.

These studies will provide valuable information allowing for both the quality improvement of the existing LCD products and the development of new ones.

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