

# Synthesis and optical properties of polynaphthalene derivatives

Takeshi Mori, Masashi Kijima\*

Institute of Materials Science, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan. E-mail: kijima@ims.tsukuba.ac.jp

## Abstract

Naphthalene-base conjugated polymers soluble in organic solvents were newly synthesized, and their optical properties were characterized. Three types of homopolymers were synthesized from 1,4-, 1,5- and 2,6-dibromonaphthalene derivatives by the Ni-catalyzed polycondensation. Alternate naphthalene copolymers with 1,4-phenylene were synthesized by Suzuki coupling. In the photoluminescence (PL) spectra, all polymers emitted bluish purple in  $\text{CHCl}_3$ . Especially, 2,6-polynaphthalene derivatives showed high quantum efficiencies ( $\phi_{\text{pl}} = 0.60$  to  $0.96$ ). In the case of thin films, 1,5- and 1,4-linked polynaphthalenes showed PL spectra similar to those in solution, while 2,6-linked polynaphthalenes had PL spectra shifted longer in wavelength than the former, which was due to  $\pi$ -interaction of the stacking naphthalene units between the polymer chains.

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## Introduction

Naphthalene molecules have frequently been taken up as a subject matter of organic semiconductor researches. For instance, solid crystals of naphthalenes are semiconducting material often showing intense photoluminescence, which is due to  $\pi$ -electronic interaction of the molecular stacks. Some stacking naphthalene derivatives such as 1,4,5,8-naphthalenetetracarboxylic dianhydride showed a good carrier mobility [1, 2]. Some thermotropic liquid crystalline naphthalenes such as

2-phenylnaphthalene derivatives have been developed as a switchable organic semiconductor [3]. In this way, the specific function can arise from the  $\pi$ -electronic interaction between the naphthalene cores. On the other hand, the naphthalene unit has been used as a component of  $\pi$ -conjugated copolymers of phenylenevinylene, fluorene, thiophene, carbazole and so on [4-10]. The principal purpose of them was development of an emissive material in organic light emitting diodes. However, these polymers having the naphthalene portion generally showed lower performances than corresponding homopolymers. Poly(naphthylenevinylene) was also synthesized as an analogue of poly(*p*-phenylenevinylene) along this line [11-14]. They showed high quantum efficiency and good solubility, but the emission color was impure due to excimeric effect. In 1983, naphthalene homopolymers with different linkages of 1,4-, 1,5-, 2,6-, and 2,7-positions were synthesized for the first time [15], but the optical and electronic characterization of the polymers were hardly carried out because of their poor solubility. Poly(binaphthyl) analogues are a kind of naphthalene homopolymers soluble in organic solvents [16-18], but they have mostly been considered as asymmetric synthetic tools with their rigid chiral conformations.

We focus again the structure of polynaphthalenes, because they have the rigid planar  $\pi$ -conjugated unit and should have much torsion between the units [19]. These structures cause extensity of the  $\pi$ -conjugation localizing in the unit, which is expected as a blue emitting polymer as polyfluorenes. On the contrary, the luminescence will bathochromically shift if the  $\pi$ -interaction between polynaphthalene chains exists. Thus in this paper, we synthesize some novel polynaphthalenes homopolymers and copolymers that should be soluble in organic solvents to investigate the electronic and optical properties in solution and thin film states.

## **Result and Discussions**

### **Synthesis**

Schemes 1-3 show the synthetic routes of the homopolymers and copolymers of 1,4-, 1,5- and 2,6-naphthalenes. All homopolymers were synthesized by the Ni-catalyzed dehalogenative polycondensation of corresponding dibromonaphthalene (**3**, **5**, **7**) without any end-treatments [20-22]. Similarly, the copolymers were synthesized by Suzuki coupling reaction of dibromonaphthalene with 1,4-benzenediboronic acid ester [23-25]. The polymerization results were summarized in Table 1.

As shown in Scheme 1, the monomer, 1,4-dibromo-2,3-dihexyloxynaphthalene **3** was synthesized by alkylation of 1,4-dibromo-2,3-dihydroxynaphthalene **2** with corresponding bromoalkane according to the procedure previously reported by Williams *et al* [26]. Poly(2,3-dihexyloxy-1,4-naphthalene) (**P14HN**) was attempted to be synthesized by Yamamoto method using Ni(cod)<sub>2</sub> and other Ni-catalyzed methods. However, the reaction was hard to be proceeded in all cases, affording only a slight yield of polymer besides some oligomeric products. The degree of polymerization estimated from the number average molecular weight ( $M_n$ ) was about 6. The low yield and the low molecular weight are due to the steric hindrance of the 2,3-dialkoxy group of the monomer **3**. Copolymerization of **3** with 1,4-benzenediboronic acid ester gave **P14HNP** with better yield than **P14HN**.

The monomer, 1,5-dibromo-4,8-dihexyloxynaphthalene **6**, was similarly prepared from 1,5-dihydroxynaphthalene **4** through alkylation and bromination (Scheme 2) [27]. The Ni-catalyzed polycondensation using NiBr<sub>2</sub> and Zn, which was referred to the paper by Colon *et al* [28], afforded poly(4,8-dihexyloxy-1,5-naphthalene) **P15HN** in the best yield. The increase of the yield than that of **P14HN** is due to absence of large substituents adjacent to the polymerization sites of 1,5-positions. However, steric hindrance of 4,8-alkoxy substituents disturbed formation of high molecular-weight **P15HN**. Copolymerization of **6** with benzenediboronic acid ester gave the better result of polymerization than the homopolymerization.

Lastly, the monomers, 2,6-dibromo-1,5-dialkoxynaphthalenes **8** were synthesized from 2,6-dibromo-1,5-dihydroxynaphthalene **7** through alkylation with corresponding bromoalkane (Scheme

3) according to the procedure previously reported by Segura *et al* [12]. Some homopolymers, poly(1,5-dihexyloxy-2,6-naphthalene) (**P26HN**), poly(1,5-bis(2-ethylhexyloxy)-2,6-naphthalene) (**P26EHN**) and poly(1,5-bis(cyclohexylmethoxy)-2,6-naphthalene) (**P26CyN**) were synthesized by the same method as **P14HN**. In the case of 2,6-polymerizations, the homopolymers and copolymers were obtained in high yields with a good degree of polymerization, which suggested that the monomer **8** was the best choice to obtain soluble conjugated polynaphthalene derivatives.

These polymerization results seem to be associated with conformations of the polymers. A geometry optimization using semiempirical technique (AM1) of polynaphthalene models suggested that the average dihedral angles ( $\phi$ ) of the triads of 1,4-linked 2,3-dimethoxynaphthalene ( $\phi = 85^\circ$ ) and 1,5-linked 4,8-dimethoxynaphthalene ( $\phi = 84^\circ$ ) are larger than that of the 2,6-linked 1,5-dimethoxynaphthalene triad ( $\phi = 47^\circ$ ). In addition,  $\phi$  of the similar model for the copolymers having the naphthalene-benzene-naphthalene sequence is smaller than that of corresponding homopolymers. It is thought that the angular variability of  $\phi$  is an indication for strain of the polymers.

### Optical properties of homopolymers

The optical data of all polymers investigated by UV-Vis absorption and fluorescence spectroscopies are summarized in Table 2. Figure 1 shows the UV-vis absorption and the photoluminescence (PL) spectra of the homopolymers (**P14HN**, **P15HN** and **P26HN**). From the UV-vis absorption spectra in solution and in the solid state, all polymers had an absorption band at around 330 nm due to  $\pi$ - $\pi^*$  transition.

All polymers in  $\text{CHCl}_3$  solution intensely fluoresced bluish purple, and their emission  $\lambda_{\text{max}}$  was about 400 nm. The relative PL intensity and the quantum yield of **P26HN** were highest among the other homopolymers. Since 2,6-polynaphthalenes is expected to have the smallest dihedral angle ( $\phi$ ) between the naphthalene units as described in the previous section, the extended  $\pi$ -conjugation along the polymer main chain might contribute the high PL quantum efficiency as well as conventional emissive

conjugated polymers. From these results, it is considered that the 2,6-linked naphthalene homopolymers are a good candidate for a novel emitting polymer material. In addition, the substitution of the flexible 1,5-dihexyloxy chains by the round bulky substituent of cyclohexylmethoxy was effective for high PL quantum efficiency.

In the case of thin cast films of the homopolymers, **P26HN** had the highest relative fluorescence intensity as expected for the same reason of the extended  $\pi$ -conjugation through the polymer chain. The PL spectra of **P14HN** and **P15HN** in the solid state were similar to those in  $\text{CHCl}_3$ , while that of **P26HN** was considerably shifted longer in wavelength from that in  $\text{CHCl}_3$  (Figure 1b). The redshift and broadening of PL bands caused decreasing color purity of the blue emission in the solid state. This result is considered that poly(2,6-naphthalene)s in the solid state had a specific  $\pi$ -electronic interaction between the polymer chains, which resulted in observation of an absorption edge of the narrow energy gap state ( $E_g=2.6$  eV) besides the usual  $E_g\approx 3.2$  eV as listed in Table 2.

Since the considerable redshift observed for **P26HN** in the thin film state is due to an excimeric radiation, the redshift might be suppressed by increasing steric hindrance between the polymer chains. The relative intensity of the PL band at around 480 nm was decreased and that at around 400 nm was increased for the thin solid films of **P26EHN** and **P26CyN** having a bulky substituent of 2-ethylhexyl and cyclohexylmethyl, respectively (Figure 2). The tendency was more remarkable for **P26EHN** than **P26CyN**, but the PL peak at 480 nm was hardly to vanish away.

### Optical properties of copolymers

Figure 3 shows the UV-vis absorption and the PL spectra of 1,4-, 1,5- and 2,6-naphthalene copolymers including 1,4-phenylene as the alternative component. The UV-vis and PL spectra were similar to those of homopolymers except observation of their slight redshift. It also should be noted that most copolymers showed higher PL quantum efficiency than corresponding homopolymers in  $\text{CHCl}_3$  (Table 2). These are due to an extension of  $\pi$ -conjugation by the copolymerization that can induce

relaxing the steric hindrance between the unit components as stated above in the geometry optimization. Exceptionally, **P26EHNHP** having the 2,5-disubstituted phenylene as the alternative component took almost perpendicular conformation, which resulted in the low quantum yield as well as the fluorene and carbazole copolymers [5, 10]. Among the hexyloxy substituted homopolymers and copolymers, **P26HNP** showed the best performance of PL in terms of the relative intensity and quantum yield in addition to the best polymerization results in terms of the yield and degree of polymerization (Table 1), but the undesired redshift and broadening of the PL spectrum in the film state remain unresolved.

In order to improve purity of the emission blue color in the solid state for **P26HNP**, the side substituent of hexyloxy was replaced by 2-ethylhexyloxy as well as the case for the 2,6-naphthalene homopolymers. The PL spectra of **P26EHNHP** were shown in Figure 4. The main peak was appeared at 390 nm that was almost same as that in solution, and the peak at around 480 nm could be much reduced. Contrary to this, introduction of a substituent into phenylene was not effective for improving purity of the emission color as the spectrum for **P26EHNHP**.

## Conclusions

We have synthesized some new naphthalene homopolymers and copolymers with the side substituents. They were enough soluble in organic solvents to investigate electronic and optical properties in the solution and thin solid film states. The 2,6-naphthalene homopolymers and copolymers were obtained in better yields than the other linkage polymers. The steric hindrance around the linkage position definitely controlled the yield, degree of polymerization and polymer conformation, respectively. The optical properties were basically controlled by the naphthalene unit, which was apparent from UV-vis and PL spectra in solution similar to each other. The polymer conformation expected from dihedral angle between the adjacent units should change the contribution of  $\pi$ -conjugation along the polymer main chain, which might affect the PL quantum efficiency of the polymers. Among the polymers, 2,6-polynaphthalenes that should have the most planar conformation

showed the highest luminescent properties in the solution and thin solid film states. However, the specific interaction between the naphthalene units was observed for the PL spectra of 2,6-polynaphthalenes in the solid state. The specific redshift of PL spectra of the 2,6-naphthalenes probably due to a stacking  $\pi$ -interaction between the planar naphthalene cores unfortunately lowering the color purity of blue emission, whose problem was hardly dissolved by introduction of the bulky substituents into the polymer side chain. These will be one of the basic results to apply for more functional materials utilizing naphthalene-base polymers.

## Experimental Section

### Measurements

UV-vis and PL spectra of the polymer samples in  $\text{CHCl}_3$  and in a form of coating thin film on quartz glass were measured on a U-3500 spectrophotometer (Hitachi) and a FP-750 spectrofluorometer (Jasco). The relative fluorescence quantum yield of the polymers in  $\text{CHCl}_3$  was estimated by using 9,10-diphenylanthracene in cyclohexane ( $\phi_f = 0.9$ ) as the standard. Average molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using the polystyrene standards in THF.

### Materials

#### 2,3-dihexyloxynaphthalene ( 2 )

The DMF solution (150 ml) of 2,3-naphthalenediol (5 g, 31.2 mmol) and  $\text{K}_2\text{CO}_3$  (43.8 g, 317 mmol) was stirred at  $125^\circ\text{C}$ , then 1-bromohexane (20.5 g, 126.7 mmol) was added dropwise. The reaction mixture was stirred at  $125^\circ\text{C}$  for 36 h. After the reaction was over, the solution was poured into water and cooled overnight. The solid was collected and washed with MeOH, obtaining 8.9 g of white solid (yield = 86 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.87 (t, 6H), 1.30 (m, 8H), 1.45 (m, 4H), 1.82 (m,

4H), 4.03 (t, 4H), 7.03 (s, 2H), 7.21 (m, 2H), 7.57 (m, 2H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.1, 22.7, 25.8, 29.1, 31.7, 68.8, 107.8, 123.8, 126.1, 129.1.  $\text{C}_{22}\text{H}_{32}\text{O}_2$  (328.49): Calcd. C 80.44, H 9.82, O 9.74; Found. C 80.63, H 9.27.

### **1,4-dibromo-2,3-dihexyloxynaphthalene ( 3 )**

The mixture of 2,3-dihexyloxynaphthalene (5 g, 15.2 mmol) and bromine (4 ml, 78.2 mmol) in AcOH (200 ml) was stirred at r.t. for 52 h. After the reaction was over, an aqueous solution of sodium thiosulfate was added to the mixture until it was colorless. The solution was extracted with  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ , and the organic layer was evaporated. The light brown oily residue was purified by column chromatography on silica gel (Hexane), obtaining 5 g of colorless oil (yield = 68 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.92 (t, 6H), 1.37 (m, 8H), 1.51 (m, 4H), 1.88 (m, 4H), 4.11 (t, 4H), 7.53 (m, 2H), 8.21 (m, 2H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.2, 22.7, 25.8, 30.3, 31.8, 74.4, 116.3, 126.8, 127.1, 130.0, 149.9.  $\text{C}_{22}\text{H}_{30}\text{Br}_2\text{O}_2$  (486.28): Calcd. C 54.34, H 6.22, Br 32.86, O 6.58; Found. C 53.77, H 6.06.

### **2,6-dibromo-1,5-bis(ethylhexyloxy)naphthalene ( 8b )**

To the refluxing EtOH (63.86 ml) solution of 2,6-dibromo-1,5-dihydroxynaphthalene (5.85 g, 18.4 mmol) and NaOEt (3.24 g, 47.6 mmol) was added dropwise 1-bromo-2-ethylhexane (9.13 g, 47.3 mmol) during a period of 10 min, which was further refluxed for 5 h. The solution was cooled to room temperature and was successively poured into 1 N aqueous NaOH solution. The isolated black solid was filtered off and dissolved in  $\text{CH}_2\text{Cl}_2$  (300 ml). After removal of an insoluble matter, the solution was evaporated, obtaining a black oil. The black oil was purified by column chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$  : hexane = 1 : 9), giving 2.1 g of a yellow oil (yield = 21 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.89, 0.97 (m, 12H), 1.33, 1.49, 1.52, 1.63 (m, 16H), 1.83 (m, 2H), 3.88 (s, 4H), 7.56, 7.66 (d, 4H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 11.3, 14.1, 23.1, 23.8, 29.2, 30.3, 40.7, 113.7, 119.2, 130.1, 131.1, 152.9.  $\text{C}_{26}\text{H}_{38}\text{Br}_2\text{O}_2$  (542.39): Calcd. C 57.57, H 7.06, Br 29.46, O 5.90; Found. C 58.95 H 7.00.



### **2,6-dibromo-1,5-bis(cyclohexylmethoxy)naphthalene ( 8c )**

Under refluxing, 2,6-dibromo-1,5-dihydroxynaphthalene (1 g, 3.1 mmol ) was added to the KOH (0.58g, 10.3 mmol) in dry EtOH (22 ml). Successively, bromomethylcyclohexane (3.7g, 20.8 mmol) was added dropwise to the solution. The mixture was stirred for 37 h under reflux. After evaporation of the solvent, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The evaporation of the solvent gave a black solid, which was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub> : hexane= 1 : 2) and recrystallization from hexane. A yellow solid was obtained in 32 % yield (0.5 g). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ = 1.29 (m, 12H), 1.70 (m, 8H), 1.99 (d, 2H), 3.84 (d, 4H), 7.59 (d, 2H), 7.70 (d, 2H), <sup>13</sup>C NMR (270 MHz, CDCl<sub>3</sub>) δ = 25.0, 26.6, 30.0, 38.8, 79.6, 113.7, 119.2, 129.9, 131.0, 152.6. C<sub>24</sub>H<sub>30</sub>Br<sub>2</sub>O<sub>2</sub> (510.30): Calcd. C 56.49, H 5.93, Br 31.32, O 6.27; Found. C 57.05, H 6.17.

### **Homopolymers and general procedures**

#### **Poly(1,5-dihexyloxy-2,6-naphthalene) ( P26HN )**

To a solution of Ni(cod)<sub>2</sub> (0.66g, 2.4 mmol) and 2,2'-bipyridine (0.38 g, 2.4 mmol) in DMF (4 ml) were added a solution of 2,6-dibromo-1,5-dihexyloxynaphthalene (0.49 g, 1 mmol) in THF (5 ml). The reaction mixture was stirred at 70°C for 69 h. The polymer was precipitated from MeOH / HCl, reprecipitated from MeOH, and dried in vacuum, affording a yellow solid in 48 % yield (0.16 g). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ = 0.72 (t, 6H), 0.87, 1.06, 1.35, 1.54 (m, 16H), 3.73 (t, 4H), 7.70 (m, 2H), 8.03 (m, 4H) <sup>13</sup>C NMR ( 270 MHz, CDCl<sub>3</sub>) δ = 14.0, 22.5, 25.6, 30.3, 31.7, 73.9, 153.0, 117.9, 127.5, 129.5, 130.0. (C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>)<sub>n</sub> (326.49)<sub>n</sub>: Calcd. C 80.86, H 9.19, O 9.80; Found. C 80.98, H 8.85.

#### **Poly(4,8-dihexyloxy-1,5-naphthalene) ( P15HN )**

Triphenylphosphine (0.087 g, 0.33 mmol), 2,2'-bipyridine (0.0018 g, 0.012 mmol), zinc powder (0.114 g, 1.74 mmol) and NiBr<sub>2</sub> (0.015 g, 0.071 mmol) in DMAc (1.5 ml) were stirred at 80°C.

After the solution color turned red brown, 4,8-dibromo-1,5-dihexyloxynaphthalene (0.37 g, 0.6 mmol) was added to the solution, which was further stirred for 3 days. The solution was washed with MeOH/HCl and MeOH, affording a precipitate. A gray solid (0.12 g) was obtained (yield = 61 %) by filtration.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.91 (s, 6H), 1.36 (s, 8H), 1.56 (s, 4H), 1.90 (m, 4H), 4.07 (s, 4H), 6.58 (m, 1H), 6.91 (m, 1H), 7.35 (m, 1H), 7.61 (m, 1H), 7.89 (m, 1H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.2, 19.2, 22.7, 26.0, 29.2, 31.7, 68.4, 69.6, 105.7, 108.2, 114.6, 125.7, 128.9, 132.1, 128.2.  $(\text{C}_{22}\text{H}_{30}\text{O}_2)_n$  (326.49) $_n$ : Calcd. C 80.86, H 9.13, O 9.74; Found. C 80.58, H 8.64.

#### **Poly(2,3-dihexyloxy-1,4-naphthalene) ( P14HN )**

Brown solid (yield = 2 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.85 (s, 6H), 1.30 (s, 8H), 1.46 (s, 4H), 1.81 (d, 4H), 4.06 (d, 4H), 7.12 (m, 2H), 7.65 (m, 2H)  $^{13}\text{C}$  NMR ( 270 MHz,  $\text{CDCl}_3$  )  $\delta$  = 14.1, 22.7, 25.8, 29.1, 31.7, 68.9, 107.6, 108.0, 123.7, 124.1, 126.6, 128.2, 129.5, 149.6.  $(\text{C}_{22}\text{H}_{30}\text{O}_2)_n$  (326.49) $_n$ : Calcd. C 74.39, H 8.45, O 9.02; Found. C 74.30, H 8.48.

#### **Poly(1,5-bis(2-ethylhexyloxy)-2,6-naphthalene) ( P26EHN )**

Yellow oil. (yield = 62 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.93, 1.01 (m, 12H), 1.39, 1.59, 1.68, 1.70 (m, 16H), 1.90 (m, 2H), 3.95 (d, 4H) 7.60, 7.71 (m, 2H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 11.3, 14.1, 23.1, 23.7, 29.2, 30.3, 40.6, 76.9, 104.8, 113.6, 119.2, 130.9, 152.6.  $(\text{C}_{26}\text{H}_{38}\text{O}_2)_n$  (382.59) $_n$ : Calcd. C 77.88, H 9.49, O 8.36; Found. C 79.73, H 9.65.

#### **Poly(1,5-bis(cyclohexylmethoxy)-2,6-naphthalene) ( P26CyN )**

Pale yellow solid (yield = 50 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.85, 1.10, 1.59 (m, 20H), 2.00 (s, 2H), 3.58 (d, 2H), 7.42, 7.49 (m, 2H), 8.07 (s, 2H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 25.9, 26.5, 29.6, 38.6, 79.4, 114.6, 117.7, 127.4, 129.8, 153.0.  $(\text{C}_{24}\text{H}_{30}\text{O}_2)_n$  (350.51) $_n$ : Calcd. C 82.17, H 8.56, O 9.13; Found. C 81.38, H 8.55.

## Copolymers and general procedures

### Poly(1,5-dihexyloxy-2,6-naphthalene-1,4-phenylene) ( P26HNP )

To a solution of 2,6-dibromo-1,5-dihexyloxynaphthalene (0.49 g, 1 mmol), 1,4-phenylenediboronic acid ester (0.25 g, 1 mmol), and tetrakis(triphenylphosphine)palladium (0.058 g, 0.05 mmol) in THF (20 ml) was added a degassed aqueous Na<sub>2</sub>CO<sub>3</sub> solution (12.5 ml). The mixture was stirred at 70°C for 74 h. After the reaction, the polymer was precipitated from MeOH/HCl, reprecipitated from MeOH, and dried in vacuum, affording a brown solid quantitatively (0.41g). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ = 0.82 (t, 6H), 1.22, 1.36, 1.51, 1.66 (m, 16H), 3.71 (s, 4H), 7.59, 8.06 (d, 4H), 7.82 (s, 4H) <sup>13</sup>C NMR (270 MHz, CDCl<sub>3</sub>) δ = 16.6, 25.1, 27.9, 32.1, 34.2, 76.6, 155.2, 132.4, 140.2, 121.1, 131.2, 131.9, 132.4. (C<sub>28</sub>H<sub>34</sub>O<sub>2</sub>)<sub>n</sub> (402.58)<sub>n</sub>: Calcd. C 80.96, H 8.19, O 7.71; Found. C 80.97, H 7.70.

### Poly(2,3-dihexyloxy-1,4-naphthalene-1,4-phenylene) ( P14HNP )

Gray solid (yield = 30 %). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ = 0.78 (m, 6H), 1.33 (m, 8H), 1.51 (s, 4H), 1.84 (m, 4H), 3.87, 4.14 (m, 4H), 7.28 (m, 2H), 7.48 (m, 4H), 7.88 (m, 2H) <sup>13</sup>C NMR (270 MHz, CDCl<sub>3</sub>) δ = 14.2, 22.8, 25.0, 30.3, 31.8, 74.3, 115.9, 124.8, 126.1, 130.6, 134.3, 149.2. (C<sub>28</sub>H<sub>34</sub>O<sub>2</sub>)<sub>n</sub> (402.58)<sub>n</sub>: Calcd. C 80.96, H 8.19, O 7.71; Found. C 74.55, H 7.66.

### Poly(4,8-dihexyloxy-1,5-naphthalene-1,4-phenylene) ( P15HNP )

Gray solid (yield = 86 %). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ = 0.78 (m, 6H), 1.14 (s, 8H), 1.51 (s, 4H), 1.89 (m, 4H), 3.71, 4.11 (m, 4H), 6.77 (m, 1H), 6.91 (m, 2H), 7.21 (m, 4H) <sup>13</sup>C NMR (270 MHz, CDCl<sub>3</sub>) δ = 14.2, 22.8, 25.9, 28.5, 31.7, 68.3, 106.1, 125.4, 127.1, 129.3, 131.8. (C<sub>28</sub>H<sub>34</sub>O<sub>2</sub>)<sub>n</sub> (402.58)<sub>n</sub>: Calcd. C 80.96, H 8.19, O 7.71; Found. C 79.64, H 7.97.

### **Poly(2,6-[1,5-bis(ethylhexyloxy)]naphthalene-1,4-phenylene) ( P26EHNP )**

Yellow solid (yield = 82 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.84, 0.87 (m, 6H), 1.25, 1.42, 1.44, 1.54 (m, 16H), 1.64 (m, 2H), 3.64 (s, 4H), 7.61, 8.11 (d, 4H), 7.85 (s, 4H)  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 11.2, 14.1, 23.1, 23.8, 29.2, 29.8, 40.7, 152.7, 129.9, 137.7, 118.5, 128.8, 129.5, 130.1.  $(\text{C}_{32}\text{H}_{42}\text{O}_2)_n$  (458.69) $_n$ : Calcd. C 83.72, H 9.16, O 6.98; Found. C 80.96, H 8.52.

### **Poly(1,5-bis(ethylhexyloxy)-2,6-naphthalene-2,5-dihexyloxy-1,4-phenylene) ( P26EHNHP )**

Yellow solid (yield = 75 %).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.83 (m, 12H), 1.25, 1.62 (m, 32H), 3.70 (s, 4H), 3.95 (m, 4H), 7.19 (m, 2H), 7.53 (m, 2H), 8.02 (d, 2H).  $^{13}\text{C}$  NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$  = 11.2, 14.0, 22.6, 23.0, 25.7, 29.3, 31.4, 40.7, 68.9, 106.4, 116.3, 116.7, 126.5, 127.1, 129.5, 129.7, 149.7, 152.7.  $(\text{C}_{44}\text{H}_{66}\text{O}_4)_n$  (659.01) $_n$ : Calcd. C 78.9, H 9.86, O 9.57; Found. C 78.14, H 9.13.

### **Acknowledgment**

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## Captions of Figures and Schemes

**Figure 1.** UV-vis and PL spectra of (a) the CHCl<sub>3</sub> solution and (b) the cast film of **P14HN** (dot-dashed line), **P15HN** (broken line), and **P26HN** (solid line).

**Figure 2.** UV-vis and PL spectra of the cast film of **P26EHN** (solid line) and **P26CyN** (broken line).

**Figure 3.** UV-vis and PL spectra of (a) the CHCl<sub>3</sub> solution and (b) the thin cast film of **P14HNP** (dot-dashed line), **P15HNP** (broken line) and **P26HNP** (solid line).

**Figure 4.** UV-vis and PL spectra of the CHCl<sub>3</sub> solution (solid line) and the thin film (broken line) of **P26EHNP** and the thin film of **P26EHNHP** (dot-dashed line ).

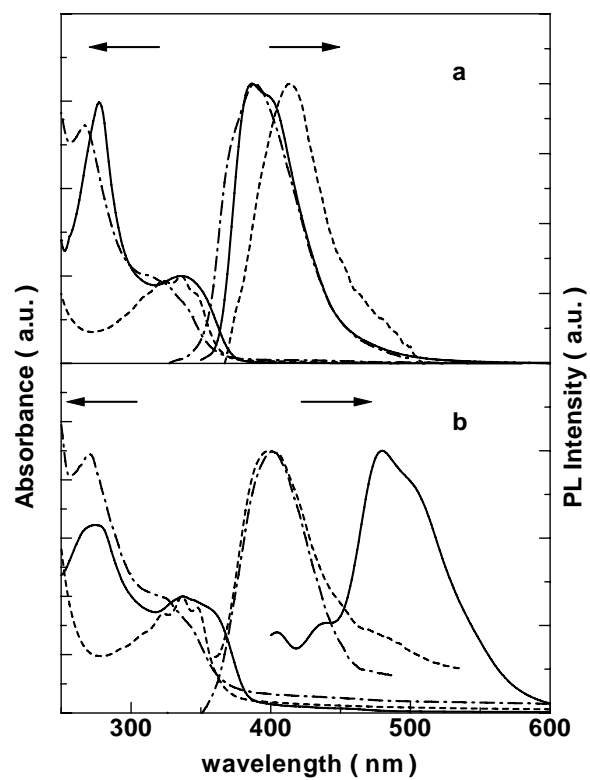
**Scheme 1.** The synthetic route of 1,4-polynaphthalene derivatives.

**Scheme 2.** The synthetic route of 1,5-polynaphthalene derivatives.

**Scheme 3.** The synthetic route of 2,6-polynaphthalene derivatives.

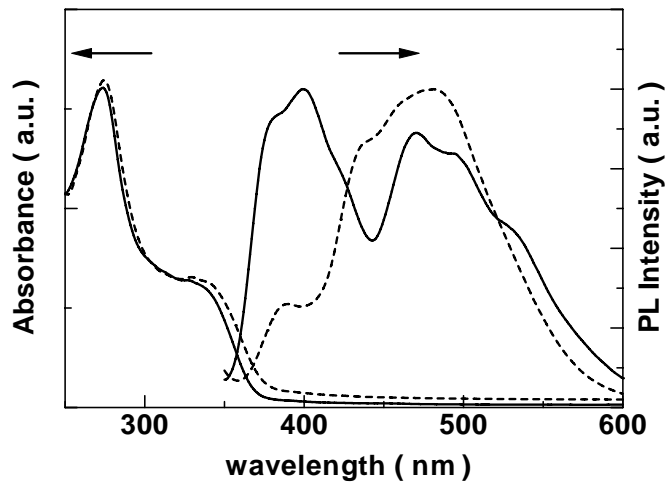
**Table 1.** Polymerization results.

**Table 2.** Optical data of polynaphthalenes.

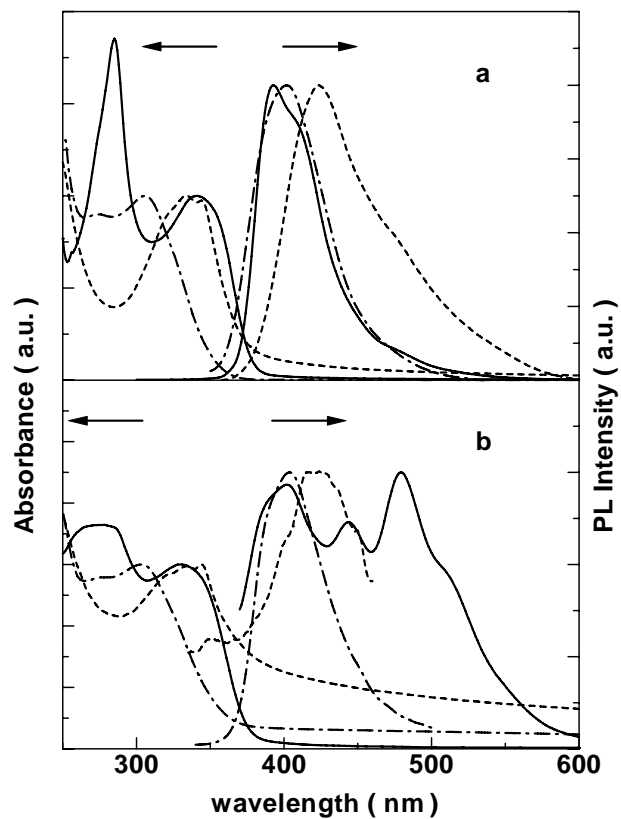


**Figure 1.** UV-vis and PL spectra of (a) the  $\text{CHCl}_3$  solution and (b) the cast film of **P14HN** (dot-dashed line), **P15HN** (broken line), and **P26HN** (solid line).

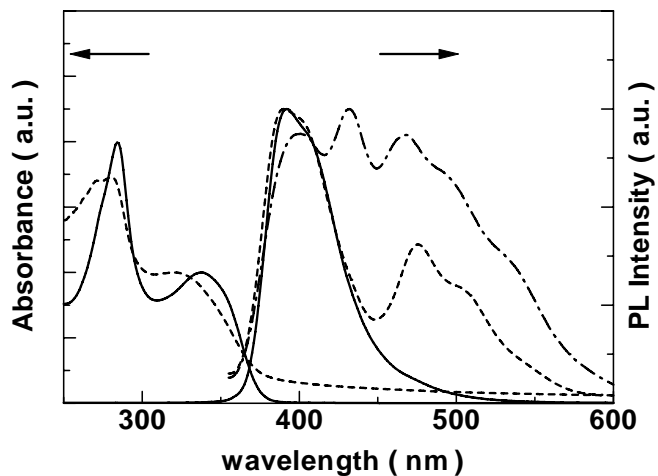




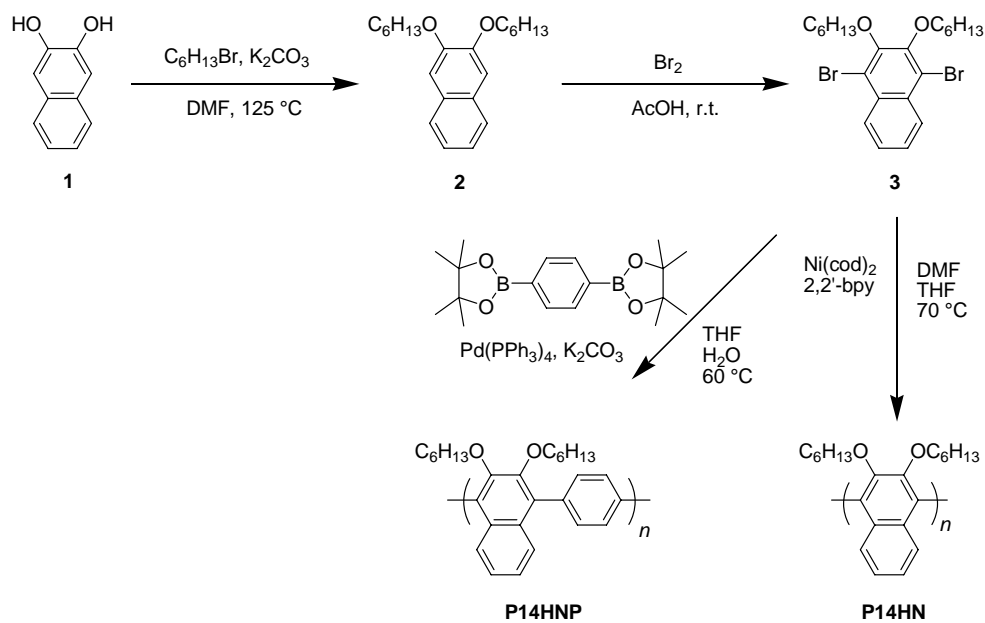
**Figure 2.** UV-vis and PL spectra of the cast film of **P26EHN** (solid line) and **P26CyN** (broken line).



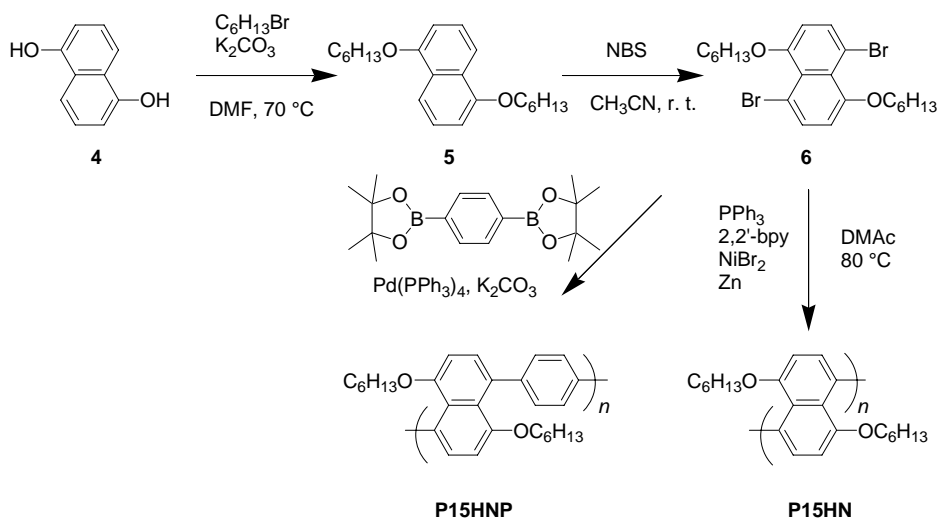
**Figure 3.** UV-vis and PL spectra of (a) the  $\text{CHCl}_3$  solution and (b) the thin cast film of **P14HNP** (dot-dashed line), **P15HNP** (broken line) and **P26HNP** (solid line).



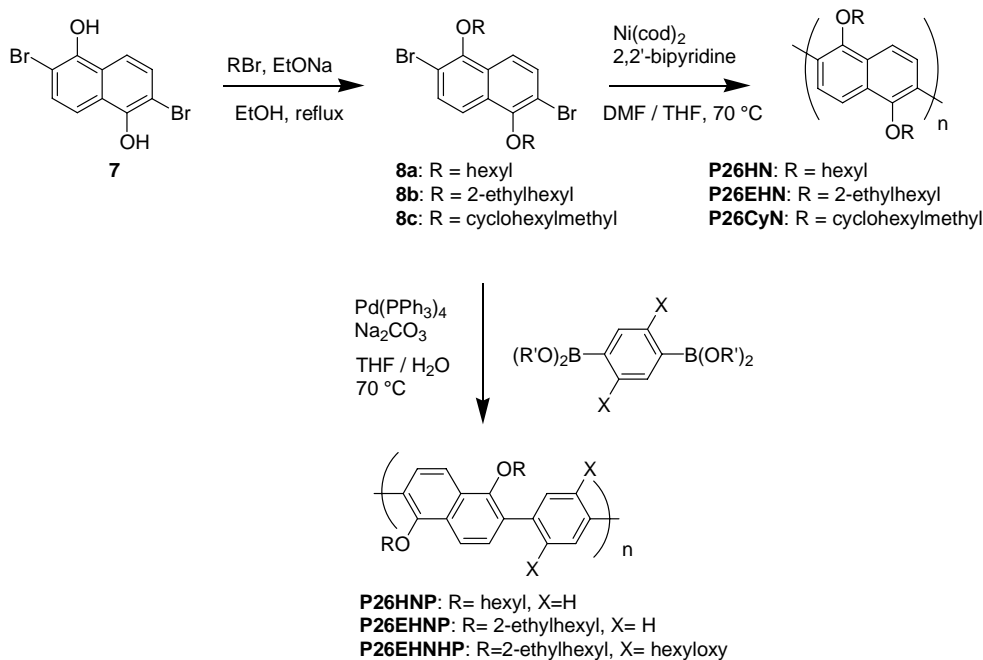
**Figure 4.** UV-vis and PL spectra of the  $\text{CHCl}_3$  solution (solid line) and the thin film (broken line) of **P26EHNP** and the thin film of **P26EHNHP** (dot-dashed line).



**Scheme 1.** The synthetic route of 1,4-polynaphthalene derivatives.



**Scheme 2.** The synthetic route of 1,5-polynaphthalene derivatives.



**Scheme 3.** The synthetic route of 2,6-polynaphthalene derivatives.

**Table 1.** Polymerization results.

polymer	yield (%)	GPC <sup>a</sup>			DP <sup>b</sup>
		$M_n$	$M_w$	$M_w/M_n$	
<b>P14HN</b>	2	2070	2460	1.2	6
<b>P14HNP</b>	30	3690	4720	1.3	9
<b>P15HN</b>	61	2240	2700	1.2	7
<b>P15HNP</b>	85	2970	4020	1.4	7
<b>P26HN</b>	48	5070	6470	1.3	16
<b>P26EHN</b>	62	3520	8300	2.4	9
<b>P26CyN</b>	50	2810	3500	1.2	8
<b>P26HNP</b>	100	5880	7180	1.2	15
<b>P26EHNP</b>	82	4850	6350	1.3	11
<b>P26EHNHP</b>	75	10800	35270	3.3	16

<sup>a</sup> Referred to polystyrene standards in THF. <sup>b</sup> Degree of polymerization.

**Table 2.** Optical data of polynaphthalenes.

polymer	UV-vis $\lambda_{\max}$ (nm)		$E_g^a$ (eV)	PL $\lambda_{\max}$ (nm)		$\phi_{\text{fl}}^b$	CIE (x, y) <sup>c</sup>	
	solution <sup>d</sup>	film		solution <sup>d</sup>	film		solution <sup>d</sup>	film
<b>P14HN</b>	(306, 336) <sup>e</sup>	(310, 340) <sup>e</sup>	3.4	388	401	0.09	0.16, 0.02	0.14, 0.08
<b>P14HNP</b>	306	304	3.3	402	404	0.28	0.15, 0.02	0.16, 0.03
<b>P15HN</b>	336	337	3.27	413	398	0.01	0.15, 0.03	0.14, 0.11
<b>P15HNP</b>	344	334	3.16	424	424	0.14	0.15, 0.11	0.16, 0.01
<b>P26HN</b>	336	337	(2.55) <sup>f</sup> , 3.28	387	480	0.71	0.16, 0.04	0.15, 0.30
<b>P26EHN</b>	327	326	(2.60) <sup>f</sup> , 3.44	392	401	0.6	0.16, 0.04	0.19, 0.27
<b>P26CyN</b>	329	329	(2.80) <sup>f</sup> , 3.36	390	481	0.96	0.16, 0.04	0.16, 0.17
<b>P26HNP</b>	341	330	(2.60) <sup>f</sup> , 3.32	393	479	0.95	0.16, 0.05	0.16, 0.20
<b>P26EHNP</b>	338	320	(2.80) <sup>f</sup> , 3.31	392	390	0.89	0.16, 0.04	0.15, 0.20
<b>P26EHNHP</b>	336	335	(2.85) <sup>f</sup> , 3.23	406	432	0.36	0.16, 0.06	0.17, 0.22

<sup>a</sup>Estimated from onset of optical absorption of thin solid films. <sup>b</sup>Relative to 9,10-diphenylanthracene in cyclohexane ( $\phi = 0.90$ ). <sup>c</sup>Tristimulus values were calculated from the fluorescence spectrum data in consideration of visibility factor. <sup>d</sup>In CHCl<sub>3</sub>. <sup>e</sup>Shoulders. <sup>f</sup>Another absorption edge at low energy state.