



## Synthesis and properties of chiral helical polymers based on optically active polybinaphthyls

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### ABSTRACT

The chiral polymer **P-1** was synthesized by the polymerization of (*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-bisoxo-1,1'-binaphthyl (**R-M-1**) with 5,5'-divinyl-2,2'-bipyridine (**M-1**) via Pd-catalyzed Heck reaction. **P-2** and **P-2'** were prepared by Wittig–Horner reaction of (*R*)-6,6'-dibutyl-2,2'-bisoxo-1,1'-binaphthyl-3,3'-dicarbaldehyde (**R-M-2**) with 5,5'-bis (diethylphosphonomethyl)-2,2'-bipyridine (**M-2**) in the presence of EtONa or NaH, respectively. **P-3** was synthesized by Wittig–Horner reaction of (*R*)-6,6'-di(4-trifluoromethylphenyl)-2,2'-bisoxo-1,1'-binaphthyl-3,3'-dicarbaldehyde (**R-M-3**) with **M-2** using NaH as a base. The four polymers have strong blue-green fluorescence due to the extended  $\pi$ -electronic structure between the chiral model compounds (*R*)-6,6'-dibutyl-/di(4-trifluoromethylphenyl)-2,2'-bisoxo-1,1'-binaphthyl (**R-1** or **R-2**) and the conjugated linker 2,2'-bipyridyl group via vinylene bridge. Both monomers and polymers were analyzed by NMR, MS, FT-IR, UV–vis spectroscopy, DSC–TGA, fluorescence spectroscopy, GPC and circular dichroism (CD) spectroscopy. Based on the great differences of specific rotation values and CD spectra, **P-1** and **P-2** may adopt a zigzag chain configuration, while **P-2'** and **P-3** may adopt a helical configuration. The responsive optical properties of the two chiral helical polymers **P-2'** and **P-3** on transition metal ions were investigated by fluorescence, UV–vis and CD spectra. The results show that Ag<sup>+</sup> and Ni<sup>2+</sup> lead to nearly complete fluorescence quenching of **P-2'** and **P-3**, Cu<sup>2+</sup> and Fe<sup>2+</sup> can cause obvious fluorescence quenching, but Zn<sup>2+</sup> and Cd<sup>2+</sup> can only produce slight fluorescence quenching. Ag<sup>+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Fe<sup>2+</sup> can also lead to the obvious changes of UV–vis spectra of **P-2'** and **P-3**. On the contrary, Zn<sup>2+</sup> and Cd<sup>2+</sup> cause little changes. Most importantly, the CD intensities and wavelengths of the chiral helical polymers **P-2'** and **P-3** exhibit the pronounced changes upon addition of Ag<sup>+</sup> and Ni<sup>2+</sup>.

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### 1. Introduction

Conjugated polymers based on  $\pi$ -conjugated organic molecules and chain backbone structures have attracted much interest during the past decade [1–6]. These functional polymers with tunable optical and electronic properties can be achieved by the careful combination of the designed monomers. They can also be used to prepare organic light-emitting diodes, electroluminescent devices, nonlinear optical materials, supramolecular sensors and other devices with colors ranging from blue to red [7–14]. Optically active 2,2'-binaphthol (BINOL) and its derivatives are one of the most important C<sub>2</sub> symmetric compounds and have often been used as the starting materials for the preparation of conjugated polymers that have a main-chain chiral configuration. Especially the

conjugated polymer incorporating optically active binaphthyl moiety in the main-chain backbone could exhibit a sort of excellent fluorescent materials with good fluorescence quantum efficiency due to the extended  $\pi$ -electronic structure between the chiral repeating unit and the conjugated linker unit. These rigid and regular chiral binaphthyl-based polymers could lead to the properties of fluorescence sensors for sensitive detection of metal ions or chiral molecules recognition [15–20], asymmetric catalysts [21–26], and optoelectronic materials [27–33] by controlling the chiral organic groups and linker structure at the well-defined molecular level.

Chiral polymers with helical chain backbone have received increasing attention due to their helicity generating from secondary interactions such as hydrogen bonds and van der Waals forces. These chiral helical polymers undergo conformational change as well as helical reversal easily. But the inherently stable helical polymers are less common so far [34–36]. Takeishi and his co-workers reported that the main chains composed of rigid segments

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are twisted to one-direction by the chiral binaphthyl linker and an ordered structure of the main-chain backbone incorporating optically pure binaphthyl could adopt the stable helical configuration [37]. As a result, there were reports on the application of some chiral helical polymers based on polybinaphthyls for electroluminescent, nonlinear optical properties and chiral sensing [21,38,39]. In view of these reports, design and synthesis of chiral helical polymers based on optically active 1,1'-binaphthyl moiety are still attractive. According to our previous report on the synthesis of polybinaphthyls, we found that a major-groove zigzag polymer and a minor-groove hexical polymer were generated while the isoquinoline moieties were introduced into the main-chain backbone by Sonogashira reaction at 6,6'- and 3,3'-positions of 1,1'-binaphthyl, respectively [40]. In this paper, we report the synthesis of four chiral polybinaphthyls incorporating 2,2'-bipyridyl moieties in the polymer main-chain backbone by Pd-catalyzed Heck reaction or Wittig–Horner reaction. As a consequence, this allows the investigation on the influence of the synthetic procedure on the chiral polymer's structure and configuration. The results indicate that **P-1** and **P-2** obtained by Heck and Wittig–Horner reaction in the presence of EtONa may adopt a zigzag form, but both **P-2'** and **P-3** synthesized by Wittig–Horner reaction using NaH as a base may exist in a helical configuration. The responsive optical properties of two chiral helical polymers **P-2'** and **P-3** on transition metal ions were investigated by fluorescence, UV–vis and circular dichroism (CD) spectra. The results show that **P-2'** and **P-3** can show distinguished sensitive sense of some transition metal ions, such as  $\text{Ag}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . Such distinct ion-responsive behaviors reveal the large differences of coordination abilities of transition metal ions with 2,2'-bipyridyl ligand receptors in the helical polymer main-chain backbone. The results also suggest that 2,2'-bipyridyl moiety can act as the recognition site of a special chemosensor for sensitive detection of transition metal ions.

## 2. Experimental part

### 2.1. Materials

All solvents and reagents were commercially available and analytical-reagent-grade. (*R*)-1,1'-Binaphthol, 3-methylpyridine and 4-trifluoromethylphenylboronic acid were purchased from Aldrich and directly used without purification. THF and  $\text{Et}_3\text{N}$  were purified by distillation from sodium in the presence of benzophenone.  $\text{CCl}_4$  and  $\text{CH}_3\text{CN}$  were distilled from  $\text{P}_2\text{O}_5$ . 5,5'-Divinyl-2,2'-bipyridine (**M-1**) was synthesized from 3-methylpyridine by a four-step reaction according to reported literatures and needed to be kept in the dark at  $-4^\circ\text{C}$  before using (Scheme 1) [18,41]. (*R*)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (**1**) [42], (*R*)-6,6'-dibutyl-2,2'-binaphthol (**3**) and (*R*)-6,6'-di(4-

trifluoromethylphenyl)-2,2'-binaphthol (**7**) [43] were prepared for the synthesis of monomers and chiral model compound according to reported literatures (Scheme 2).

### 2.2. Measurements

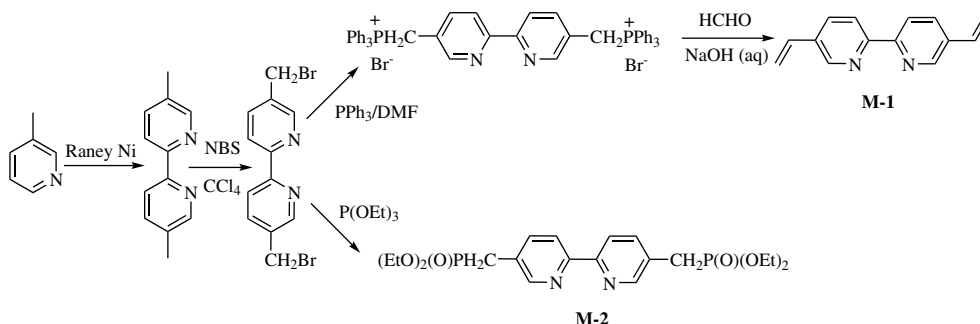
NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for  $^1\text{H}$  NMR and 75 MHz for  $^{13}\text{C}$  NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV–vis spectra were obtained from a Perkin–Elmer Lambda 25 spectrometer. Fluorescent spectra were obtained from a 48000 DSCF spectrometer. DSC–TGA was performed on a Perkin–Elmer Pyris-1 instrument under  $\text{N}_2$  atmosphere. CD spectrum was determined with a Jasco J-810 spectropolarimeter. Specific rotation was determined with a Ruololph Research Analytical Autopol I. MS was determined on a Micromass GCT. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards.

### 2.3. Preparation of **M-2** (Scheme 1)

Compound **M-2** was prepared according to a reported method [44,45]. A mixture of 5,5'-bis(bromo methyl)-2,2'-bipyridine [41] (0.93 g, 2.72 mmol) and triethylphosphite (1.94 g, 12.76 mmol) was refluxed for 4 h. After removal of the excess triethylphosphite under reduced pressure, the residue was recrystallized from the mixture of  $\text{CHCl}_3$  and *n*-hexane (1:10, v/v) to afford a white solid 5,5'-bis(diethylphosphonomethyl)-2,2'-bipyridine (**M-2**) in 80.5% yield. Mp:  $107\text{--}109^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59 (t, 2H,  $J = 1.8$  Hz), 8.37 (d, 2H,  $J = 8.4$  Hz), 7.84–7.80 (m, 2H), 4.14–4.04 (m, 8H), 3.25 (s, 2H), 3.18 (s, 2H), 1.29 (t, 12H,  $J = 7.2$  Hz).

### 2.4. Preparation of model compound **R-1** (Scheme 2)

A mixture of (*R*)-6,6'-dibutyl-2,2'-binaphthol (**3**) (0.98 g, 2.46 mmol),  $\text{K}_2\text{CO}_3$  (2.38 g, 17.23 mmol), and *n*- $\text{C}_8\text{H}_{17}\text{Br}$  (1.90 g, 9.84 mmol) was dissolved in 20 mL of anhydrous  $\text{CH}_3\text{CN}$ . The solution was refluxed overnight. After being evaporated to dryness, the residue was extracted with ethyl acetate ( $2 \times 30$  mL). The solution was washed with water and brine twice and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the cruder product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (50:1, v/v) as an eluent to afford a yellow liquid (*R*)-6,6'-dibutyl-2,2'-bis(octoxy)-1,1'-binaphthyl (**R-1**) in 83.0% yield (1.27 g).  $[\alpha]_D^{25} = -20.4$  ( $c$  0.54, THF).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d, 2H,  $J = 8.4$  Hz), 7.66 (s, 2H), 7.15 (d, 2H,  $J = 8.4$  Hz), 7.10 (dd, 2H,  $J = 9.0$  Hz, 1.5 Hz), 4.00–3.90 (m, 4H), 2.76 (t, 4H,



Scheme 1. Synthesis procedures of **M-1** and **M-2**.

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