



# Synthesis and liquid-crystalline properties of methacrylate monomers carrying a *p*-terphenyl laterally substituted with one or two cyano groups



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## ABSTRACT

Two methacrylate monomers, carrying a *p*-terphenyl laterally substituted with one or two cyano groups, were synthesized and studied from the liquid crystal and optical points of view. The synthetic route involved several reactions, including the Suzuki reaction that allows the coupling of aryl groups. The chemical structure of these new monomers, as well as that of their corresponding precursors, was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. The mesomorphic behavior of both monomers and precursors was studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) analyses. Molecules bearing one cyano group melt at lower temperature and display a mesomorphic behavior over larger temperature intervals as compared to those bearing two cyano groups. The four compounds (two monomers and two precursors) showed only non-ordered smectic phases. By X-ray diffraction it was determined that molecules stack in single layers within the smectic phase, except for one of the monomers that stacks in double layers. The electrochemical characterization reveals that these molecules behaves as *p* type materials, and that their electronic nature (band gap) can be modulated by introducing CN groups. The molecules absorb and emit in the blue spectral range, a region of high energy light. The large Stokes' shifts indicate that the geometry of the molecules changes from aromatic in the electronic ground state to a more coplanar quinoid structure in the first excited state. The fluorescence quantum yield is high (70–80%) suggesting that these new monomers can be used as precursors for the synthesis of fluorescent liquid crystal polymers, which is a work in progress.

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## 1. Introduction

In the 1970s, liquid crystals (LC) provided a technological breakthrough to the visual display industry: the capacity to commercially produce light-weight flat-panel displays driven by electric-field stimuli [1]. Among the first known electric-field responsive liquid crystals (nematic) for flat-panel display applications are the cyano-substituted biphenyl and *p*-terphenyl derivatives [2]. These two types of liquid crystals are normally combined to each other to get a nematic order over extended temperature ranges around room temperature; [3] a condition that is virtually mandatory for LC display applications. Unlike biphenyl derivatives, *p*-terphenyls possess remarkable photo-physical properties associated to their extended  $\pi$ -conjugation length, as for instance, a high quantum efficiency of photoluminescence (>0.9) and short decay times (around 1 ns) [4]. Thus, *p*-terphenyl-based

compounds have shown to be good candidates not only for use in flat-panel LC displays, but also in their competing organic light-emitting diode (OLED) displays [5], and in many other applications like scintillators [6], wavelength shifters [7,8], UV-laser dyes, [9,10] and so on [11]. The structure – mesomorphic properties (mesophase types, transition temperatures, order parameter, etc.) relationship for *p*-terphenyl liquid crystals have been studied along the years since the 70s [2,12,13]. Different chemical groups have been incorporated into the *p*-terphenyl group to change its thermal and optical behavior, or to induce new properties [14,15]. The cyano (or nitrile) group remains one of the most tested as it is highly polar, thermally and chemically stable, and tolerates a wide variety of chemical groups. It induces a dipole moment and promotes dipole–dipole interactions that may have an important effect on the molecular stacking [16,17], as well as on the optical properties [18], depending on their number and position in the aromatic core. Short chemical substituents have proven to have a strong influence on the mesomorphic behavior of rigid rod-like mesogenic groups [19]. They could adversely affect the mesophase, either reducing its temperature interval or inhibiting its development [20]. In this paper, the synthesis and liquid-crystalline properties of two methacrylate monomers (and their precursors), substituted with one or two cyano

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groups, are presented and discussed. Preliminary optical studies are also reported for their possible combined luminescent and thermotropic behavior, for which the frontier orbitals HOMO and LUMO as well as the band gap were determined by cyclic voltammetry.

## 2. Experimental

### 2.1. Materials

Bromododecane, dibromododecane, bromophenol, 5-bromo-2-hydroxy-benzonitrile, 1.6 M butyllithium in hexanes (1.6 M BuLi), triisopropyl borate (TIPBO), hydrochloric acid, tetrakis (triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub> or Pd[0]), sodium carbonate, potassium carbonate, potassium iodide, hydroquinone (HQ), potassium hydrogen carbonate, methacrylic acid (MA) and electrochemical grade tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) were purchased from Sigma-Aldrich and used as received. Chloroform (CHCl<sub>3</sub>), deuterated chloroform (CDCl<sub>3</sub>), dimethylformamide (DMF), methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>), tetrahydrofuran (THF), triethylamine (TEA) acetone, ethyl ether and hexanes were purchased from J. T. Baker. TEA (over KOH), THF (over a Na/benzophenone complex) and acetonitrile (silica and CaH) were freshly distilled right before use.

### 2.2. Synthesis

The route for the synthesis of the monomers bearing a didodecyloxy-*p*-terphenyl group substituted with one or two cyano groups is depicted in Scheme 1. For the sake of brevity, monomers were labeled as mCN and m2CN. As noted in Scheme 1, the final intermediates (here named terphenyl precursors) were labeled as tCN and t2CN. Intermediates 1a–c and 2a–c were prepared as described in a previous report for similar compounds [17]. Procedures for the synthesis of the intermediates 3a,c and 4a, as well as those for the preparation the *p*-terphenyl precursors (tCN and t2CN) and monomers (mCN and m2CN), are detailed below.

#### 2.2.1. 4-Bromo-4'-(dodecyloxy)-1,1'-biphenyl (3a)

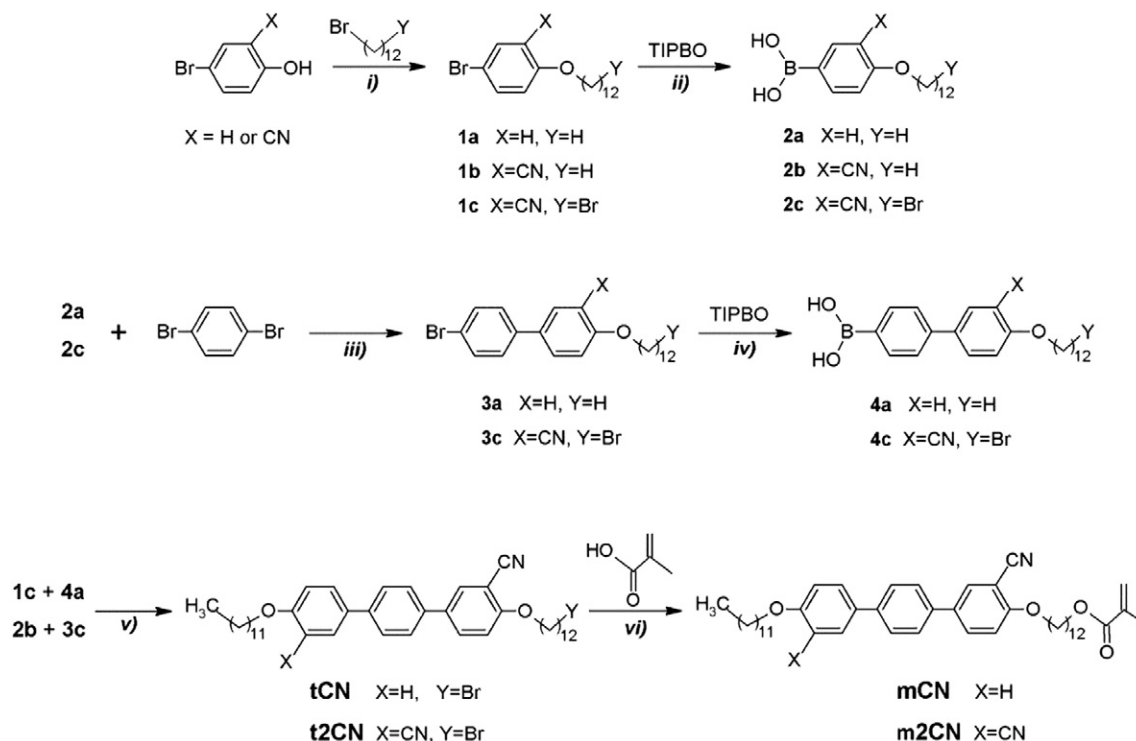
In a 250 mL two-neck round-bottom flask, under argon atmosphere, 1.15 g (4.90 mmol) of 1,4-dibromobenzene, 0.17 g (0.15 mmol) of Pd[0], and 80 mL of THF (freshly distilled) were introduced, and the mixture was stirred to complete dissolution. Next, 31.8 mL of aqueous Na<sub>2</sub>CO<sub>3</sub> 2 M and 1 g (3.26 mmol) of 2a were added and the solution was heated to 65 °C and held under stirring overnight. The reaction mixture was then allowed to reach the room temperature to then be transferred to a separation funnel containing water and chloroform. The organic layer was subsequently washed with water until neutral pH, dried over MgSO<sub>4</sub>, filtered, and evaporated. The crude product was finally passed through a silica-gel chromatographic column using hexanes:chloroform (6:4) as a mobile phase. 3a was obtained as a white powder (Yield: 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ = ppm): 0.91 (t, CH<sub>3</sub>, 3H, *J* = 6.9 Hz); 1.54–1.22 (m, CH<sub>2</sub>, 18H); 1.87–1.79 (m, CH<sub>2</sub>, 2H); 4.02 (t, CH<sub>2</sub>, 2H, *J* = 6.5 Hz); 6.99 (d, CH, 2H, *J* = 8.8 Hz); 7.44 (d, CH, 2H, *J* = 8.5 Hz); 7.50 (d, CH, 2H, *J* = 8.5 Hz); 7.55 (d, CH, 2H, *J* = 8.5 Hz).

#### 2.2.2. 4'-Bromo-4-((12-bromododecyl)oxy)-[1,1'-biphenyl]-3-carbonitrile (3c)

A similar procedure to that described for 3a was followed, but using 2c instead of 2a. White solid (Yield: 66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ = ppm): 1.54–1.18 (m, CH<sub>2</sub>, 16H); 1.89–1.82 (m, CH<sub>2</sub>, 4H); 3.43 (t, CH<sub>2</sub>, 2H, *J* = 6.9 Hz); 4.11 (t, CH<sub>2</sub>, 2H, *J* = 6.6 Hz); 7.02 (d, CH, H, *J* = 8.8 Hz); 7.37 (d, CH, 2H, *J* = 8.8); 7.56 (d, CH, 2H, *J* = 8.5 Hz); 7.68 (dd, CH, H, *J* = 8.8, 2.2 Hz); 7.72 (d, CH, H, *J* = 2.2 Hz).

#### 2.2.3. (4'-(Dodecyloxy)-[1,1'-biphenyl]-4-yl)boronic acid (4a)

In a 250 mL three-neck round-bottom flask, equipped with two addition funnels (100 mL) under argon atmosphere and stirring, 5 g (12 mmol) of 3a were dissolved in 50 mL of freshly distilled THF. This solution was then cooled down to –40 °C (over a dry ice–isopropanol bath) before adding 6.9 mL (30 mmol) of triisopropyl borate under vigorous stirring. Next, 2.8 mL (30 mmol) of 1.6 M BuLi (dissolved in about 20 mL of freshly distilled THF) were added dropwise keeping the solution at –40 °C. The reaction mixture was stirred during 24 h allowing



**Scheme 1.** Synthesis route for the preparation of methacrylate monomers bearing a *p*-terphenyl moiety substituted with one or two cyano groups. i) K<sub>2</sub>CO<sub>3</sub>, KI, acetone, 48 h; ii) BuLi, –70 °C, HCl 2 M; iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub> 2 M, THF, 60 °C, 48 h; iv) BuLi, –40 °C, HCl 2 M; v) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub> 2 M, THF, 60 °C, 48 h; and vi) KHCO<sub>3</sub>, HQ, DMF, 20 °C, 24 h.

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