Keynote Paper

Light-emitting Liquid-crystal Displays Constructed from AIE Luminogens

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ABSTRACT

Liquid crystal displays (LCDs) are widely used for diverse purposes in many aspects in daily life from handle personal devices to professional applications and large-panel LCD televisions. Since LCD is a passive emission display device, it usually shows narrow viewing angle and reduced brightness. Nowadays, LCDs with light-emitting properties is suggested as a less energy consuming displays. To date, fluorescent materials with dichroic properties and strong fluorescence emission are required. However, many molecular emitters, which are highly efficient in solution, will suffer from heavy aggregation-caused quenching (ACQ) effect in the aggregate state, which has greatly limited their applications.

In order to overcome these weaknesses, we have designed and synthesized a novel luminescent liquid crystalline compound consisting of a tetraphenylethene (TPE) core, TPE-PPE, as a luminogen with mesogenic moieties. As a result, the TPE-PPE exhibits both the aggregate-induced emission (AIE) and thermotropic liquid crystalline characteristics. By dissolving 1 weight% (wt%) of TPE-PPE into the nematic LC host PA0182, a linearly polarized emission was obtained on the unidirectional orientated LC cell. The photoluminescence polarization ratio of the LC cell has reached to 4.16 between the directions perpendicular and parallel to the rubbing direction. Utilizing the emissive anisotropic TPE-PPE, we have fabricated the photoluminescent liquid crystal display (PL-LCD). This approach has simplified the device design, lowered the energy consumption and increased brightness of the LCD.

Keywords: liquid crystal displays, aggregation-induced emission (AIE), polarized emission, anisotropy, alignment, PL-LCD, tetraphenylethene (TPE)

1. INTRODUCTION

Liquid crystal displays (LCDs) still occupy the dominant position in the display industry. LCDs take the advantages in low energy consumption and the flat panel fabrication compared with the cathode ray tube monitors. However, the LCD panels themselves cannot produce light. As such, they require an external light source for visualizing the images. Therefore, the luminescent LCD is a favorable alternative.[1-3] It is a type of emissive display, which can simplify the device design and substantially increase the device brightness, contrast, efficiency and viewing angle.[4–6] Their LC phase temperature range should be low enough for the LCD fabrication requirement.

However, the complicated synthetic routes make this approach becoming too expensive for industrial mass production.[7] Furthermore, the luminescence efficiency in the liquid crystalline phase is the other challenge. Many molecular luminescence emitters are highly emissive in solution but emit weakly or non-emissive in their solid-state. This notorious

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effect is coined aggregation-caused quenching (ACQ) effect.[8,9] Their fluorescence emission is quenched by π-π stacking once they have formed aggregates. To date, we have reported a luminescent LCD devices fabricated with an aggregation-induced emission (AIE)-active LC mixture. AIE is a novel phenomenon opposite to the ACQ effect commonly suffered by the conventional luminogens. The aggregate formation of AIE molecules will enhance their fluorescence emission by restricting their intramolecular rotation.[10–13] The excitation energy is relaxed through radiative decay rather than the non-radiative channels, such as rotation and vibration. We have firstly prepared the luminescent liquid crystalline compound TPE-PPE, consists of AIE active luminogen, tetraphenylethene (TPE), and mesogenic moieties. By doping TPE-PPE into the nematic LC host, a linearly polarized emission was obtained with the unidirectionally orientated LC cell. In addition, the PL-LCD devices were fabricated by utilizing the fluorescence emissive anisotropy of TPE-PPE. The details will be presented below.

2. METHODOLOGY

2.1 Material

The target molecule TPE-PPE was prepared according to the synthetic route shown in Figure 1. TPE4Br was firstly prepared as a key intermediate in high yield through McMurry coupling. Subsequently, TPE-PPE was obtained through Sonogashira-coupling of TPE4Br with 4-Ethynylpropylbenzene. Other raw materials were purchased from Aldrich. Nematic LC PA0182 was purchased from Dainippon Ink and Chemicals (DIC).

2.2 Measurements

^{1}H NMR spectra were measured on a Bruker ARX 400 spectrometer in chloroform-*d* with tetramethylsilane (TMS, $\delta = 0$) as the internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) high-resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer. Emission spectra were recorded on a Perkin-Elmer spectrofluorometer LS 55. An Olympus BX 60 polarized optical microscope (POM) equipped with a Linkam TMS 92 hot stage was used to observe the anisotropic optical textures. Polarized fluorescence spectra were excited using second-harmonic generation from Ti: Sapphire mode-lock laser. The excitation laser source was intrinsically polarized so no extra polarizer was required. A rotatable polarizer in the angle range of 0–360 was inserted between the sample and the detector. The excitation wavelength was 370 nm.

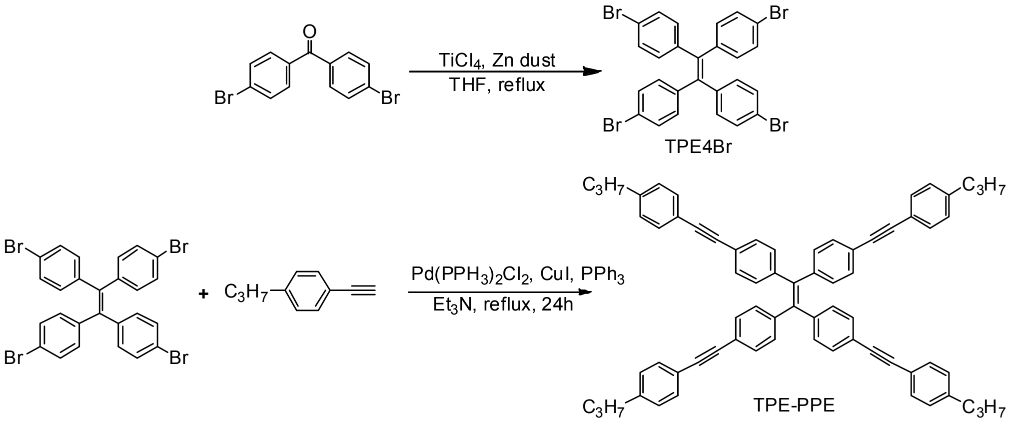

Figure 1. Synthetic route to compound TPE-PPE.

2.3 Characterization

Data of TPE4Br: ^{1}H NMR (400 MHz, DMSO-d6, δ): 7.28–7.26 (m, 8H, aromatic protons ortho to –Ar-Br), 6.86, 6.84 (m, 8H, aromatic protons meta to –Ar-Br).

Data of TPE-PPE: ^{1}H NMR (400 MHz, CDCl3), δ (TMS, ppm): 7.42-7.28 (m, 16H), 7.15-6.99 (m, two 16H), 2.58 (t, 8H), 1.54 (m, 8H), 0.93 (t, 12H). HRMS (MALDI-TOF): Calcd. for $C_{10}H_{60}$: 900.47. Found: 900.4686 [M^+].

3. RESULTS

The liquid crystalline (LC) properties of TPE-PPE were demonstrated with polarized optical microscopy (POM). Figure 2 shows the POM photograph of TPE-PPE. When it was heated above 218 ºC, an anisotropic mesomorphic texture was clearly observed. However, the mesomorphic texture could not be observed upon cooling the TPE-PPE which indicated that it is a monotropic disc LC.

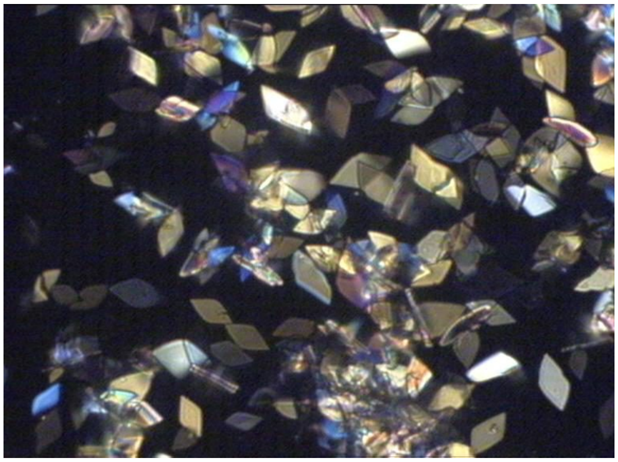

Figure 2. POM photograph recorded on heating TPE-PPE to 223ºC（×200).

TPE is a well-known AIE luminogen. To investigate whether TPE-PPE is AIE-active, photoluminescence (PL) spectra in THF and THF/water mixtures were measured. As shown in Figure 3, the solution state of TPE-PPE in pure THF is non-emissive under UV illumination. Addition of the water into the THF solution, however, has induced the formation of the aggregate and enhanced the fluorescence emission of TPE-PPE. It still emits weakly in the aqueous mixtures at the low water fractions (~50%) but becomes stronger afterwards. Water is the poor solvent for TPE-PPE, thus, it should aggregates in high water content. Since the aggregate of TPE-PPE is formed, the restriction of intramolecular rotation (RIR) is activated and the radiative decay of the excitons becomes populated. That is why the fluorescence emission of TPE-PPE is enhanced. The polarity inside the aggregate is lower than the medium outside due to the tight packing of the hydrophobic molecules. As such, the blue-shifted fluorescence enhancement in its aggregate state is observed.

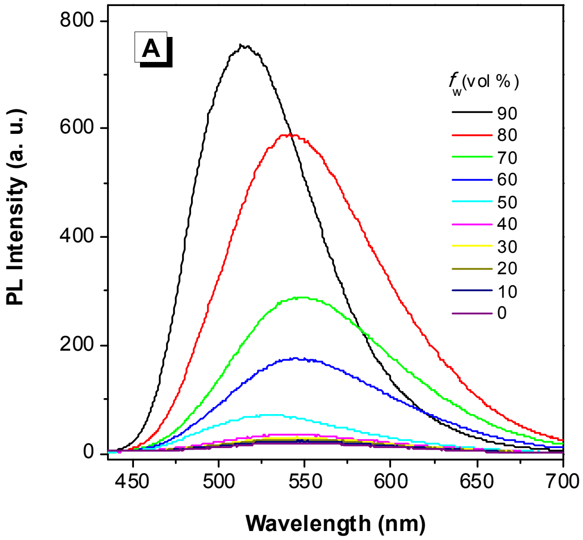

Figure 3. Fluorescence spectra of TPE-PPE in the THF/water mixtures with different fractions (f_w) of water; Excitation wavelength: 319 nm. [TPE-PPE] = 10 μM.

Since TPE-PPE is a fluorophore with liquid crystalline properties, we wonder if its polarized emission could be achieved. A polarized emissive LC mixture containing commercial nematic LC host and TPE-PPE was prepared. 0.1 wt% of TPE-PPE was dissolved into the host nematic LC PA0182. The LC mixture was then filled into the planar oriented LC cell with homogeneously rubbed alignment layer. Figure 4 shows the polar diagram of the fluorescence signal from the nematic LC/TPE-PPE mixture. The LC cell reveals a maximum signal value along the direction of 90° to 270° , which is perpendicular to the rubbing direction. However, a minimum signal value along the direction of 0° to 180° which is parallel to the rubbing direction. This anisotropic properties indicate again that the TPE-PPE molecules are unidirectional oriented. Simultaneously， the polarized luminescence was proved to be achieved with the nematic LC/TPE-PPE mixture. The dichroic ratio of the polarized fluorescence of the LC cell is shown to be 4.1.

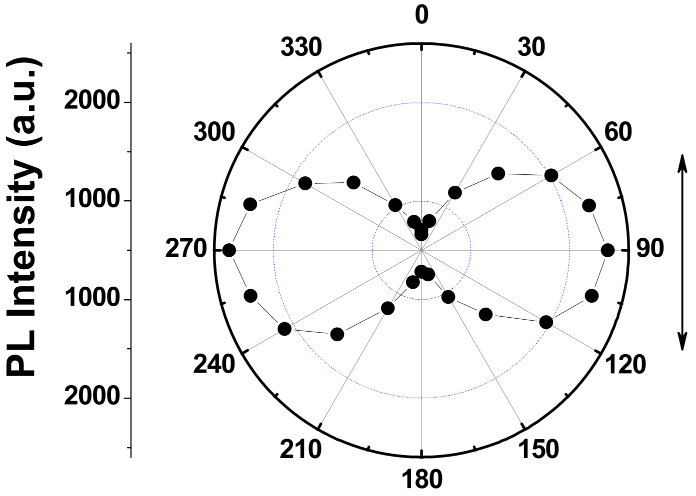

Figure 4. Polar diagram of PL intensity of the LC cell. The LC mixture is consisted of nematic LC PA0182+0.1 wt % TPE-PPE.

Based on the results of the polarized fluorescence measurements, the PL-LCD was fabricated. In the PL-LCD, the LC cell was fabricated with the patterned ITO glass substrates. The unidirectionally aligned LC cell was obtained through rubbing the polyimide alignment layer. If there was no electric field applied to the LC cell, no any light emission was observed under UV irradiation. Once electric field (1 KHz, 8v) was applied to the LC cell, the light emission from the patterned ITO region will be clearly visualized. Figure 5 shows the photograph of the light emitting LCD fabricated with the mixture of TPE-PPE and the nematic LC host PA0182 which was perceived by eye. The PL-LCD demonstrated the switching from dark state to the bright yellowish-green state.

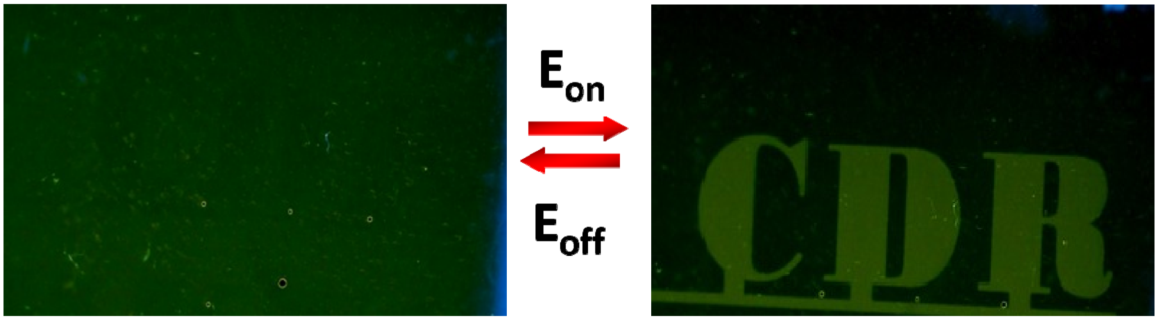

Figure 5. Photograph of the luminescent liquid crystal device with patterned electrode in the (left) electric field-off and (right) field-on states under UV irradiation using light-emitting LC mixture. The LC mixture =Nematic LC PA0182 + 0.1 wt % TPE-PPE.

4. CONCLUSION

In summary, TPE-PPE with AIE-active TPE core and peripheral mesogens was successfully synthesized and characterized. The compound exhibits monotic liquid crystalline behavior upon heating as well as the AIE properties in the THF/water mixture. By dissolving TPE-PPE into the nematic LC host PA0182, the LC mixture exhibits anisotropy in the measurement of polarized emission. The guest-host PL-LCD was consequent fabricated, based on the patterned electrode. Under an UV source irradiation, the luminescent molecules were excited and emission was controlled electrically by the alignment of the liquid crystal.

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