# Sacha Legrand\*, Milja Hannu-Kuure and Ari Kärkkäinen Design, synthesis, and characterization of 6-[(trimethyl) silylethynyl]naphthalene-2-ethene: a new precursor for the preparation of high-refractive-index organic materials

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**Abstract:** A new polymerizable naphthalene derivative has been designed, prepared, and characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and MS. The new monomer synthesis has successfully been accomplished from a cheap commercially available raw material, in only four steps with good yields. The four steps can be easily scaled up for manufacturing purposes. It is anticipated that the new precursor can be very useful in the preparation of valuable materials with high refractive index for numerous opto-electronic applications.

**Keywords:** high refractive index; monomer; Sonogashira; synthesis; Wittig.

# **1** Introduction

The needs for materials with high-refractive-index (high*n*) values are becoming more and more important. Such polymers, with high optical transparency, are currently required in a wide range of applications, including antireflecting coatings [1], display and opto-electronic devices [2], complementary metal oxide semiconductor image sensors, and micro lens components for charge coupled devices [3], to mention but a few.

Recently, Higashihara and Ueda reviewed macromolecules with high refractivities, together with their application studies [4]. For example, sulfur-containing polyimides [5], poly(arylene sulfide)s [6], polyphenylquinolaxines [7], TiO<sub>2</sub> inverse opal photonic crystals [8], polymer–inorganic hybrid materials [9–12], polyimide hybrids [13], and nanocomposites have been shown to exhibit high-*n* values with good optoelectronic performances [14]. Halogen-containing high-refractive-index polymers can also be found in the literature [15]. However, European Union has limited the use of such halogen-containing materials as microelectronic devices due to their potential pollution of the environment [16]. Polysiloxane polymers also exhibit excellent opto-electronic applications [17]. These hybrid organic–inorganic materials can be easily prepared using the sol-gel process.

Various polymeric materials having a high refractive index, such as thermoplastics for camera, pick-up, projector lenses [18] and thermoset resins for eyeglasses applications [19, 20], are now commercially available. Nevertheless, their manufacturing procedures can be challenging and very laborious. As a result, there is still a high need of developing effective new materials, which can be easily produced with excellent yields and scaled up without major difficulties for commercial purposes.

Herein, we report the design, synthesis, and characterization using <sup>1</sup>H, <sup>13</sup>C NMR, GC, and MS of a new polymerizable monomer, which can be employed in the preparation of very valuable materials having high refractive indices. The target molecule can be synthesized from a cheap commercially available raw material, in only four steps with high yields.

Badur et al. demonstrated the possibility to predict the final refractivity of a polymer based on the refractive indices of its components [21]. Indeed, high-*n* polymers can be designed according to the Lorentz–Lorenz equation (Eq. (1))

$$n = \sqrt{\frac{1 + \frac{2[R]}{V_0}}{1 - \frac{[R]}{V_0}}}$$
(1)

where *n* is the refractive index of the material, [R] the molar refraction, and  $V_0$  the molecular volume of the polymer repeating unit [22]. Therefore, the refractive index value of a polymer should be high when its substituents have high molar refractivities and low molar volumes, such as aromatic rings, halogen atoms (except fluorine), and C=C or C=C bonds [23]. Accordingly, a polymer repeating unit which consists of an aromatic ring substituted with both C=C and C=C bonds should have such property. A suitable example of a precursor containing one naphthalene ring and both C=C and C=C bonds is depicted in Fig. 1.

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**Fig. 1:** Example of a polymer repeating unit with substituents having high molar refractivities and low molar volumes.

Moreover, polymerization of such monomers can easily occur via radical polymerization, since the C=C moiety can react together with an azo-based radical initiator such as 2,2'-azobis(2-methylpropionitrile), 1,1'-azobis (cyclohexanecarbonitrile), 2,2'-azobis(2-methylpropane), or 4,4'-azobis(4-cyanovaleric acid), for example. This type of radical polymerization process has been shown to be very effective in the preparation of macromolecules with high commercial values, such as water-soluble polymers for the paper industry [24-27], polysiloxanes for optoelectronic applications [28, 29], and promising chiral stationary phases for the pharmaceutical industry [30]. However, despite the relative simplicity of the general chemical structure depicted in Fig. 1, the preparation of such precursors and their applications have been poorly reported in the literature. Therefore, there is an urgent need to develop such monomers for valuable applications in organic, polymer, or material chemistry.

### 2 Results and discussion

Our synthesis started with the commercially available ester methyl 6-bromo-2-naphthoate (1), which was treated with diisobutylaluminum (DIBAL) at low temperature (–78°C), giving the corresponding primary alcohol **2** in quantitative yield [31]. Selective oxidation of this primary alcohol in the presence of MnO<sub>2</sub> gave the aldehyde **3** in excellent yield. A Wittig reaction between this aldehyde and Ph.PCH.Br in the presence of the base KO'Bu yielded the vinyl derivative 4 [32]. Finally, the Sonogashira coupling was used to introduce the C=C moiety [33]. The treatment of the bromo derivative 4 with Me,SiC=CH in the presence of the palladium catalyst PdCl,, the co-catalyst CuI, the ligand PPh<sub>2</sub>, and the base triethylamine (TEA) gave the desired target molecule 5 in quantitative yield. The purity of the monomer 5 was found to be >98% according to GC measurements. The main impurity was determined by GC-MS and was found to be Me<sub>2</sub>Si-C=C-SiMe<sub>2</sub>. This impurity was most probably formed by the intermolecular reaction of the radical Me<sub>2</sub>Si-C=C with itself, which was created during the Pd cycle of the Sonogashira coupling mechanism. The general synthetic pathway of 6-[(trimethyl)silylethynyl]naphthalene-2-ethene (5) is shown in Scheme 1.

Importantly, all the steps presented in Scheme 1, the reduction and the oxidation steps, the Wittig reaction, and the Sonogashira coupling, can be easily scaled up for production purposes. The alkyne group present in **5** was not deprotected because of our envisaged applications. The largest possible number of silicon atoms should be present in our polymer backbone made partly from **5** for our opto-electronic purposes. In addition, our composition comprises a siloxane prepolymer with a backbone exhibiting chemical groups, which are capable of being deprotonated in an aqueous base solution. Consequently, it is necessary to keep the alkyne group protected with Si(CH<sub>3</sub>)<sub>3</sub> and to avoid its deprotection during the polymerization process, which would result in a loss of one silicon atom.

It is important to mention that naphthalene derivatives substituted with one or several ethynyl moieties protected



Scheme 1: Reactions condition: (i) DIBAL, THF,  $-78^{\circ}C \rightarrow RT$ ; (ii) MnO<sub>2</sub>, THF, RT; (iii) Ph<sub>3</sub>PCH<sub>3</sub>Br, KO'Bu, THF,  $-20^{\circ}C \rightarrow RT$ ; (iv) PdCl<sub>2</sub>, Cul, PPh<sub>3</sub>, Me<sub>3</sub>SiC=CH, TEA, RT  $\rightarrow$  50°C.



Scheme 2: Reactions condition: (i) PdCl<sub>2</sub>, Cul, PPh<sub>2</sub>, Me<sub>2</sub>SiC≡CH, TEA, RT → 50°C. (ii) TBAF, THF, RT.

with the Si(CH<sub>3</sub>)<sub>3</sub> group can be easily deprotected anyway. A typical example is shown in Scheme 2. The dibromo derivative **6** was first treated with Me<sub>3</sub>SiC=CH in the presence of the palladium catalyst PdCl<sub>2</sub>, the co-catalyst CuI, the ligand PPh<sub>3</sub>, and the base TEA, yielding the di(alkyne)-containing group **7** in excellent yield. Deprotection of the ethynyl moieties in **7** was successfully accomplished after treatment with tetrabutylammonium fluoride (TBAF) at room temperature, yielding 2,6-diethynylnaphthalene (**8**) in good yield.

We are now aiming to use the new monomer **5** with other suitable precursors for the preparation of new valuable polysiloxanes. By using the sol-gel technology and a radical polymerization process, new hybrid organic– inorganic polymers will be prepared in suitable organic solvents. After their deposition (using, for example, spincoating techniques) on specific substrates such as silicon wafers, the resulting films will then be characterized by an ellipsometer in order to determine both the thickness and the refractive properties of the final material [34].

# **3** Conclusion

We report the design, synthesis, and characterization, including <sup>1</sup>H and <sup>13</sup>C NMR, together with MS, of a new polymerizable precursor. By means of GC measurements, we also prove the very high purity of the isolated monomer. We anticipate the high value of this new precursor for the preparation of polymers with high refractivities. Importantly, the preparation of this new monomer can be achieved in good yield and can be easily scaled up for manufacturing purposes. Our current work consists of the preparation, characterization, and applications studies of macromolecules based on the new monomer presented in this study.

# **4** Experimental section

Flash chromatography was performed on silica gel (Merck 60). NMR spectra were recorded on the Bruker DMX

spectrometer (200 MHz for <sup>1</sup>H and 50 MHz for <sup>13</sup>C). CDCl<sub>3</sub> was used as a solvent, and the signal of the solvent served as the internal standard. Chemical shifts were expressed in ppm, followed by their multiplicity (s, singlet; t, triplet; d, doublet; m, multiplet) and number of protons. The mass spectra of positive ions obtained by the electron impact (EI, 70 eV) were measured on the Varian Saturn ws GC-MS instrument. GC measurements were performed using Agilent 6890N apparatus equipped with a TCD detector. The reactions were performed in an inert atmosphere (N<sub>2</sub>). TEA was dried over CaH<sub>2</sub>, and THF was dried over Na/ benzophenone before use. The other starting materials employed were purchased from commercial suppliers and were used without further purification.

#### 4.1 6-Bromonaphthalene-2-methanol (2)

Methyl 6-bromo-2-naphthoate (1) (50 g, 188.6 mmol) was dissolved in THF (350 mL). DIBAL (1.0 M in hexane, 452 mL, 452 mmol) was added dropwise to the reaction mixture at T = -78 °C. The reaction mixture was stirred at T = -78 °C for 1 h and then at room temperature for additional 1 h. The reaction mixture was then cooled to  $T = -30^{\circ}$ C, and MeOH (60 mL) was added dropwise. Potassium sodium tartrate salt (concentrated aqueous solution, 470 mL) was added in portions, and the reaction mixture was stirred at room temperature for 30 min. Then the phases were separated, and the aqueous phase was extracted with EtOAc ( $2 \times 100$  mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtrated. The solvents were evaporated to give 6-bromonaphthalene-2-methanol (2) as a paleyellow solid (44 g, 98%), which was used without further purification in the next step. – <sup>1</sup>H NMR (200 MHz, CDCl.,  $20^{\circ}$ C):  $\delta = 7.91$  (s, 1H, H\_), 7.62–7.25 (m, 5H, H\_), 4.90 (s, 2H, CH<sub>2</sub>O). The spectroscopic data found were in accordance with those published by Gingras and Collet [31].

#### 4.2 6-Bromonaphthalene-2-carbaldehyde (3)

The primary alcohol **2** (2.50 g, 10.5 mmol) was dissolved in THF (50 mL). MnO<sub>2</sub> (4.58 g, 527 mmol) was added in small portions at room temperature, and the reaction mixture was then stirred at this temperature for 24 h in a dark environment. The reaction mixture was then filtered, and the solvent was evaporated to give the corresponding aldehyde **3** (2.20 g, 90%) as a slightly brown solid, which was used without purification in the next step. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 20°C):  $\delta$  = 10.15 (s, 1H, CHO), 8.31 (s, 1H, H<sub>ar</sub>), 8.07 (s, 1H, H<sub>ar</sub>), 8.01–7.96 (app. d, 1H, H<sub>ar</sub>), 7.89–7.82 (dt, 1H, H<sub>ar</sub>), 7.69–7.64 (dd, 2H, H<sub>ar</sub>). The spectroscopic data found were in accordance with those published by Granzhan and Teulade-Fichou [35].

#### 4.3 6-Bromonaphthalene-2-ethene (4)

Ph,PCH,Br (71 g, 199 mmol) was mixed with THF (100 mL). KO'Bu (20.62 g, 184 mmol) was added in small portions and the reaction mixture was stirred at room temperature for 15 min. The reaction mixture was then cooled to T = -20 °C, and the aldehyde **3** (36 g, 153 mmol) dissolved in THF (270 mL) was added dropwise. Then, the reaction mixture was allowed to reach room temperature and was stirred overnight at this temperature. The reaction was then quenched by the addition of deionized water (200 mL). The phases were then separated, and the aqueous phase was extracted with EtOAc (2×150 mL). The combined organic phases were dried over MgSO,, filtrated, and evaporated. The crude product was then purified by flash chromatography on silica gel, using EtOAc-n-hexane (1:4, v/v) as an eluent, to give the ethene-containing compound 4 (25.35 g, 71%) as a slightly yellow solid. –  $^{1}$ H NMR (200 MHz, CDCl<sub>2</sub>, 20°C):  $\delta = 8.10$  (s, 1H, H<sub>2</sub>), 7.76–7.73 (m, 4H, H<sub>a</sub>), 7.66–7.65 (app. d, 1H, H<sub>a</sub>), 7.03–6.89 (dd, 1H, CH<sub>gem</sub>=CH<sub>2</sub>), 6.03-5.94 (d, 1H, CH=CHH<sub>cis</sub>), 5.50-5.44 (d, 1H, CH=CH<sub>trans</sub>H). The spectroscopic data found were in accordance with those published by Fakhouri et al. [36].

### 4.4 6-[(Trimethyl)silylethynyl]naphthalene-2-ethene (5)

The bromo derivative **4** (10 g, 43 mmol) was mixed together with  $PdCl_2$  (187.3 mg, 1.05 mmol), CuI (408.6 mg, 2.1 mmol), and  $PPh_3$  (996 mg, 3.8 mmol). Me\_3SiC=CH (12 mL, 986 mmol) was added at room temperature, followed by TEA (90 mL, 645 mmol). Then, the reaction mixture was stirred at T=50°C overnight. After cooling to room temperature, the solution was filtrated, and the solvents were evaporated to give a brown solid. The crude product was purified by flash chromatography on silica gel, using EtOAc–*n*-hexane (1:4, v/v) as an eluent to give

the target molecule **5** (11 g, 99%) as a slightly orange solid. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 20°C):  $\delta$  = 8.08 (s, 1H, H<sub>ar</sub>), 7.83–7.77 (m, 4H, H<sub>ar</sub>), 7.66–7.65 (m, 1H, H<sub>ar</sub>), 7.03–6.89 (dd, 1H, CH<sub>gem</sub>=CH<sub>2</sub>), 6.03–5.94 (d, 1H, CH=CHH<sub>cis</sub>), 5.50–5.44 (d, 1H, CH=CH<sub>trans</sub>H), 0.42 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si). – <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub> 20°C):  $\delta$  = 136.91, 136.17, 133.29, 132.76, 132.65, 129.04, 128.22, 128.20, 126.38, 124.04 (10×C<sub>ar</sub>), 120.53 (C=CH<sub>2</sub>), 115.00 (C=CH<sub>2</sub>), 105.63 (C=C-Si), 95.00 (C=C-Si), 0.00 ((CH<sub>3</sub>)<sub>3</sub>Si). – MS (EI, 70 eV): *m/z* (%) = 250 (100), 235, 220, 205, 177, 152, 128, 102, 87, 75, 51.

### 4.5 2,6-Bis[(trimethyl)silylethynyl] naphthalene (7)

2,6-Dibromonaphthalene (**6**) (3 g, 10.5 mmol) was mixed together with PdCl<sub>2</sub> (81 mg, 0.45 mmol), CuI (204 mg, 1.05 mmol), and PPh<sub>3</sub> (510 mg, 1.9 mmol). Me<sub>3</sub>SiC=CH (4.36 mL, 31.4 mmol) was added at room temperature, followed by TEA (30 mL, 214 mmol). Then, the reaction mixture was stirred at T=50°C overnight. After cooling to room temperature, the solution was filtrated, and the solvents were evaporated to give an orange solid. The crude product was purified by flash chromatography on silica gel, using EtOAc–*n*-hexane (1:4, *v*/*v*) as an eluent to give the compound **7** (3.05 g, 91%) as a slightly orange solid. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 20°C):  $\delta$ =7.95 (s, 2H, H<sub>ar</sub>), 7.73–7.68 (app. d, 2H, H<sub>ar</sub>), 7.52–7.48 (app. d, 2H, H<sub>ar</sub>), 0.29 (s, 18H, 2×(CH<sub>3</sub>)<sub>3</sub>Si). The spectroscopic data found were in accordance with those published by Yamaji et al. [37].

#### 4.6 2,6-Diethynylnaphthalene (8)

The starting material 7 (3 g, 9.37 mmol) was dissolved in THF (30 mL). TBAF (1.0 м in THF, 28.1 mL) was added dropwise to the reaction mixture at room temperature. The reaction was slightly exothermic, and the color of the reaction mixture changed from deep brown to very dark green. The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated to give very viscous dark oil, which solidified under high vacuum. The crude product was purified by flash chromatography using CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane (1:1, v/v) as an eluent, yielding the deprotected ethynyl-containing naphthalene 8 (1.17 g, 71%) as a slightly orange solid. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>2</sub>,  $20^{\circ}$ C):  $\delta = 8.00$  (s, 2H, H<sub>a</sub>), 7.80–7.70 (app. d, 2H, H<sub>a</sub>), 7.60– 7.52 (app. d, 2H, H<sub>a</sub>), 3.20 (s, 2H, C≡CH). – MS (EI, 70 eV): m/z (%) = 176, 163, 145 (100), 118, 103, 88, 73, 58, 43. The spectroscopic data found were in accordance with those published by Kim et al. [38].

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