

## Research Article

# Synthesis and Study of Chemical, Thermal, Mesomorphic, and Optical Properties of Terphenyls Modified with Nitrile Groups

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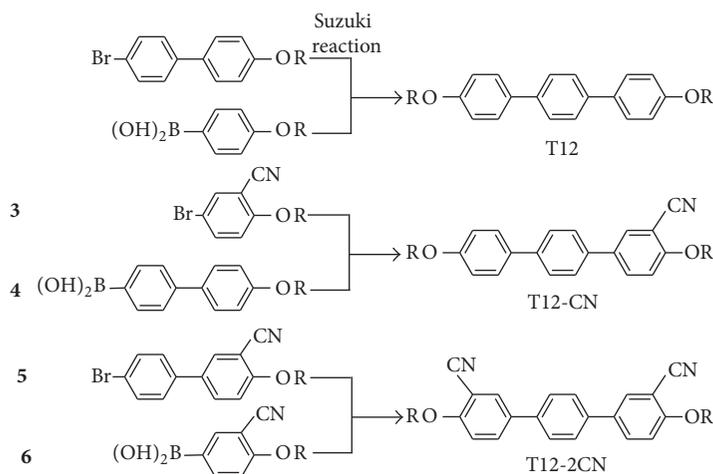
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We report the synthesis, characterization, and the thermotropic and photoluminescence properties of dialkoxyterphenyls with (T12-CN and T12-2CN) and without (T12) nitrile groups. These terphenyls were prepared through the Suzuki-Miyaura cross-coupling reaction using a palladium-based catalyst. The products obtained were analyzed as powders or after being drop-casted or spin-coated on glass. Nuclear Magnetic Resonance (<sup>1</sup>H NMR) and Fourier Transform Infrared (FTIR) spectroscopy techniques confirmed the structure and purity of the synthesized terphenyls. The mesomorphic behavior was studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). T12 developed various mesophases, whereas T12-CN and T12-2CN displayed one single mesophase of low order over a wide temperature range. The films topology was studied by AFM and the optical properties were determined by ultraviolet-visible (UV-Vis) spectroscopy and spectrofluorometry. Higher roughness was found for the films prepared with the asymmetric terphenyl (T12-CN). The photoluminescence (PL) spectrum obtained for the asymmetric terphenyl (T12-CN) exhibited the expected characteristics with an emission band centered at 381 nm and an overtone around 760 nm.

## 1. Introduction

In the recent years,  $\pi$ -conjugated organic molecules have been the subject of increasing attention due to their unique electrical and optical properties, which make them suitable active materials for photovoltaic cells [1], photodiodes [2, 3], and molecular sensors [4–7], among other optoelectronic devices [8–11]. The oligo-*p*-terphenylenes are of particular interest because the smallest (terphenyl, quaterphenyl, and quinqueterphenyl) are able to not only radiate a high energy light in the blue region of the spectrum but also display a rich thermotropic polymorphism. These oligomers are commonly modified with flexible chains [12, 13] and other groups [14, 15]

to disrupt the  $\pi$ -interactions that hold them close together. Such disruption increases their entropy and improves the number of conformations that can take place to effectively decrease their melting point and improve their solubility. Another outstanding aspect of the oligo-*p*-phenylenes is their ability to form flexible and resistant films by spin coating and dip coating methods which can be used as active layers in organic light-emitting diodes (OLEDs) of relatively large area [16]. Among the  $\pi$ -conjugated fluorescent materials [17], the oligo(*p*-phenylenes) and poly(*p*-phenylenes) are considered promising organic materials for blue light generation [18]. Moreover, the light emitted can be easily converted to other colors enabling single-source lighting in a wide range of



SCHEME 1: Precursors 1–6 and terphenyls with (T12-CN and T12-2CN) and without (T12) cyano groups. R: dodecyl chain.

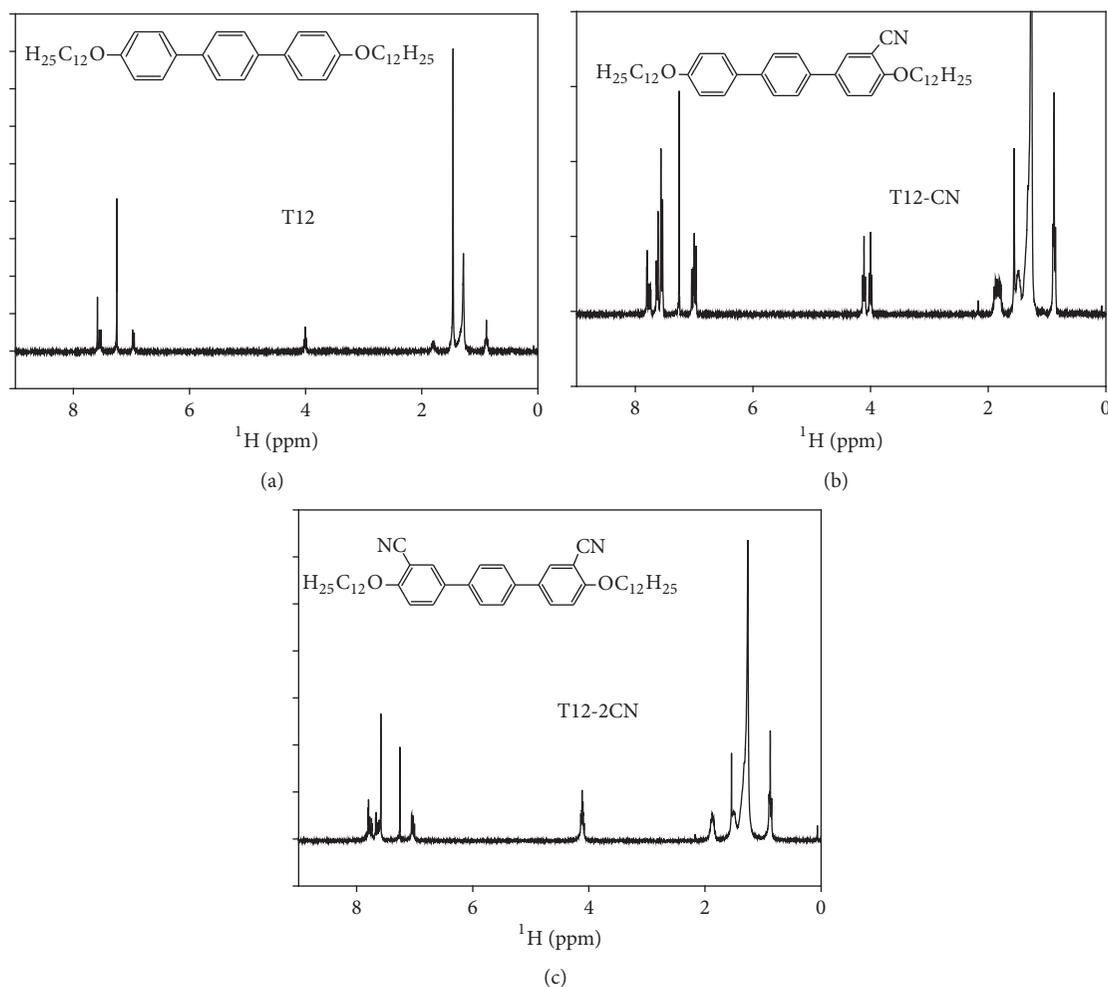
wavelengths [19]. The mesomorphic behavior of organic molecules carrying  $\pi$ -conjugated groups has also gained high interest due to the fact that light emission characteristics are dependent on the orientation of the molecular emitters [20].  $\pi$ -Conjugated molecules with cyano groups have also been studied because of their electron withdrawing character which leads the wavelength of the emitted light to be shifted [21]. The red or blue shifting depends on the number of cyano groups and also on the *ortho*position, *meta*position, or *para*position on the benzene rings [22]. Photodiodes based on fluorescent organic compounds have been seen as a viable alternative to artificial lighting [23, 24]. Our approach is to design a series of liquid crystal cyanoterphenyls harnessing their spontaneous alignment to potentially improve their luminescent properties. In this paper, we report the synthesis as well as the chemical, thermal, mesomorphic, and optical characterization of the three obtained terphenyls with and without a nitrile group. Thin films were deposited over a glass substrate in order to evaluate their photoluminescence for potential applications in organic semiconductor devices.

## 2. Materials and Methods

**2.1. Synthesis.** Hydroquinone 99%, hydrochloric acid 37%, sodium hydroxide 97%, potassium carbonate 99%, 5-bromo-2-hydroxybenzonitrile, 1-bromododecane, benzene-1,4-diboronic acid 95%, butyllithium ( $C_4H_9Li$ ) in hexanes 1.6 M, triisopropyl borate 98%, and tetrakis(triphenylphosphine)palladium(0) Pd[0], dimethylformamide (DMF), carbon tetrachloride, chloroform, methanol, methylene chloride, hexane, and ethyl acetate were acquired from Sigma-Aldrich and/or J.T.Baker and used as received. Tetrahydrofuran (THF) was distilled over a Na/benzophenone complex. Deuterated solvents including chloroform ( $CDCl_3$ ), tetrahydrofuran 99% ( $THF-d_8$ ), and toluene 99.5% ( $C_7D_8$ ) were used as received for NMR spectroscopic analysis. The precursors used for the synthesis of terphenyls are shown in Scheme 1. Arylboronic acids were coupled with aryl halides using a Suzuki reaction mediated with a palladium catalyst.

Terphenyls (T) were labeled as T12, T12-CN, and T12-2CN, where the number 12 corresponds to the length of each of the two alkyl chains and CN and 2CN correspond to either one or two nitrile groups, respectively. Terphenyls were purified in silica-gel chromatographic columns and resulting compounds were crystallized. Preliminary thin layer chromatography tests were conducted to determine the presence of impurities. Precursors 1 to 5 were synthesized according to previously reported procedures [25, 26]. The synthesis of boronic acid (6) and final products (T12, T12-CN, and T12-2CN) are detailed in Scheme 1. The chemical structure of precursors 1–6 was verified by  $^1H$  NMR using a 300 MHz Jeol spectrometer (JNM-ECO300) and  $CDCl_3$  as solvent (see supplementary material (available here)). Five separate runs of the synthesis protocol were performed and the obtained materials were analyzed under the same conditions; the results were found to be in good agreement.

**2.2. 5-Dodecyloxy-2-benzonitrile Boronic Acid.** First, 8 g (21.8 mmol) of 5-bromo-2-dodecyloxybenzonitrile and 150 mL of freshly distilled THF were added to a 250 mL three-neck round-bottom flask, equipped with two addition funnels (100 mL) and sealing septa. The formed solution was cooled down to  $-68^\circ C$  and then 17.5 mL (28 mmol) of butyllithium (BuLi) in hexane (1.6 M) was added dropwise over a 20 min period. The reaction mixture was stirred before adding 11 mL (47.8 mmol) of triisopropyl borate over a similar period of time. The solution was then maintained under stirring for 18 h; during this time, the solution was allowed to warm up to room temperature. Next, HCl (2N) was added and the solution was stirred for 120 min to hydrolyze the product. The acidified solution was then transferred to a separation funnel, where diethyl ether was added. The organic phase was recovered and washed with water until neutral pH was obtained. The solvent was evaporated and the residual product suspended in chloroform, washed with water, filtered, and dried. Finally, the aryl boronic acid 3 was obtained as a white powder (Yield: 35.3%).  $^1H$  NMR (300 MHz,  $THF-d_8$ ,  $\delta$  = ppm): 0.9 (t,  $J$  = 6.7 Hz, 3H,  $-CH_3$ );

FIGURE 1:  $^1\text{H}$  NMR spectra of terphenyls.

1.3–1.5 (m, 20H,  $-(\text{CH}_2)-\text{CH}_3$ ); 1.7 (m, 2H,  $\text{OCH}_2-\text{CH}_2$ ); 4–4.2 (t,  $J = 6.5$  Hz, 2H,  $\text{OCH}_2-$ ); 6.8 (s,  $J = 8.8$ , 2H, Ar); 7.6 (d, 4H,  $\text{B}(\text{OH})_2$  Ar) and 8–8.3 (d, 4H, Ar *ortho* to the  $\text{B}(\text{OH})_2$ ).

**2.3. Terphenyl without Cyano Group: T12.** 1.415 g (3.3 mmol) of **1** and 50 mL of freshly distilled THF were introduced in a 250 mL two-necked round-bottom flask equipped with a stirring element and saturated with argon; the solution was stirred until visible dissolution was achieved. Then 0.1318 g (0.11 mmol) of tetrakis(triphenylphosphine)palladium(0) and 25 mL of  $\text{Na}_2\text{CO}_3$  (2 M) were added. Next 1.15 g (3.7 mmol) of precursor **2** was added and the reaction mixture was heated to  $65^\circ\text{C}$  and stirred during 48 h. Once this period elapsed, the reaction was allowed to cool down to room temperature to be then transferred to a separation funnel, where diethyl ether was added. The organic layer was washed with water and the product (gray precipitate) which remained near the interface was recovered and recrystallized from chloroform. (Yield: 72.6%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$   $\delta = \text{ppm}$ ): 0.9 ppm (t,  $J = 6.7$  Hz, 6H,  $-\text{CH}_3$ ); 1.3–1.5 ppm (m, 36H,  $-(\text{CH}_2)-\text{CH}_3$ ); 1.7 ppm (m, 4H,

$-\text{CH}_2-\text{CH}_3$ ); 4 ppm (t,  $J = 6.5$  Hz, 4H,  $\text{OCH}_2-$ ); 6.9 ppm (d,  $J = 8.8$ , 4H, Ar) and 7.5 ppm (t, 8H, Ar) (Figure 1).

**2.4. Terphenyl with One Cyano Group: T12-CN.** 0.850 g (0.028 mmol) of precursor **3** and 50 mL of freshly distilled THF were introduced in a 250 mL two-necked round-bottom flask equipped with a stirring element and filled with an argon atmosphere. Then 0.029 g (0.0087 mmol) of tetrakis(triphenylphosphine)palladium(0) and 27.6 mmol of  $\text{Na}_2\text{CO}_3$  (2 M) were added and the solution was heated to  $65^\circ\text{C}$ . Next, 1.025 g (0.028 mmol) of precursor **4** was added and the reaction mixture was held under stirring and heating ( $65^\circ\text{C}$ ) over 48 h. The reaction mixture was cooled down to room temperature before being transferred to a separation funnel, where diethyl ether was added. The organic layer was washed with water. Finally, the crude product was purified by using a silica-gel chromatographic column ( $\text{CHCl}_3$ : hexane (1:2) as eluent), where the catalyst and other residual solids were removed. The product was obtained as a white solid (40% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$   $\delta = \text{ppm}$ ): 0.9 ppm (t,  $J = 6.7$  Hz, 6H,  $-\text{CH}_3$ ); 1.3–1.5 ppm (m, 36H,  $-(\text{CH}_2)-\text{CH}_3$ ); 1.7 ppm (m, 4H,  $\text{O}-\text{CH}_2-\text{CH}_2$ ); 3.9 ppm (t,  $J = 6.5$  Hz, 2H,

OCH<sub>2</sub>-); 4.1 ppm (t,  $J = 6.5$  Hz, 2H, OCH<sub>2</sub>-); 6.9 ppm (d,  $J = 8.8$ , 2H, Ar); 7 ppm (d,  $J = 8.8$ , H, Ar); 7.5 ppm (d,  $J = 8.8$ , 2H, Ar); 7.6 ppm (d,  $J = 8.8$ , 2H, Ar) and 7.5 ppm (t, 4H, Ar) (Figure 1).

**2.5. Terphenyl with Two Cyano Groups: T12-2CN.** This terphenyl was synthesized and purified through the already-described procedure for the synthesis of T12-CN; however, the quantities of the reactants were adjusted as follows: 0.450 g (1.0 mmol) of precursor 5, 0.632 g (1.5 mmol) of precursor 6, 0.045 g of Pd[0], and 8.5 mL of Na<sub>2</sub>CO<sub>3</sub> (2 M). White powder (50% yield) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta = 7.7$  ppm (t, 4H, Ar),  $\delta = 7.5$  ppm (d,  $J = 8.8$ , 4H, Ar),  $\delta = 7$  ppm (d,  $J = 8.8$ , 2H, Ar),  $\delta = 4.1$  ppm (t,  $J = 6.5$  Hz, 4H, OCH<sub>2</sub>-),  $\delta = 1.8$  ppm (m, 4H, O-CH<sub>2</sub>-CH<sub>2</sub>-),  $\delta = 1.3$ -1.4 ppm (m, 36H, -(CH<sub>2</sub>)-CH<sub>3</sub>),  $\delta = 0.8$  ppm (t,  $J = 6.7$  Hz, 6H, -CH<sub>3</sub>) (Figure 1).

**2.6. Chemical, Thermal, and Structural Analysis.** The chemical structure of terphenyls was verified by <sup>1</sup>H NMR using a 300 MHz Jeol spectrometer (JNM-ECO300) and CDCl<sub>3</sub> as solvent. Infrared spectroscopic measurements were carried out using a Magna-IR Nicolet infrared spectrometer model 550 with a MIRacle ATR, PIKE, equipped with a Germanium crystal. The thermal stability of the compounds was determined in vacuum-dried samples and using a thermal analyzer from Dupont Instruments (TGA 951) connected to a nitrogen vector gas with a heating rate of 10°C/min from 30 to 800°C. DSC traces were obtained in a differential scanning calorimeter from TA Instruments (MDSC 2920); the scanning rate was 10°C/min and heating-cooling cycle ranged from -20 to 250°C; the reported data corresponds to the second heating cycle. Optical textures of mesophases were captured upon cooling using a polarized optical microscope (POM) from Olympus (BX60) coupled with a temperature-controlled stage from Mettler (FP82HT) and a digital camera from Hitachi. The phase behavior of molecules was investigated using hot-stage polarizing optical microscopy. The study was done between untreated glass slides using heating and cooling rates of 10°/min. Despite the relatively high transition temperatures, some mesophases remain stable under room temperature for a relatively long period. X-ray diffraction analysis was performed in an SWAXS from Anton-Paar (SAXSess mc<sup>2</sup>) equipped with a sample holder unit (TCS 300-C), image plate detector, and a temperature-controlled unit (TCU50).

**2.7. Thin Film Deposition and Characterization.** The final products were deposited by the spin coating technique over glass substrates at 500 RPM over a 30 s run. The UV-visible absorption spectra were registered with a 6850 JENWAY spectrophotometer. The PL experiments were performed with a PerkinElmer LS50B luminescence spectrometer; films were excited using radiation at 300 nm in the range from 370 to 900 nm with a 2.5 nm resolution. The average roughness was measured with an Atomic Probe Microscope from Veeco, Model 3100 Dimension V, at a frequency of 320–359 kHz.

TABLE 1: FTIR bands of terphenyls as identified elsewhere [17–27].

Vibration	Bond	cm <sup>-1</sup>
A. Stretching	C-H (aromatic)	2910
B. Stretching	C-H (aliphatic)	2860
C. Stretching	C≡N	2210
D. Annular stretching	C=C	1600 and 1455
E. Asymmetric stretching	C-O-C	1245
F. Out of plane	C-H	800

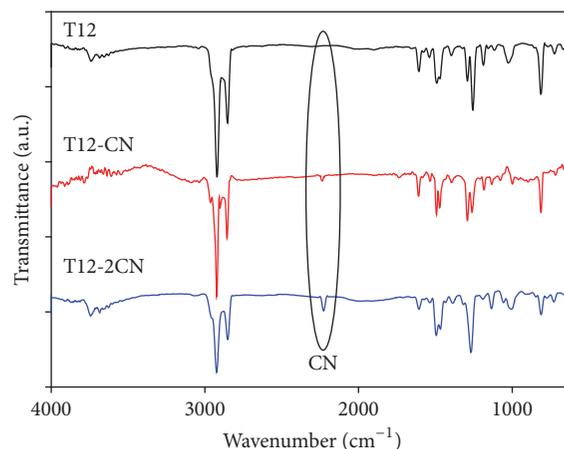


FIGURE 2: FTIR spectra of synthesized terphenyls.

### 3. Results and Discussion

**3.1. Chemical Characterization.** As described in Materials and Methods, the <sup>1</sup>H NMR spectroscopy verified the structure and purity of the synthesized terphenyls; the spectra obtained for T12, T12-CN, and T12-2CN have been presented in Figure 1.

The obtained FTIR results were satisfactory (Figure 2) to differentiate between absence and presence of one or two cyano groups. Such differentiation was made through the characteristic stretching band of the nitrile group at 2210 cm<sup>-1</sup>. In T12, this band is absent, but in T12-2CN it is twice as intense as for T12-CN. The other groups were identified as described in Table 1.

**3.2. Thermal Stability.** The obtained TGA thermograms are depicted in Figure 3. It can be noticed that the terphenyls start to decompose around 200°C and lose <5 wt% below 280°C. The presence of the nitrile groups in the terphenyls seems to improve their thermal stability. T12-2CN is around 25°C more stable than T12-CN, and this is in turn more stable than T12. The thermal analysis of terphenyls is used to determine the limiting temperature for the thermotropic examination performed by different techniques such as DSC, POM, and XRD. Terphenyls showed only one transition in the TGA thermograms, indicating a simple process of decomposition and suggesting the absence of byproducts.

**3.3. Mesomorphic Behavior.** The DSC thermograms of the terphenyls are shown in Figure 4. Two or more thermal

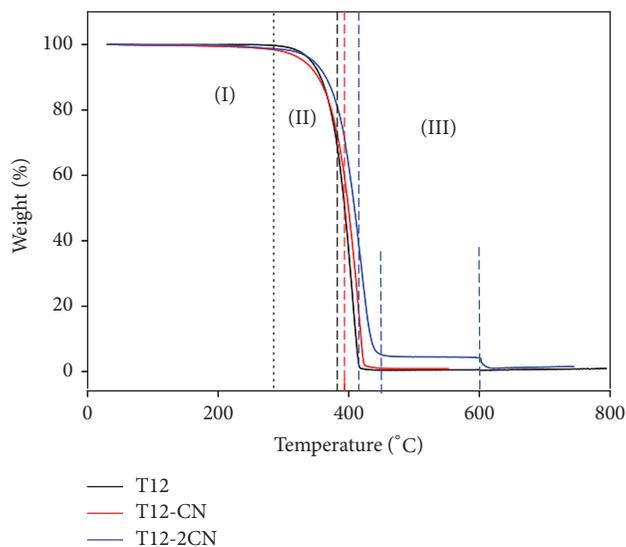


FIGURE 3: TGA thermograms for the synthesized terphenyls.

transitions in the DSC trace suggest a mesomorphic behavior. All mesophases are enantiotropic, since they are observed in both heating and cooling scans. A decrease in the melting point is observed for T12-CN and T12-2CN as compared to T12. T12 showed a rich polymorphism with transitions at 130, 164, 182, and 190°C. Adding one or two nitrile groups in the *orthoposition* to the alkoxy group changes the mesomorphic behavior towards only one mesophase in a large temperature interval. According to POM observations, T12-CN displays a smectic-A phase of low order having a strong tendency to form a homotropic texture upon cooling from its isotropic state. Only one POM image is included (inset) for each terphenyl in Figure 4. According to microscopy observations, the isotropic temperatures of each of the molecules are found between 218°C and 245°C, between 170°C and 185°C, and between 146°C and 200°C for T12, T12-CN, and T12-2CN, respectively.

Symmetric terphenyls (T12 and T12-2CN) displayed a focal-conic fan texture, whereas the asymmetric one (T12-CN) developed an unconventional texture showing high mobility. This result suggests that the tightly held liquid crystal (T12) is able to develop a rich polymorphism, whereas those having one or two lateral groups (T12-CN and T12-2CN) are to certain degree decoupled and display only a less ordered phase at lower temperatures. For our asymmetric terphenyl (T12-CN), only one extended mesophase (over 118°C) was observed. The XRD patterns of the terphenyls are shown in Figure 5. In the small degree region of the X-ray pattern, all terphenyls display a sharp Bragg reflection, indicating a smectic order. The rich polymorphism of T12 was confirmed by different changes produced upon cooling (or heating) in the X-ray patterns (Figure 5(a)). At high temperature (218°C), this terphenyl displayed a broad peak (centered around  $2\theta = 20^\circ$ ), suggesting the presence of a low-ordered smectic phase (SmA or SmC). Upon cooling, the presence of one or more sharp peaks at this region is

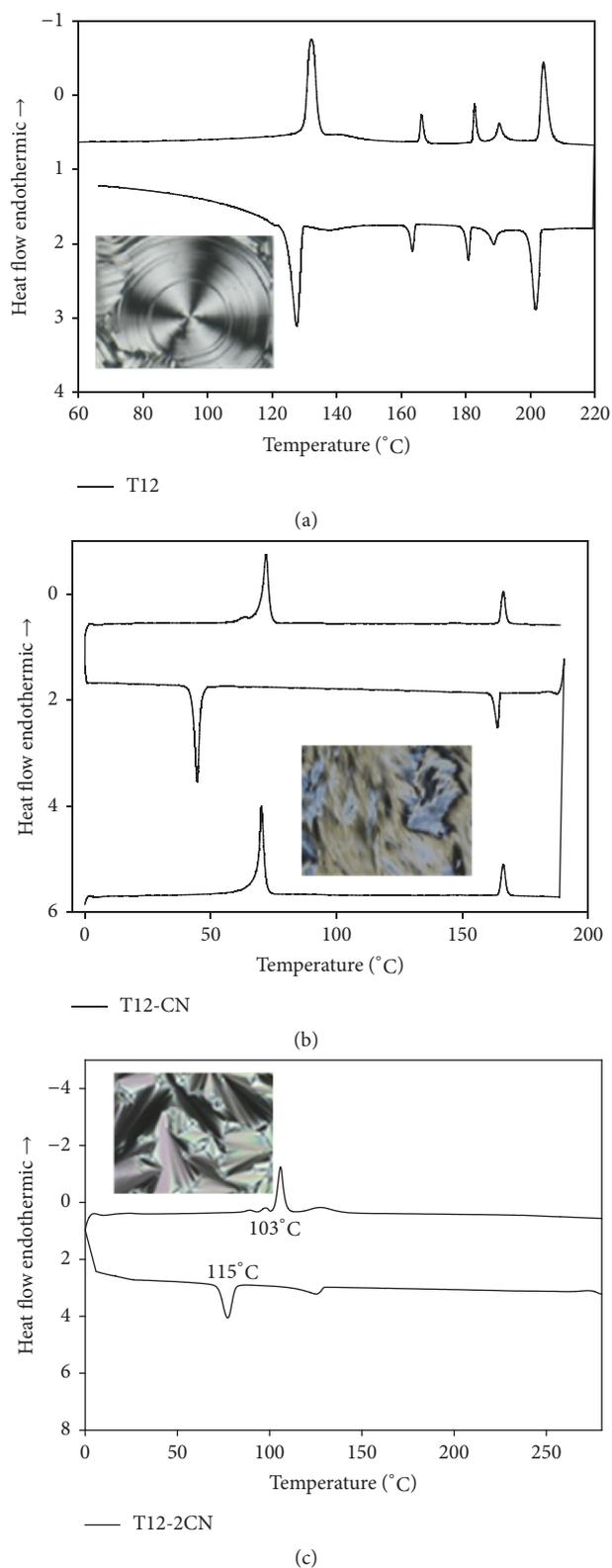


FIGURE 4: DSC thermograms of the terphenyls. The inset shows a POM texture. Micrographs temperatures are as follows: T12, 68°C, T12-CN, 89°C, and T12-2CN, 108°C.

indicative of high-ordered smectic crystalline phases. T12-CN remained unchanged over a broad temperature range

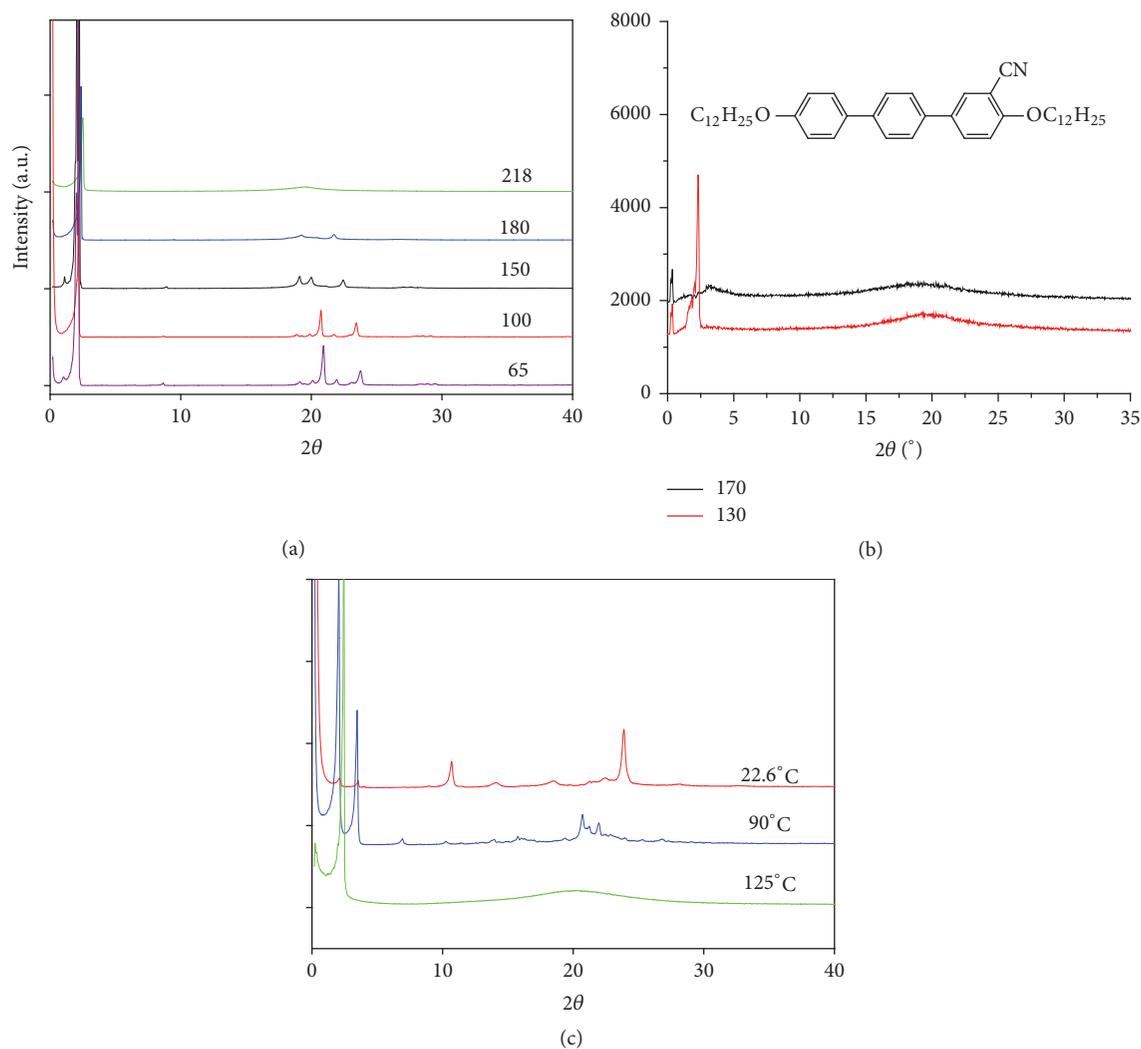


FIGURE 5: XRD patterns of the terphenyls (a) T12, (b) T12-CN, and (c) T12- 2CN.

(from 170 to 50 °C). Such behavior is typical of a smectic liquid crystal of low order. Finally, T12-2CN displayed a smectic phase of low order over a relatively small temperature range (from 125 to 190 °C).

**3.4. Optical Behavior.** The UV-Vis absorption spectra of the terphenyls in chloroform solution are depicted in Figure 6. The absorption maxima for terphenyls with and without one CN group are located at 295 nm; the sample with one CN group shows a hyperchromic effect. The absorption maximum of T12-2CN is shifted to 286 nm (hypsochromic effect as discussed elsewhere [14, 28]). From this characterization, it is possible to confirm that only one CN group is necessary for luminescent applications as demonstrated by PL characterization. In contrast, presence of two functional groups resulted in decreased absorption. The inclusion of nitrile groups correlates to the stability of the molecules, which decreases according to the molecular symmetry.

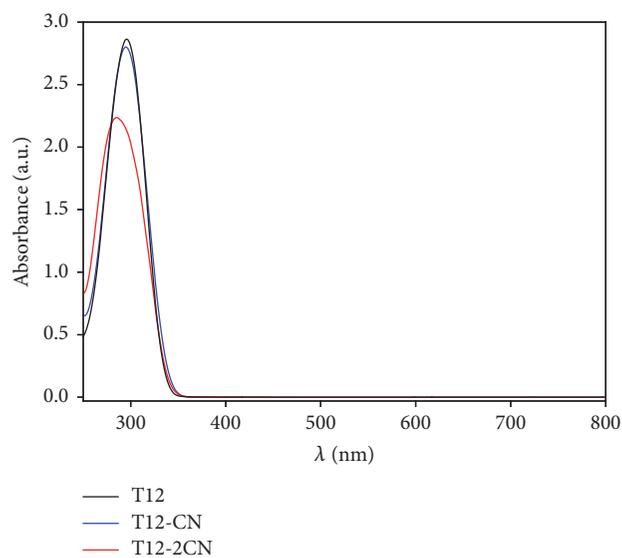


FIGURE 6: UV-Vis absorption spectra of terphenylenes.

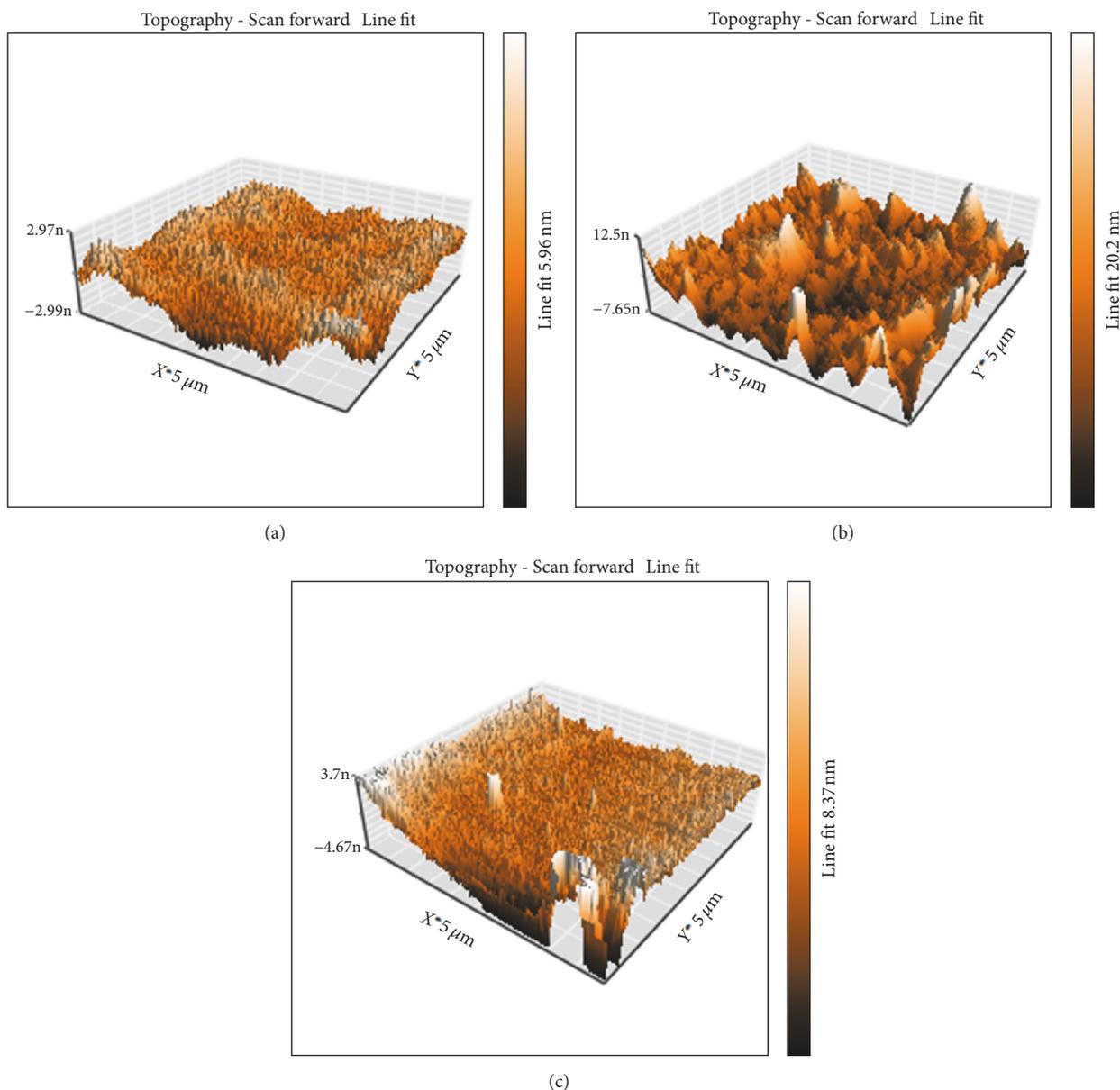


FIGURE 7: AFM images of terphenyls deposited over glass substrates: (a) T12, (b) T12-CN, and (c) T12-2CN.

**3.5. Topography Characteristics.** Figure 7 shows the AFM images of the fabricated thin films. The calculated roughness of the symmetrical terphenyl films (T12 and T12-2CN) is 0.509 and 0.547 nm, respectively, whereas for the asymmetrical one (T12-CN) it is 1.492 nm. There is not a considerable difference in roughness between T12 and T12-2CN due to the similar molecular geometry and its association with their stacking ability to produce ordered structures. The topography study was performed at room temperature and over untreated substrates. Further studies will be necessary to improve the quality of the films. High roughness in this type of materials can strongly affect the electrooptical properties as discussed by Hoven et al. [29].

**3.6. Photoluminescence Properties.** Deposition of organic functional materials based on small molecules on solid

surfaces is important for their feasible use in electronic devices. T12-CN was deposited over a glass substrate by spin coating (one layer) or by drop casting (1.5 ml of dispersion, dropwise); their corresponding photoluminescence spectra are shown in Figure 8. The spectrum (reference) of the glass substrate was also included in this figure. The emission spectra are recorded using an excitation wavelength of 300 nm (see supplementary material). The PL spectrum of T12 showed two emission peaks at 381 and 760 nm. Here we report, for the first time, the emission peak at 760 nm (overtone band) with stronger PL.

#### 4. Conclusions

The effect of one and two nitrile groups in the mesomorphic and optical properties of terphenyls was studied. Such

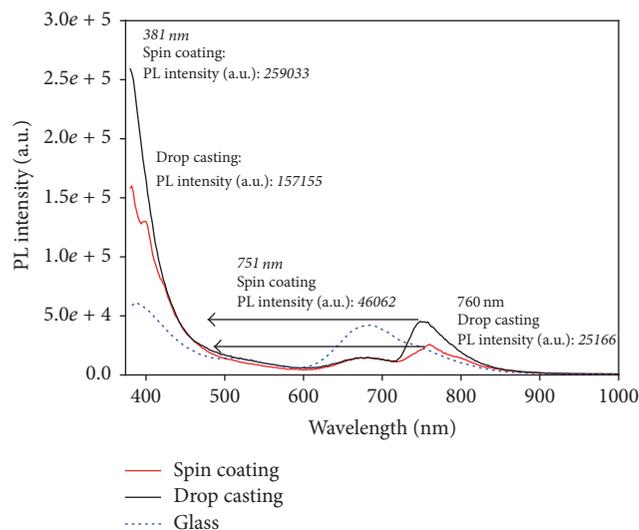


FIGURE 8: Photoluminescence emission spectra of T12 p-terphenyls deposited by spin coating and drop casting and glass substrate as reference.

terphenyls were synthesized through the Suzuki-Miyaura cross-coupling reactions between aryl boronic acids and bromoaryls, mediated by Pd[0]. The chemical structure and purity of the terphenyls were confirmed by  $^1\text{H}$  NMR and FTIR. The terphenyl without nitrile group develops a rich mesomorphism. The introduction of one or two nitrile groups in the terphenyls decouples  $\pi$ -interactions, resulting in a less ordered mesophase at lower temperature. The presence of a smectic phase of low order for such nitrile containing terphenyls was confirmed by POM and XRD. Films deposited by spin coating and drop casting techniques showed similar PL characteristics to the spectra peaking at 381 and 760 nm. The light emission is much more intense for the film deposited by drop casting; however, further studies are needed to expand on this subject.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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## Supplementary Materials

Scheme S1: precursors (1–6) and terphenyls with (T12-CN and T12-2CN) and without (T12) cyano groups. R: dodecyl chain. Figure S1:  $^1\text{H}$  NMR spectra for precursors. Precursors

I, III, and V in  $\text{CDCl}_3$ , IV in TDF, and VI in methanol-D4. Figure S2: photoluminescence spectra of T12-CN p-terphenyl deposited by spin coating and drop casting on silicon substrate. Figure S3: photoluminescence spectra of T12-CN p-terphenyl deposited by spin coating on glass substrate. (*Supplementary Materials*)

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