# Photochromic properties of liquid crystalline dithienylperfluorocyclopentenes for photo- and electro-tunable coloration

# Hiroyuki Yoshida<sup>1</sup>, Hao Chun Yang<sup>2</sup>, Hanwen Kuo<sup>2</sup>, and Hsiu-Hui Chen<sup>2</sup>

yoshida@eei.eng.osaka-u.ac.jp

<sup>1</sup>Division of Electrical, Electronic, and Infocommunications Engineering, 2-1 Yamadaoka Suita, Osaka 565-0871 Japan <sup>2</sup>Institute of Organic and Polymeric Materials and Research and Development Center for Smart Textile Technology, National Taipei University of Technology, Taipei, Taiwan

Keywords: Liquid Crystal, photochromism, electro-optic effect

#### ABSTRACT

Photochromic materials, which undergo a structural transition upon light absorption such that their colour changes, are attractive materials from the point of view of optical applications. Here, a series of Dithienylperfluorocyclopentenes with high miscibility in standard nematics are presented and their electro-optic properties characterized.

#### 1 Introduction

Photochromic materials, which undergo a structural transition upon light absorption such that their color (i.e., absorbance) changes, are attractive materials from the point of view of optical applications. The color change is usually associated with a conjugation change in the molecule due to some photoinduced intramolecular cyclization/cyclo-reversion. On the other hand, liquid crystals (LCs), typically composed of a rigid planar central moiety and flexible alkyl chains, are materials which exhibit liquid crystalline phase with long range molecular ordering within certain temperature range. In the nematic phase, the molecules are aligned along an average direction known as the director, and show uniaxial anisotropy in various physical properties such as the refractive index and dielectric constant. In addition, their fluid nature enables the director to be reoriented, leading to advanced materials with properties that can be tuned by external fields.

Photochromic nematic which LCs, contain photochromic moiety and liquid crystalline structural feature in their framework, are particularly interesting. Upon light absorption and thus structure transition, they may either maintain its original LC phase or transform into another LC phase. Design and synthesis of photochromic LCs, which undergo photoinduced phase transitions, photoalignment, and photoorientation of LCs have emerged as novel system and have been reported in systems involving spirooxazines, spiropyrans, bisindenyldenediones, and dithienylcyclopentenes [1-4]. Dithienylperfluorocyclopentenes are one member of the dithienylcyclopentenes family and show excellent fatigue resistance, thermal stability, fast photocyclization, and electrical conductivity. They have found applications in the field of molecular electronics, such as high-speed rewritable recording devices, fluorescence imaging, and sensors. While photochromism of dithienylperflorocyclopentene has been investigated in LC environment through guest-host systems, where a small amount of photochromic dye was doped in a LC host, direct observation of photochromism in their LC state may give enhanced absorption and switching speed. In this work, we synthesized diarylethene (DAE) derivatives with biphenyl groups connected directly to the DAE backbone and investigated their thermodynamic, crystalline and optical properties. We found that the introduction of the biphenyl group can enhance the  $\pi$ - $\pi$  interaction of central DAE moieties and lead to an LC phase. The system also showed excellent photo-switching property in the nematic phase, with the LC properties being modulated successfully by terminal alkoxyl chains of different lengths. [5]

#### 2 Experiment

#### 2.1 Synthesis

Figure 1 describes the synthesis route of the final compounds synthesized in this work (Compounds 3a-3d). All compounds used for synthesis were obtained commercially and used without further purification.

#### 2.2 Material characterization

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy (NMR) (Bruker, Fourier-300, Germany) spectra of the synthesized compounds were recorded in CDCl<sub>3</sub>. Column chromatography was carried out on silica gel (60–200 mesh). Analytical thin layer chromatography (TLC) was performed on pre-coated 60 mesh F254 glass plates. Spots were rendered visible by exposing the plate to UV light. Elemental analysis (EA) (Elementar, UNICUBE, Germany) was performed at the Core Facility Center of National Cheng Kung University. Mass spectra (MS) (Bruker, Microflex JEOL/JMS-700, Germany) were obtained on a Bruker Microflex spectrometer using fast atom bombardment (FAB) and matrix-assisted laser



Figure 1 Synthesis

desorption ionization (MALDI). Infrared (IR) (Thermo Fisher Scientific, Nicolet 6700 FT-IR Spectrometer, America) spectra were measured on a Nicolet 6700 FT- IR Spectrometer. X-ray diffraction (XRD) experiments were performed on the wiggler beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The optical textures and transition temperatures were observed using a polarizing microscope (POM) (Nikon, Eclipse LV100N, Japan) equipped with a Linkam T95-HS (Japan) temperature controller. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC8000 calorimeter, United States of America (U.S.A). The UV-visible spectra were recorded using a Hitachi UH5300 (Japan) spectrophotometer. Fluorescence (FL) measurements were performed on a Shimadzu RF-6000 (Japan) fluorescence spectrophotometer with a controlled slit excitation of 5 nm and a scan range from 300 to 800 nm. Light irradiation studies were carried out using a highpressure 100 W xenon lamp (Asahi spectra Co Ltd., Japan) with a mirror module of UV and a visible range of 300-400 and 400-700 nm with respective cut-off filters. An ultra-low temperature bath, Panchum Scientific CORP., UR-850, Taiwan, was used.

#### 2.3 Optical characterization in sandwich cell

The materials prepared were examined for use as transmissive polarization modulators in the colorless state and as dichroic absorbers in the colored state. As a representative material, the optical properties of compounds 3c and 4c (Fig. 1) were characterized in a glass sandwich cell (ITO glass length 10 mm, width 5 mm

and 5  $\mu$ m thick), whose surface was coated with polyimide and rubbed unidirectionally (EHC Co., KSRP-10/D607P1NSS05, Japan). The cell was placed so that the rubbing axis was at 45° to the crossed polarizers, and the optical texture was recorded every minute as the sample temperature was reduced from 130 °C to 115 °C at a rate of 2 °C/min. A long-pass filter with a cut-off at ~480 nm was inserted in the optical path to prevent unwanted photochromic reaction by the white light of the microscope.

The birefringence,  $\Delta n$ , of compound 3c was measured in the LC phase as a function of temperature. The sample was first rapidly heated to 180 °C and cooled to 130 °C to give a completely molten isotropic liquid and then cooled at a rate of 2 °C/min to room temperature. The transmittance spectrum was measured with the alignment direction of the sample oriented at 45° to the crossed polarizers, and the transmittance spectrum was analyzed according to Eq. (1), which gives the theoretical transmittance of a uniaxially anisotropic medium placed between crossed polarizers,

$$T = T_0 \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)....(1)$$

In Eq. (1), *d* is the thickness of the cell, which was ~ 4.3  $\mu$ m as evaluated from interference fringes that appeared



Fig. 2 POM textures of compound 3c



Fig.3 Temperature dependence of birefringence at 500 nm for compound 3c.

in the empty cell, and  $T_0$  is a coefficient that accounts for losses due to surface reflections and scattering.

To evaluate the properties of compound **4c** as a dichroic absorber, the transient increase in absorbance due to photoisomerization to the closed form was measured at 115 °C. A UV light (~ 365 nm, 2.8  $\mu$ W) from an LED (Thorlabs, M365L3) impinged on the sample through a fluorescent filter cube equipped with a bandpass filter (330-380, Nikon), dichroic mirror (Semrock, FF389-Di01-25×36×1.5), and long-pass glass filter (Schott, GG400) for 10 s and the transmittance spectra parallel and perpendicular to the director were measured after turning off the LED. Measurements were made up to a total irradiation time of 100 seconds.

#### 3 Results

Analysis of the synthesized materials showed that addition of alkoxy chains on the dithienylperfluorocyclopentene core induces a nematic LC phase that varies in temperature range depending on the chain length. However, all materials studies were monotropic, only showing the liquid crystal phase upon cooling the sample from the isotropic phase.

Figure 2 shows POM images of compound 3c observed between crossed polarizers. From the initially dark state, regions of yellow-orange hue gradually developed and grew to fill the entire field of view at ~126 °C. The texture soon became uniform and gradually changed color, corresponding to a change in birefringence of the compound. The optical texture showed no noticeable change at 115 °C, but after keeping the sample at the same temperature for ~ 40 min., the crystal phase gradually grew to fill the field of view, reflecting the metastable nature of the LC phase.

Figure 3 shows typical transmittance spectra, and the obtained birefringence ( $\Delta n$ ) at a wavelength of 500 nm. The birefringence is between 0.1-0.2, which is comparable to standard LC materials used in optical applications.

Figure 4 shows the absorbance spectra parallel and perpendicular to the director at different irradiation times, where the absorbance was calculated by normalizing the transmittance to the spectrum without UV irradiation. For both polarizations, the absorbance showed a monotonic increase until 60 s; however, the dichroic ratio gradually



Fig. 4 (a)Relative absorption spectra of compound 3c undergoing photoisomerization to the closed form for polarizations parallel and perpendicular to the LC director. (b) Relative absorbance and dichroic ratio at 610 nm. (c) Microscope images showing the onset and disappearance of linear dichroism with increasing UV irradiation times.

decreased from approximately 3 to 2 (Figure 4 (b)). At 60 s, the dichroic ratio dropped sharply and approached 1, which suggests that the compound had undergone a photoinduced nematic to isotropic phase transition causing the anisotropy to disappear. The onset and

disappearance of linear dichroism was clearly observed in the microscope using polarized light. (Fig. 4(c)). Despite the relative high temperature range of the LC phase, the DAE derivatives prepared here showed potential as tunable dichroic dyes.

## 4 Conclusions

A series of DAE derivatives showing monotropic LC behavior were synthesized and their thermodynamic, structural and optical properties were investigated. The materials showed good thermostability in both the colored and transparent states, offering the possibility of using them in coloration purposed with both optical and electrical switching modes.

### References

- I. Cabrera, V. Krongauz, H. Ringsdorf, "Photoand Thermochromic Liquid Crystal Polysiloxanes". Angew. Chem., Int. Ed. Engl. 1987, 26, 1178–1180
- [2] H. Hattori, T. Uryu, "Synthesis and Characterization of Polymerizable Photochromic Liquid Crystals Containing a Spirooxazine Group". Liq. Cryst. 1999, 26, 1085–1095.
- [3] I. Cabrera, A. Dittrich, H. Ringsdorf, "Thermally Irreversible Photochromic Liquid Crystal Polymers." Angew. Chem., Int. Ed. Engl. 1991, 30, 76–78.
- [4] Frigoli, M.; Mehl, G. H. "A Photochromic Liquid Crystal System". ChemPhysChem 2003, 4, 101–103.
- [5] H. Chen et al., "Photo-switching behaviour in liquid crystalline materials incorporating a nonplanar dithienylcyclopentene core and their birefringence properties", Liq. Cryst., (2022). https://doi.org/10.1080/02678292.2022.204452 9