ARTICLES

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# Effects of substitution and terminal groups for liquid-crystallinity enhanced luminescence of disubstituted polyacetylenes carrying chromophoric terphenyl pendants

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Liquid-crystalline and light-emitting poly(2-alkyne)s containing terphenyl cores with hexamethyleneoxy spacers, and cyano or *n*-propoxy tails  $-\{[CH_3C=C(CH_2)_6O\text{-terphenyl-R}]\}_n$ , where R=CN, **CH3PA6CN**, R=OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>. **CH3PA6OPr**, were synthesized. The effects of the substitution and terminal groups on the properties, especially the mesomorphic and optical properties of the polymers, were investigated. The disubstituted acetylene monomers (**CH3A6CN**, **CH3A6OPr**) were prepared through multistep reaction routes and were polymerized by WCl<sub>6</sub>-Ph<sub>4</sub>Sn in good yields (up to 82%). All the monomers and **CH3PA6CPr** formed a bilayer SmA<sub>d</sub> packing arrangement. Upon excitation at 330 nm, strong UV and blue emission peaks at 362 and 411 nm were observed in **CH3PA6OPr** and **CH3PA6CN**, respectively. The luminescent properties of **CH3PA6CN** and **CH3PA6CN** ( $\Phi$ =74%) was found to be higher than that of **CH3PA6OPr** ( $\Phi$ =60%). Compared to polyacetylene parents, both **CH3PA6OPr** and **CH3PA6CN** showed a narrower energy gap. This demonstrated that the electrical conductivities of polyacetylenes could be enhanced by attaching appropriate pendants to the conjugated polyene backbones.

disubstituted polyacetylenes, liquid crystallinity, phase transition, photoluminescence

## 1 Introduction

Conjugated polymers are quintessential materials for the "plastic electronics" revolution and have been extensively studied for their potential applications in light-emitting diodes, electrochemical cells, field effect transistors, lasers, and photovoltaic cells [1–6]. Liquid crystalline (LC) materials play a significant role in the modern optical display systems and show a variety of characteristic properties in the application of electric and magnetic fields [7, 8]. Combination of the anisotropic properties of liquid crystals with conjugated polymers' properties may endow new materials with novel functional properties, which are promising can-

didates as high-performance engineering materials. Inspired by these prospects, a variety of LC conjugated polymers have been widely investigated because they are of both theoretical and practical interest [9–11]. In particular, a large number of monosubstituted polyacetylenes (PAs) and some disubstituted PAs containing LC groups in their side chains have been considered with growing interest due to their excellent properties and their optical and electrical properties are expected to be controlled by the molecular orientation of the LC side chain [12–16].

Despite the fascinating functionalities, monosubstituted polyacetylenes, however, still suffer from the instability problem during storage, especially when they were in the solution state. The polymers could be readily oxidized when the solutions are exposed to air without the protection of nitrogen [13]. This has seriously restricted the scope of their

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potential technological applications. In sharp contrast to monosubstituted PAs, disubstituted PAs possess many advantages: high thermal stability, good film forming, mechanically strong and excellent luminescence [17-19]. Terphenyl is not only an efficient chromophore but also a good mesogenic core. It has been widely employed in constructing low molecular mass gelators and optically helical polymers [20–22]. Melding of optically active terphenyl mesogenic cores with electronically active PAs at the molecular level may endow liquid crystalline polyacetylenes (LCPAs) with both optical and electronic activities. The spontaneous orientation and luminescent property of the terphenyl mesogens might result in polymers with excellent photoelectric properties. Attachment of the chromophoric and mesogenic terphenyl pendants onto the disubstituted polyacetylene backbones may further enhance their fluorescence quantum yields through the energy transfer from the pendant to the backbone.

In our previous work, we synthesized a group of monosubstituted PAs containing terphenyl mesogenic pendants and found that the polymer with one methylene spacer was nonmesomorphic, while the polymer with six methylene units showed good mesomorphism and better luminescence property (Chart 1) [23]. In other words, the long spacer is good for both mesomorphism and luminescence of PAs bearing terphenyl pendants. Although it is challenging to synthesize and even polymerize disubstituted PAs. Attracted by the potential of generating new functional polymers with enhanced emissions, good mesomorphic and excellent heat stable properties, we decided to extend our investigations and take the challenge to design and synthesize disubstituted PAs containing terphenyl pendants with six methylene spacers and different terminal groups. We found that structural variations exhibit much influence on the liquid crystallinity behaviors and the optical properties of the polymers CH3PA6CN and CH3PA6OPr. The luminescence and thermal stabilities of CH3PA6CN and CH3PA6OPr were better than those of monosubstituted PAs with terphenyl mesogenic pendants.





#### 2 Experimental

## 2.1 Materials

4-Bromo-4'-hydroxybiphenyl, WCl<sub>6</sub>, Ph<sub>4</sub>Sn, n-butyllithium

(2.2 M in hexane, packaged under argon in resealable), and tetrakis(triphenylphosphine)palladium(0) were purchased from Alfa Aasar. Trimethyl borate, 4-bromobenzonitrile, sodium acetylide, and 1,6-dibromehexane were purchased from Aldrich, and used as received. 4-Iodophenol (Aladdin), 1-bromopropane (Aladdin), and CH<sub>3</sub>I were prepared in our laboratory. Tetrahydrofuran (THF) was dried over sodium and then distilled under nitrogen. Other chemicals were obtained from Shanghai Reagent Co. Ltd., and used as received.

#### 2.2 Methods

The infrared (IR) spectra were recorded on a Shimadzu IR-Prestige-21 Fourier transform infrared (FTIR) spectrophotometer by drop-casting sample solutions on KBr substrates. The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR and Bruker AV 600 NMR spectrometer with deuterated chloroform or THF or DMSO as the solvent and with tetramethylsilane ( $\delta = 0$ ) as the internal standard. Thermogravimetric analysis (TGA) was performed on a TA Q600 SDT for thermogravimetry at a heating rate of 10 °C/min under nitrogen with a sample size of 8-10 mg. Texture observations by polarizing optical microscopy (POM) were carried out with a Nikon E600POL polarizing optical microscope equipped with an Instec HS 400 heating and cooling stage. Differential scanning calorimetry (DSC) was used to determine phase-transition temperatures on a SHIMADZU DSC-60 differential scanning calorimeter with a constant heating/cooling rate of 10 °C/min. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ( $\lambda = 1.54$  Å) and at a scanning rate of 1°/min. The UV spectra of the samples were recorded on a Hitachi UV-2300 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Shimadzu RF-5301 PC with a xenon lamp as the light source. The gel permeation chromatography (GPC), i.e., size-exclusion chromatography (SEC) analysis, was conducted with a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm  $\times$  300 mm, 10<sup>3</sup> + 10<sup>4</sup> Å), to separate molecular weight (MW) ranging from  $10^2$  to  $10^6$ . Electrochemical measurements were made carried out in a standard threeelectrode cell by an electrochemical analyzer (CH Instruments, Model CHI660C) using Ag/AgCl, platinum and platinum wires as the reference, working electrode and counter electrode, respectively, with a solution of a polymer  $(10^{-3} \text{ M})$  and Tetra-*n*-butylammonium Tetrafluoroborate (0.1 M) in THF. Elemental analyses (EA) were characterized by means of elemental analysis with Vario Elementar

III. The mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole mass spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas.

#### 2.3 Synthesis of the monomers

The synthesis and structures of the monomers are outlined in Scheme 1.



Scheme 1 Illustration of procedures for synthesis of CH3A6CN, CH3A6OPr, CH3PA6CN and CH3PA6OPr.

#### 8-Bromo-1-octyne

To a two-necked 250 mL flask equipped with a nitrogen inlet, a pressure-equalized dropping funnel, and a magnet stirrer were added 30 mL of DMF and 1, 6-dibromohexane (65 g, 0.27 mol). The mixture was heated to 40 °C, and a solution of sodium acetylide (22 g, 18 wt% in xylene, 0.08 mol) was added slowly over a period of 20 min. After the reaction mixture was refluxed for 24 h. The formed solid was filtered, and the solvent was evaporated. Vacuum distillation yielded 9.95 g of colorless oily product (60–62 °C/88 Pa). Yield: 66.0%. IR (KBr cm<sup>-1</sup>): v 3301 ( $\equiv$ C–H), 2116 (C $\equiv$ C), 637 ( $\equiv$ C–H bending). <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>, ppm):  $\delta$  3.42 (t, 2H, CH<sub>2</sub>Br), 2.20 (m, 2H, HC $\equiv$ CCH<sub>2</sub>), 1.95 (t, 1H, HC $\equiv$ ), 1.87 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.43–1.54 (m, 6H, CH<sub>2</sub>).

#### 9-Bromo-2-nonyne

The *n*-BuLi (2.2 M in *n*-hexane; 5.0 mL, 11.0 mmol) was added slowly to a solution of 8-bromo-1-octyne (1.89 g, 9.98 mmol) in THF (20 mL) at -78 °C under nitrogen, and the resulting solution was stirred at the same temperature for 1 h. A solution of CH<sub>3</sub>I (1.52 mL, 25.2 mmol) in THF (20 mL) was slowly added to the solution at -78 °C, and the resulting mixture was subsequently warmed to room temperature and stirred overnight. The formed solid was filtered, and the solution was concentrated by rotary evaporator. Vacuum distillation yielded 1.42 g of colorless oily product (100–102 °C/130 Pa). Yield: 69.8 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  3.37 (t, 2H, CH<sub>2</sub>Br), 2.22 (t, 2H, CH<sub>3</sub>C≡ CCH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.78 (t, 3H, CH<sub>3</sub>C≡C), 1.47–1.40 (m, 2H, C≡CCH<sub>2</sub>CH<sub>2</sub>), 1.26–1.16 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br).

#### 4-Iodo-n-propoxybenzene

A mixture of 4-iodophenol 44.00 g (0.20 mol),  $K_2CO_3$  (46.00 g, 0.33 mol) and acetone 200 mL were was added in a 500 mL flask. 40.50 g 1-Bromopropane (0.33 mol) was added dropwise to the stirred refluxing mixture. The stirred solution was heated under reflux for 24 h. The potassium carbonate was filtered off, water was added to the filtrate and the product was extracted two times with diethyl ether. The combined ethereal extracts were washed with water, 5% sodium hydroxide, and dried with anhydrous MgS0<sub>4</sub>. Vacuum distillation yielded 40.90 g of light-yellow oily product (80–82 °C/40 Pa). Yield: 78.0 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.50 (d, 2H, Ar-H, *J*=8.4 Hz), 6.68 (d, 2H, Ar-H, *J*=8.0 Hz), 3.84 (t, 2H, OCH<sub>2</sub>), 1.80 (m, 2H,  $-CH_2CH_3$ ), 1.02 (t, 3H,  $-CH_2CH_3$ ).

#### 4-n-Propoxyphenylboronic acid

1.90 g 4-Iodo-n-proposybenzene (0.0072 mol) and 21 mL of anhydrous THF were added in a 250 mL two-neck flask equipped with a dropping funnel, thermometer, and nitrogen inlet-outlet. The solution was cooled to -78 °C with liquid nitrogen and ethanol. 5.50 mL n-butyllithium (2.2 M in hexane) was added dropwise over 0.5 h to the stirring mixture, with the temperature maintained below -78 °C. B(OCH<sub>3</sub>)<sub>3</sub> (1.86 mL) in 5.20 mL of anhydrous THF was added dropwise to the stirring mixture, with the temperature maintained below -78 °C. The reaction mixture was subsequently warmed to room temperature and stirred overnight. The dilute HCl (8.20 mL) was added over a period of 20 min, and the mixture was stirred for 1 h. The solution was extracted two times with EtOAc and the combined organic layer was dried over MgSO<sub>4</sub> and filtered, and the filtrate was concentrated in vacuum. The crude solid was purified by recrystallization from water to yield a white powder 0.59 g (yield 50.0 %), which was used in the next step without further purification and characterization.

#### 4-Hydroxy-4'-n-propoxy-p-terphenyl

4-Bromo-4'-hydroxybiphenyl (1.64 g, 6.58 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.19 g), 1 M Na<sub>2</sub>CO<sub>3</sub> (9 mL) and toluene (12 mL) were added to a 100 mL three-neck flask under nitrogen atmosphere. 4-n-Propoxyphenylboronic acid (2.70 g, 16.45 mmol dissolved in 18 mL 95% ethanol) was added dropwise over 1 h at 80 °C. The reaction mixture was stirred at the same temperature overnight. The mixture was cooled to room temperature and diluted with chloroform and water to form two phases. The organic layer was separated, dried over MgSO<sub>4</sub>, and filtered and the solvent was distilled with a rotary evaporator. The resulting product was purified by column chromatography (silica gel, dichloromethane/hexane) to yield 1.03 g (51.3%) of white powder. IR (KBr,  $cm^{-1}$ ): v 1351 (CH<sub>3</sub>), 3371 (-OH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.65 (d, 4H, Ar-H, J=8.0 Hz), 7.62 (d, 2H, Ar-H, J=6.4 Hz), 7.46 (d, 2H, Ar-H, J=6.4 Hz), 7.32 (d, 2H, Ar-H, J= 4.4 Hz ), 6.83 (d, 2H, Ar-H, J=8.4 Hz), 4.91 (s, 1H, OH), 3.96 (t, 2H, OCH<sub>2</sub>, J = 4.4 Hz ), 1.76 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>, J =4.4 Hz), 0.96 (t, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J = 6.4 Hz).

## 4-Cyanophenylboronic acid

1.82 g 4-Bromobenzene carbonitrile (0.010 mol) and 100 mL of anhydrous THF were added in a 250 mL two-neck flask equipped with a dropping funnel, thermometer, and nitrogen inlet-outlet. The solution was cooled to -78 °C with liquid nitrogen and ethanol. 21.10 mL n-BuLi (2.2 M in hexane) was added dropwise over 0.5 h to the stirring mixture, with the temperature maintained below -78 °C. B(OCH<sub>3</sub>)<sub>3</sub> (7.44 mL) in 21.00 mL of anhydrous THF was added slowly to the stirring mixture, with the temperature maintained below -78 °C. The reaction mixture was subsequently warmed to room temperature and stirred overnight. 40.20 mL dilute HCl was added dropwise, and the mixture was stirred for 1 h. The solution was extracted two times with Et<sub>2</sub>O, washed with water, dried over MgSO<sub>4</sub> and filtered, and the solvent was evaporated to yield a white powder. The powder was dissolved in THF, precipitated in hexane, and filtered to yield 1.36 g white powder (yield 75.1%), which was used in the next step without further purification and characterization.

#### 4-Hydroxy-4'-cyano-p-terphenyl

This compound was obtained using a method similar to that described for 4-hydroxy-4'-*n*-propoxy-p-terphenyl. Quantity used: 4-bromo-4'-hydroxybiphenyl (1.64 g, 6.58 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.19 g), 1 M Na<sub>2</sub>CO<sub>3</sub> (9 mL), toluene (12 mL) and 4-cyanophenylboronic acid (1.34 g, 0.0085 mol dissolved in 9 mL 95% ethanol). The resulting product was purified by column chromatography (silica gel, dichloromethane/

hexane). Yield: 52.1 % (white powder). IR (KBr, cm<sup>-1</sup>):  $\nu$  2230 (C=N), 3351 (–OH). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.73 (d, 4H, Ar-H, J = 8.0 Hz), 7.65 (d, 4H, Ar-H, J = 6.4 Hz), 7.53 (d, 2H, Ar-H, J = 6.8 Hz), 6.93 (d, 2H, Ar-H, J = 8.4 Hz ), 4.91 (s, 1H, OH).

#### 9-[(4'-n-Propoxy-4-terphenyl)oxy]-2-nonyne

A Schlenk flask was charged with 1.52 g 4-hydroxy-4'-npropoxy-p-terphenyl (0.0050 mol), 1.52 g 9-bromo-2-nonyne (0.0075 mol), 1.12 g anhydrous potassium carbonate (0.012 mol), KI (0.083 g, 0.5 mmol) and 75 mL acetone. The mixture was refluxed at 75 °C for 24 h under nitrogen atmosphere. After the mixture was cooled to room temperature, the solution was filtered off, and the filtrate was evaporated. The crude product was purified by column chromatography (silica gel, dichloromethane/hexane) to yield 1.52 g of pale yellow solid (yield: 71.2%, mp 182-184 °C). IR (KBr, cm<sup>-1</sup>):  $\nu 2070$  (C=C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ 7.60 (d, 4H, Ar-H, J = 5.2 Hz), 7.56 (d, 4H, Ar-H, J = 8.0Hz), 6.98 (d, 4H, Ar-H, J = 6.4 Hz), 4.02 (m, 4H, OCH<sub>2</sub>), 1.85–1.78 (t, 5H,  $-CH_2C \equiv CCH_3$ ), 1.51–1.28 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>, −CH<sub>2</sub>CH<sub>2</sub>C≡CCH<sub>3</sub>), 1.08–1.04 (m, 4H, OCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.89 (t,3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  158.81 (aromatic carbon linked to OCH<sub>2</sub>), 139.21 (terphenyl core carbons), 133.20 (terphenyl core carbons), 128.25 (aromatic carbon meta to OCH<sub>2</sub> and terphenyl core carbons), 127.97 (aromatic carbon para to OCH<sub>2</sub>), 114.92 (aromatic carbon orth to OCH<sub>2</sub>). MS (CI): m/e 425.1 [(M<sup>+</sup>), calcd 426. Anal. calcd for C<sub>30</sub>H<sub>34</sub>O<sub>2</sub>: C, 84.51; H, 7.98. Found: C, 84.62; H, 8.02.

#### 9-[(4'-Cyano-4-terphenyl)oxy]-2-nonyne

This compound was prepared using a method similar to that described for 9-[(4'-n-propoxy-4-terphenyl)oxy]-2-nonyne. Quantity used: 2.71 g 4-hydroxy-4'-cyano-p-terphenyl (0.010 mol), 3.04 g 9-bromo-2-nonyne (0.015 mol), 2.04 g anhydrous potassium carbonate (0.024 mol), KI (0.163 g, 1.0 mmol) and 130 mL acetone. Yellow solid: 2.78 g (yield 70.8%, mp 156–157 °C). IR (KBr, cm<sup>-1</sup>): v 2229 (C=C, C=N). <sup>1</sup>H NMR (400 MHz, THF, ppm):  $\delta$  7.76 (d, 4H, Ar-H, J = 5.6 Hz), 7.65 (d, 4H, Ar-H, J = 8.4Hz), 7.51 (d, 2H, Ar-H, J=6.4 Hz), 6.89 (d, 2H, Ar-H, J=6.4 Hz), 3.91 (t, 2H, OCH<sub>2</sub>), 1.70–1.60 (t, 5H,  $-CH_2C \equiv CCH_3$ ), 1.40 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 1.26–1.18 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>,  $-CH_2CH_2C \equiv CCH_3$ ). <sup>13</sup>C NMR (400 MHz, THF, ppm):  $\delta$ 158.92 (aromatic carbon linked to OCH<sub>2</sub>), 144.45 (aromatic carbon para to CN), 137.52 (terphenyl core carbons), 132.06 (aromatic carbons ortho to CN), 127.24-126.42 (aromatic carbons meta and para to OCH<sub>2</sub>, aromatic carbons meta to CN and terphenyl core carbons), 122.10 ( $-C \equiv N$ ), 119.12 (aromatic carbon ortho to OCH<sub>2</sub>), 114.25 (aromatic carbon linked to CN). MS (CI): *m/e* 391.8 [(M<sup>+</sup>), calcd 393. Anal. calcd for C<sub>28</sub>H<sub>27</sub>ON: C, 85.50; H, 6.87. Found: C, 85.39; H, 6.79.

#### 2.4 Polymerization and characterization

All of the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or an inert atmosphere glovebox (vacuum atmospheres), except for the purification of the polymers, which was carried out in an open atmosphere. A typical experimental procedure for the polymerization of **CH3A6OPr** was as follows.

In the sidearm, 339.0 mg CH3A6OPr (0.8 mmol) was added in a baked 20 mL Schlenk tube with a stopcock. The tube was evacuated under vacuum and flushed with dry nitrogen three times through the sidearm. Freshly distilled THF (2 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 16.0 mg of tungsten (VI) chloride and 17.5 mg of tetraphenyltin in 2 mL of THF. The two tubes were aged at 60 °C for 15 min and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 °C under nitrogen for 24 h. The solution was then cooled to room temperature, diluted with 5 mL of chloroform, and added dropwise to 500 mL of acetone through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered with a Gooch crucible. The polymer was washed with acetone and dried in a vacuum oven to a constant weight.

#### CH3PA60Pr

White powder: yield 82.5%. <sup>1</sup>H NMR (400 MHz, THF, ppm):  $\delta$  7.50 (d, 4H, Ar-H, *J*=5.6 Hz), 7.44 (d, 4H, Ar-H, *J*=7.2Hz), 6.86–6.69 (d, 4H, Ar-H, *J*=6.4 Hz), 3.90 (m, 4H, OCH<sub>2</sub>), 1.71–1.62 (t, 5H, –CH<sub>2</sub>C=CCH<sub>3</sub>), 1.40 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>C, –CH<sub>2</sub>CH<sub>2</sub>C=CCH<sub>3</sub>), 1.22–1.18 (m, 4H, OCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.95 (t, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, THF, ppm):  $\delta$  158.51–157.02 (aromatic carbon linked to OCH<sub>2</sub>), 138.95 (terphenyl core carbons), 132.56–131.34 (terphenyl core carbons and CH<sub>3</sub>C=C), 127.05 (aromatic carbon meta to OCH<sub>2</sub> and terphenyl core carbons), 126.07–125.98 (aromatic carbon para to OCH<sub>2</sub> and CH<sub>3</sub>C=C), 115.06–114.18 (aromatic carbon orth to OCH<sub>2</sub>). Anal. calcd for (C<sub>30</sub>H<sub>34</sub>O<sub>2</sub>)<sub>n</sub>: C, 84.51; H, 7.98. Found: C, 84.47; H, 7.90.

## CH3PA6CN

White powder: yield 83.4 %. IR (KBr, cm<sup>-1</sup>): v 2230 (C=N). <sup>1</sup>H NMR (400 MHz, DMSO, ppm):  $\delta$ 7.82–7.78 (d, 4H, Ar-H, *J*=8.0 Hz), 7.67–7.64 (d, 4H, Ar-H, *J*=6.4 Hz), 7.62 (d, 2H, Ar-H, *J*=6.4 Hz), 7.02 (d, 2H, Ar-H, *J*=8.4 Hz), 4.01 (t, 2H, OCH<sub>2</sub>), 1.76–1.72 (t, 5H, –CH<sub>2</sub>C=CCH<sub>3</sub>), 1.46–1.42 (m, 2H,OCH<sub>2</sub>CH<sub>2</sub>), 1.24 (m, 6H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (600 MHz, THF, ppm):  $\delta$  154.48 (aromatic carbon linked to OCH<sub>2</sub>), 141.02 (aromatic carbon para to CN), 135.15 (terphenyl core carbons and CH<sub>3</sub>C=C),

132.05 (aromatic carbons ortho to CN), 126.90–126.42 (aromatic carbons meta to OCH<sub>2</sub>, aromatic carbons meta to CN and terphenyl core carbons), 118.13 ( $-C \equiv N$  and C=*C*CH<sub>3</sub>), 115.32 (aromatic carbon ortho to OCH<sub>2</sub>). Anal. calcd for (C<sub>28</sub>H<sub>27</sub>ON)<sub>n</sub>: C, 85.50; H, 6.87. Found: C, 85.61; H, 6.92.

## 3 Results and discussion

#### 3.1 Synthesis of the monomers

Scheme 1 illustrates the synthetic routes for the monomers CH3A6CN and CH3A6OPr. CH3A6OPr was synthesized as follows. First, 4-iodo-*n*-propoxybenzene was prepared by the reaction of 4-iodophenol with the corresponding 1-bromopropane using K<sub>2</sub>CO<sub>3</sub> as a catalyst. 4-n-propoxyphenylboronic acid was obtained by 4-iodo-n-propoxybenzene, n-BuLi (2.2 M in hexane) and B(OCH<sub>3</sub>)<sub>3</sub> in 50.0% yield. 4-Hydroxy-4'-n-propoxy-p-terphenyl was prepared between 4-bromo-4'-hydroxybiphenyl and 4-n-propoxyphenylboronic acid using tetrakis(triphenylphosphine)palladium (0) as the catalyst by the Suzuki coupling reaction. 8-Bromo-1-octyne was prepared by the etherification of 1,6-dibromohexane with sodium acetylide in DMF. 9-Bromo-2-nonyne was also obtained by the etherification reaction. 4-Hydroxy-4'-n-propoxy-p-terphenyl was transformed to CH3A6OPr 9-[(4'-n-propoxy-4-terphenyl)oxy]-2-nonyne by the etherification reaction with 9-bromo-2-nonyne in the presence of a mixture of K<sub>2</sub>CO<sub>3</sub>, KI and acetone. CH3A6CN was prepared using a procedure similar to that described for CH3A6OPr. The intermediates and the final monomers were confirmed by FT, IR, and NMR. All the terphenyl-containing hexyloxy spacer monomers showed good solubility in common solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, and DMSO. An IR spectrum of CH3A6OPr and its corresponding polymer is shown in Figure 1 as an example. A peak at about 2070 cm<sup>-1</sup> associated with C=C stretching vibrations was observed in CH3A6OPr, which disappeared



Figure 1 IR spectra of (a) CH3A6OPr and (b) CH3PA6OPr.

in the IR profile of **CH3PA6OPr**. The disappearance of the acetylene absorption band in the spectrum of **CH3PA6OPr** indicates that the triple bonds have been transformed to the polyene double bonds.

#### 3.2 Synthesis of the polymers

Transition-metal compounds  $TaCl_5$  and  $NbCl_5$  are the most widely used catalysts for the polymerization of disubstituted acetylenes [24]. However, because of the "toxic" interactions of the ester and ether functional groups with the transition metal mixtures, these transition-metal catalysts are often found to be ineffective for the polymerization of substituted acetylene monomers containing polar functional groups, such as ester and ether units [25–26].

The polar cyano functional group is known to be "toxic" to the classical metathesis catalysts for acetylene polymerization [27–30]. Therefore, it is challenging to polymerize disubstituted acetylenes containing polar functional groups.

However, Tang et al. found that the transition metal initiator WCl<sub>6</sub>-Ph<sub>4</sub>Sn could be an effective catalyst for the polymerization of substituted acetylenes with polar cyano groups or ester units [13, 14, 31–33]. We thus attempted to polymerize **CH3A6OPr** in the presence of WCl<sub>6</sub>-Ph<sub>4</sub>Sn at 60 °C for 24 h, using THF as the solvent, which yielded a polymer with a moderate molecular weight in > 80% yield. **CH3A6CN** was also polymerized under similar conditions. The polyacetylenes **CH3PA6OPr** and **CH3PA6CN** polymerized by WCl<sub>6</sub>-Ph<sub>4</sub>Sn showed narrow polydispersities with moderate molecular weights (shown in Table 1) (weight-

Table 1 Molecular weights of the polymers

Polymers	$M_{\rm n}$	$M_{ m w}$	MWD <sup>a)</sup>	DP <sup>b)</sup>
CH3PA6OPr	7300	8200	1.12	17.1
CH3PA6CN	7400	8600	1.16	18.8
	1 1.1.1	( 1) ( <sup>2</sup> 1) E		1

a) MWD, molecular weight distribution; b) DP, degree of polymerization calculated by  $M_n$ /mru (mru, molecular weight of the molecular repeat unit).

average molecular weight  $M_w = 8200$  and number-average molecular weight  $M_n = 7300$  for CH3PA6OPr;  $M_w = 8600$  and  $M_n = 7400$  for CH3PA6CN).

#### 3.3 Structural characterization

The intermediates, monomers and the final purified polymerization products gave satisfactory spectroscopic data corresponding to their expected molecular structures (see Experimental Section for details). CH3A6OPr exhibited a weak absorption at 2070 cm<sup>-1</sup> which is assignable to the  $C \equiv C$  stretching vibrations and completely vanished in the spectrum of its polymer (Figure 1(b)). The disappearance of the acetylene absorption band in the spectrum of CH3PA6OPr implies that the triple bonds have been transformed to the polyene double bonds after polymerization. Figures 2 and 3 depict the <sup>1</sup>H NMR spectra of CH3A6OPr (in CDCl<sub>3</sub>-d), **CH3PA6OPr** (in THF- $d_6$ ), **CH3A6CN** (in THF- $d_6$ ) and **CH3PA6CN** (in DMSO- $d_6$ ) All the resonance peaks could be well assigned and no other unexpected signals are observed in the <sup>1</sup>H NMR spectra of the polymers and monomers, demonstrating that the molecular structures of the polymers are indeed CH3PA6OPr and CH3PA6CN (shown in Chart 1). The structures of the monomers and the corresponding polymers were further characterized by <sup>13</sup>C NMR (Figures 4 and 5). While the acetylenic carbon atoms of **CH3A6OPr** resonate at  $\delta$  75.1 and 67.9. These peaks were totally absent in the spectrum of CH3PA6OPr. Because of the transformation of the acetylenic triple bonds to the olefinic double bonds by the acetylene polymerization, the resonance peaks of the acetylenic methyl carbons ( $CH_3C \equiv C$ ) at  $\delta$  6.79 and the propargyl carbon ( $\equiv$ C–*C*H<sub>2</sub>) at  $\delta$  19.2 all vanished (Figure 4). As in CH3PA6CN, after polymerization the resonant peaks of acetylene carbon atoms centered at  $\delta$  75.0 and 65.2 ppm disappeared completely. The peaks



Figure 2<sup>-1</sup>H NMR spectra of (A) CH3A6OPr (in CDCl<sub>3</sub>-d), and (B) its polymers CH3PA6OPr (in THF-d<sub>6</sub>).



Figure 3 <sup>1</sup>H NMR spectra of (A) CH3A6CN (in THF-*d*<sub>6</sub>), and (B) its polymers CH3PA6CN (in DMSO-*d*<sub>6</sub>).



Figure 4 <sup>13</sup>C NMR spectra of CH3A6OPr (in CDCl<sub>3</sub>-d), and its polymers CH3PA6OPr (in THF-d<sub>6</sub>).



Figure 5 <sup>13</sup>C NMR spectra of CH3A6CN (in THF-*d*), and its polymers CH3PA6CN (in THF-*d*<sub>6</sub>).

at  $\delta$  6.54 and 18.5, which are assignable to acetylenic methyl carbons and the propargyl carbon in **CH3A6CN**, vanished in the figure of **CH3PA6CN** (Figure 5). However, the absorptions of the olefinic carbons of the polyene backbone in **CH3PA6OPr** and **CH3PA6CN** cannot be readily observed owing to their overlapping with those of the terphenyl carbons. The NMR and IR results discussed above are enough to demonstrate that the acetylene triple bond has been consumed by the polymerization reaction.

#### 3.4 Thermal stability and liquid crystallinity

As shown in Figure 6, all the polymers possess good thermal stability. **CH3PA6CN** and **CH3PA6OPr** showed a 5% weight loss at 336 and 316 °C, respectively. The combination of terphenyl pendants with the polyacetylene backbone has apparently enhanced the resistance of the polymer to thermolysis, which is ascribed to that the terphenyl pendants may have well wrapped the polyacetylene backbones plus the additional shielding effect contributed by the methyl directly linked to the polyene backbone, thus protecting them from the attack by the degradative species.

Figure 7 shows the POM microphotographs of the mesomorphic textures of the monomers and their polymers **CH3PA6OPr** and **CH3PA6CN**. All the monomers and polymers exhibited enantiotropic liquid-crystalline optical anisotropy. When **CH3A6OPr** is cooled from the isotropic state to 210 °C, many anisotropic entities are formed but their development into the focal conic texture of SmA phase is very difficult. Upon cooling **CH3A6CN** to 198 °C, anisotropic entities with birefringent textures were formed, but the exact nature of the mesophase is also problematic to identify. With the aid of X-ray diffraction (XRD) measurements, the textures of **CH3A6OPr** and **CH3A6CN** are assignable to SmA (discussed later). Upon cooling **CH3PA6OPr** from the isotropic state, many small bâtonnets started to emerge from the dark background. The bâtonnets grew to



Figure 6 TGA thermograms of CH3PA6CN and CH3PA6OPr recorded under nitrogen at a heating rate of 10 °C/min.



**Figure 7** Mesomorphic textures observed upon cooling (a) **CH3A6OPr** to 210 °C, (b) **CH3A6CN** to 198 °C, (c) **CH3PA6OPr** to 235 °C, (d) **CH3PA6CN** to 238 °C from their isotropic melts.

bigger larger domains when the polymer was fur ther cooled, resulting in the formation of a typical focal conic fan texture of SmA phase. The cousin polymer **CH3PA6CN** with different tails shows focal-conic fan smectic phase (Figure 7(d)). Small optically anisotropic entities emerged from the dark background of the isotropic liquid when the **CH3PA6CN** was cooled to the anisotropic state, suggesting that **CH3PA6CN** was better packed than its homologous monomer **CH3A6CN**. The polymer chain plays a constructive role in the alignment and packing of the mesogenic pendants [12, 34].

Differential scanning calorimetry (DSC) measurements were carried out to evaluate the thermal transition temperatures. Figure 8 shows the DSC thermograms of monomers and polymers under nitrogen during the first cooling and the second heating scans at a rate of 10 °C/min. The isotropization transition and melting temperature of CH3A6OPr in the first cooling curve were observed at 227.4 and 185.1 °C, respectively. The associated k-SmA and SmA-i transitions were discovered at 196.1 and 231.4 °C, respectively. The thermogram recorded in the first cooling scan of CH3PA6OPr displays a sharp exothermic peak associated with the i-SmA transition at 240.3 °C, and a strong exothermic peak appeared at 225.3 °C associated with the SmA-g transition. In the second heating profile, two transitions were found at 230.3 and 251.3 °C. CH3PA6CN enters the SmA mesophase from its isotropic state at 256.7 °C and the mesophase is stable in a wide temperature range over 86.6 °C. The corresponding g-SmA and SmA-i transitions are detected at 175.1 and 279.5 °C in the second heating profile. The DSC thermogram of CH3A6CN exhibits two broad endothermic peaks at 157.1 and 250.6 °C in the second heating cycle, and the i-SmA and SmA-k transitions are detected at 229.6 °C and 155.6 °C, respectively. The polymer



Figure 8 DSC thermograms of mesomorphic monomers and polymers recorded under nitrogen during the (a and c) first cooling and (b and d) second heating scans at a scan rate of 10 °C/min.

with polar cyano tail **CH3PA6CN** undergoes an enantiotropic SmA transition over a wide temperature range (103 °C), but its counterpart with less polar n-propoxy tails **CH3PA60Pr** goes through enantiotropic SmA<sub>d</sub> transition in a much narrower temperature range (21 °C), which may be attributed to the former with polar cyano stabilizing the ordering of the mesogenic groups.

In order to gain more information on the mesomorphic structures and molecular packing arrangements in the mesomorphic phases of the monomers and polymers, the XRD thermograms of the monomers and polymers are shown in Figure 9. The monomer CH3A6CN shows an XRD pattern consisting of two broad low-angle peaks and several high angle peaks. The broad peak in the low angle indicates that CH3A6CN was not well packed in the mesophase, which was in agreement with the broadness of its transition peaks (Figure 8(d)) and the difficulty in growing the anisotropic fine textures into large-size textures upon further cooling (cf., Figure 7(b)). The broad low angel centered at  $2\theta =$ 3.34° gives a spacing  $d_1 = 26.46$  Å, which is shorter than the fully extended molecular length of the monomer unit (l =30.39 Å), but close to that of the unit containing the cyanoterphenyl and -(CH<sub>2</sub>)<sub>4</sub>O- groups. According to Tang's study [12], the CH3A6CN forms a monolayer SmA structure. The diffractogram of CH3A6OPr exhibits strong



Figure 9 X-ray diffraction patterns of the mesogenic polyacetylenes and monomers quenched with liquid nitrogen from their liquid crystalline states.

reflections at low and high angles. The *d* spacing derived from the low-angle  $(2\theta = 2.68^{\circ})$  peak is 32.97 Å, which is close to the calculated mesogenic length for the repeat unit of **CH3A6OPr** at its most extended conformation (32.34 Å). The peak at high angle  $2\theta = 19.90^{\circ}$  gives an average distance (d<sub>5</sub>) of 4.46 Å (Table 2) associated with the lateral packing arrangement of the pendants. The **CH3A60Pr** 

Compounds	<i>T</i> (°C)	$d_1(\text{\AA})$	$d_2$ (Å)	$d_3$ (Å)	$d_4(\text{\AA})$	$d_5$ (Å)	l (Å) <sup>b)</sup>	Ratio $(d_1/l)$	Phase
CH3A6CN	195	26.46	18.15	4.33			30.39	0.87	SmA
CH3PA6CN	236	18.04	8.33	4.35			26.76	0.67	SmA
CH3A6OPr	208	32.97	26.46	11.78	5.92	4.467	32.34	1.02	SmA
CH3PA6OPr	234	35.77	25.11	13.08	5.96	4.48	28.71	1.25	$SmA_d$

Table 2 X-ray diffraction analysis data of CH3A6CN, CH3PA6CN, CH3A6OPr and CH3PA6OPr <sup>a)</sup>

a) The mesophases in the liquid crystalline states at given temperatures were frozen by rapid freezing with liquid nitrogen. b) Calculated from molecular length of monomers in their fully extended conformations.

shows a monolayer structure of the SmA phase. CH3PA6OPr shows a sharp reflection in the low-angle region  $(2\theta = 2.47^{\circ})$ corresponding to a layer spacing of 35.77 Å, which is in considerable excess of the molecular length (28.71 Å). The mesophase in CH3PA6OPr thus involves a bilayer SmA<sub>d</sub> packing arrangement, in which the n-propoxy tails are interdigitated in an antiparallel fashion (shown in Figure 10). The mesogen pendant of CH3PA6OPr was packed so regularly that a very steep reflection at  $2\theta = 6.75^{\circ}$  ( $d_3 =$ 13.08 Å) was detected. It may be associated with the ordering of the terphenyl cores (d = 11.78 Å), because its homogenous monomer CH3A6OPr has a similar peak at  $2\theta$ =  $7.50^{\circ}$  ( $d_3 = 11.78$  Å). However, the polymer with cyano tail CH3PA6CN displays Bragg reflections at low and high angles. The intense reflection at the low angle  $2\theta = 4.89^{\circ}$  is associated with a layer spacing of  $d_1 = 18.04$  Å, which is shorter than the molecular length (26.76 Å). The mesophase in CH3PA6CN thus involves a monolayer packing arrangement. The molecular structures for polymers CH3PA6OPr and CH3PA6CN are almost identical, except for that the former and latter have n-propoxy and cyano tails, respectively. This seemingly subtle structural difference exhibits much influence on the layer structures and the arrangements of mesogenic packing in liquid crystalline polyacetylenes, with the former ordered in a bilayer structure in an interdigitated fashion, namely, interdigitated smectic A phase (SmA<sub>d</sub>), while the latter packs in a monolayer structure.

#### 3.5 Electronic absorption and photoluminescence

The UV spectra of the monomers and polymers are given in Figure 11. **CH3A6OPr** and **CH3A6CN** exhibit strong K-band of the terphenyl mesogen pendants at 308 and 319 nm and



Figure 10 Smectic layer structure of CH3PA6OPr.



Figure 11 UV spectra of THF solutions of the monomers and the mesogenic polyacetylenes.

no absorptions were detected in the long wavelength region. Polymers CH3PA6OPr and CH3PA6CN absorb UV light strongly at 320 and 322 nm, indicating that the absorptions are ascribed to the mesogen pendants. However, the polyene backbone absorptions of the polymers CH3PA6OPr and CH3PA6CN are not strong. Tang reported that the polyene backbone absorptions of polymers -{[CH<sub>3</sub>C=C(CH<sub>2</sub>)<sub>m</sub>OCObiphenyl-O(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>] $_{n}$ -, m = 4,9 were very weak [32]. This suggests that the UV absorptions of CH3PA6OPr and CH3PA6CN are consistent with those of Tang's. The low absorptivity of the polyacetylenes main chain in the UV spectra may be due to the steric effect of the bulky methyl group directly linked to the polyene backbone, which twists the double bonds and reduces the effective conjugation length along the main chain. The attachment of mesogenic and chromophoric pendants to the polyacetylene backbone may enhance their quantum yields and find unique technological applications [35]. We thus investigated the fluorescence properties of the polymers and monomers in THF solutions and the polymer films at different temperatures (Figure 12). When CH3A6OPr and CH3A6CN are photoexcited at 330 nm, they emit strong UV light at 361 and 410 nm. The UV light emitting bands of their corresponding polymers CH3PA6OPr and CH3PA6CN are shifted to the longer regions with the higher intensity than those of the monomers CH3A6OPr and CH3A6CN. It suggests that the UV light emission originated from the polyene backbone and the terphenyl mesogen pendants. The fluorescence



Figure 12 Photoluminescence spectra of (a) the monomers and the mesogenic polyacetylenes in THF solutions (0.05 mM) and (b) the polymers frozen with liquid nitrogen from their liquid crystalline state and its solid thin films at room temperature.

quantum of the famous highly luminescent disubstituted polyacetylene poly(1-phenyl-1-octyne) {PPO;  $-[(C_6H_5)C=$  $C(C_6H_{13})]n-\}$  was 43 % when its polyene backbone was photoexcited at 355 nm. Compared to the well-known luminescent polymer PPO, both CH3PA6OPr and CH3PA6CN show higher photoluminescence quantum yields when induced at 330 nm. By using quinine sulfate dihydrate as the reference, the emission efficiency of CH3PA6CN was calculated to be 74 %, which is much higher than that of CH3PA6OPr (60 %) by the 330 nm excitation. The fluorescence quantum yield of CH3PA6CN is slightly higher than that of the polymer  $-\{[CH_3C=C(CH_2)_4OCO\text{-biphenyl-}$  $O(CH_2)_6CH_3]_n$  (69%) reported by Tang [32]. The quantum yields of CH3PA6CN and CH3PA6OPr are much higher than those of their associated monosubstituted polyacetylenes  $-\{[HC=C(CH_2)_6O\text{-terphenyl-R}]\}_n$ , where R=CN (64%) and R=OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (49%) demonstrating that the fluorescent quantum efficiencies were enhanced by the attachment of the methyl group to the monosubstituted polyene backbone. The photoluminescence spectrum of CH3PA6CN was found to have a red shift of 49 nm with higher intensity than that of CH3PA6OPr. It may be because the terphenyl chromophore pendant of CH3PA6CN was well polarized by the push-pull interaction of the electron-donating hexamethyleneoxy and the electron-accepting cyano. Figure 12(b) shows the photoluminescence (PL) spectra of CH3PA6OPr and CH3PA6CN films frozen from their liquid crystalline state. The PL spectra of CH3PA6OPr and CH3PA6CN films at room temperature are also given in the same figure for comparison. Upon photoexcitation at 330 nm, the UV light emitting bands of CH3PA6OPr and CH3PA6CN films frozen from their liquid crystalline state at 235 °C with liquid nitrogen were stronger and red-shifted compared with their homogenous films at room temperature. This may be because the polymers CH3PA6OPr and CH3PA6CN form ordered smectic phase at 235 °C, making the backbone more coplanar with a better conjugation, thus resulting in the observed hyperchromic effects. Figure 13 shows the fluorescence photo graphs of the monomers and polymers excited by irradiation of UV light of 330 nm, and the pure THF is also given for the purpose of comparison. All the polymers emitted intensely than their monomers. Compared with **CH3PA6OPr**, the emission intensity of **CH3PA6CN** is much stronger. It is in accordance with the results of photoluminescence.

#### 3.6 Electrochemical properties

The electrochemical activities of CH3PA6OPr and CH3PA6CN were analyzed by cyclic voltammetry (CV) in a standard three-electrode cell with a platinum wire counter electrode and an Ag/AgCl reference electrode (Figure 14). The oxidation process corresponds to the removal of charges from the HOMO energy level whereas the reduction cycle corresponds to the electron addition to the LUMO energy level. The oxidation and reduction of CH3PA6OPr and CH3PA6CN showed irreversible waves in all four cases. Irreversible oxidation of the polymers (Figure 14(c) and (d)) occurred at 1.19 and 1.24 V for CH3PA6CN and CH3PA6OPr, respectively. The first reduction peaks of CH3PA6CN and CH3PA6OPr were observed at -0.24 and -0.51 V (vs. Ag/Ag<sup>+</sup>) (shown in Table 3). The electrochemical energy gap (HOMO-LUMO) of the polymers were calculated from the difference in the onsets of the first



Figure 13 The photographs of blue fluorescence of the polymers and monomers in the THF solution and pure THF (right), excited by irradiation of UV light of 330 nm.



Figure 14 Cyclic voltammograms of polymers (a, c) CH3PA6CN and (b, d) CH3PA6OPr measured at a scan rate of 0.1 V/s, vs.  $Ag/Ag^+$  in a  $(C_4H_9)_4$  NBF<sub>4</sub> solution.

Table 3 Electrochemical data for polymers <sup>a)</sup>

Polymers	$E_{1red}(V)$	$E_{2red}(V)$	$E_{1 \text{ox}} (\mathbf{V})$	HOMO (eV) <sup>b)</sup>	LUMO (eV) b)	$Eg (eV)^{c)}$
CH3PA6CN	-0.24 <sup>d)</sup>	$-1.75^{(d)}$	1.19	5.50	4.23	1.27
CH3PA6OPr	-0.51 <sup>d</sup> )	-1.36 <sup>d)</sup>	1.24	5.54	4.14	1.40

a) Experimental conditions are the same as those given in Figure 14. b) HOMO and LUMO values are calculated from the onset of the first peak of the corresponding redox wave,  $E_{\text{LUMO/HOMO}} = E^{\text{onset (red/ox)}} + 4.4 \text{ eV. c}) Eg$  is the LUMO-HOMO energy gap. d) Irreversible peak.

oxidation and reduction peaks. The onset oxidation and reduction potentials were determined by the intersection of the two tangents drawn at the rising current and background charging current of the CV's. The onset reduction potential of the **CH3PA6CN** was -0.17 V, and the corresponding onset potential of the oxidation was 1.10 V (vs. Ag/Ag<sup>+</sup>). The onset reduction and oxidation of **CH3PA6OPr** were at -0.26 and 1.14 V. The HOMO and LUMO energy levels were calculated from the following equation [36–37]:

## $E_{\text{LUMO/HOMO}} = E^{\text{onset (red/ox)}} + 4.4 \text{ eV}$

Using the equation, the electrochemical energy gaps (*E*g) of **CH3PA6OPr** and **CH3PA6CN** were calculated to be 1.40 and 1.27 eV, respectively. An interesting comparison is the electrochemical value of the HOMO-LUMO gap with respect to the optical energy band gap of unsubstituted polyacetylene 1.50 eV (825 nm). Compared to unsubstituted polyacetylene, both **CH3PA6OPr** and **CH3PA6CN** showed

a narrower electrochemical energy gap. It indicates that the electrical conductivities of polyacetylenes were enhanced by introducing the mesogen pendants onto the polyacetylenes backbone.

## 4 Conclusions

In this work, a group of disubstituted acetylene monomers bearing chromophoric and mesogenic terphenyl pendants with different tails were designed and synthesized. The monomers were polymerized by  $WCl_6-Ph_4Sn$  in high yields (>82%). The structural variations on the properties of the monomers and polymers were investigated. All the polymers are thermally stable, irrespective of the type of the tails. The monomers and polymers are all enantiotropic liquid crystalline. The polymers show better developed mesomorphic textures than their associated monomers. This demonstrates that the polyacetylene backbone plays an active role in the alignment and packing of the mesogenic pendants. LC temperature range ( $\Delta T$ ) for the polymer with polar cyano tail **CH3PA6CN** is approximately five times wider than that for the polymer with less polar n-propoxy tail **CH3PA6OPr**. The terminal groups in the structures of **CH3PA6CN** and **CH3PA6OPr** result in a big change in the mesogenic packing: The mesostructure of the former involves a monolayer arrangement, while the mesophase of the latter is associated with a bilayer mesogenic alignment.

The disubstituted polyacetylenes **CH3PA6CN** and **CH3PA6OPr** emitted more strongly than those of their counterpart monosubstituted polyacetylenes, and their quantum yields were enhanced by attaching the methyl substitution. Both **CH3PA6CN** and **CH3PA6OPr** emit UV light with high efficiency ( $\geq 60\%$ ) upon excitation at 330 nm. Polymer **CH3PA6CN** is a better fluorophore than **CH3PA6OPr** because of the push-pull interaction by the electron-donating and the electron-accepting groups of the former. The band gap calculations of the polymers **CH3PA6OPr** and **CH3PA6CN** were lower than that of unsubstituted polyacetylene, showing that the conductivities of polyacetylenes could be increased by the attachment of mesogen pendants onto the polyacetylenes backbone.

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