CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc
Europe

DOI: 10.1002/chem.201302726

A New Chiral Binaphthalene-Based Fluorescence Polymer Sensor for the Highly Enantioselective Recognition of Phenylalaninol

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Abstract: A new (*S*)-binaphthalene-based polymer (**P-1**) was synthesized by the polymerization of 5,5′-((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2-hydroxy-3-(piperidin-1-ylmethyl) benzaldehyde (**M-1**) with (*S*)-2,2′-dimethoxy-(1,1′-binaphthalene)-3,3′-diamine (**M-2**) through the formation of a Schiff base; the corresponding chiral polymer (**P-2**) could be obtained by the reduction of polymer **P-1** with $NaBH_4$. Chiral polymer **P-1** exhibited a remarkable "turn-on" fluorescence-enhancement response towards (D)-phenylalaninol and excellent enantioselective recognition behavior with enantiomeric fluorescence difference ratios (*ef*) as high as 8.99. More importantly, chiral polymer **P-1** displays a bright blue fluorescence color change upon the addition of (D)-phenylalaninol under a commercially available UV lamp, which can be clearly observed by the naked eye. On the contrary, chiral polymer **P-2** showed weaker enantioselective fluorescence ability towards the enantiomers of phenylalaninol.

Keywords: binaphthalenes · enantioselectivity · molecular recognition · polymers · sensors

Introduction

Molecular chirality is of great importance because of its applications in stereochemistry in the sugar industry (sugars are *D* isomers), optical spectroscopy (the basis of optical rotation, circular dichroism, and circularly polarized luminescence), and pharmaceuticals (naturally occurring amino acids are *L* isomers). Chiral enantioselective recognition is attracting significant research interest, because it is one of the most fundamental and crucial properties of various natural systems.[1] Recently, numerous efforts have been devoted to the design of new chiral fluorescence sensors that can provide a real-time and reversible analytical method for chiral enantiomer detection or recognition, owing to its importance for understanding the interactions in biological molecules, developing useful separation processes, designing systems for asymmetric catalysis, and screening high-throughput chiral catalysts. Moreover, these chiral fluorescence sensors can not only greatly facilitate the rapid determination of enantiometric composition of chiral compounds with high sensitivity, but also easily achieve high-throughput screening (HTS).[2]

Optically active binaphthalene derivatives, such as 2,2′-binaphthol (BINOL) and 2,2′-binaphthyladiamine (BINAP), are two of the most important C_2-symmetric compounds. The rigid structure and C_2 symmetry of chiral binaphthalene molecules can play an important role in their inherent chiral induction. Their chirality is derived from the restricted rotation of the two naphthalene rings.[3] The skeletal structure of BINOL can be systematically modified on a well-defined molecular level by the introduction of various functional groups at the 3,3′-, 5,5′-, and 6,6′-positions, which can lead to a variety of polybinaphthyl compounds with a stable chiral configuration, as well as high chiral induction and chiral discrimination for fluorescence sensors and asymmetric catalysis.[4] Recently, Pu and co-workers found that the use of a (*S*)-BINOL-based trifluoromethylketone molecule as a fluorescence sensor could simultaneously determine both the enantiomeric composition of a chiral diamine, *trans*-1,2-diaminocyclohexane, and the concentration of its enantiomers through three reaction processes, that is, nucleophilic addition, elimination, and cyclization, between the trifluoromethylketone groups at the 3,3′-positions of (*S*)-BINOL and the chiral diamine substrate.[5] However, most reports have mainly focused on chiral small-molecule sensors and, as such, binaphthalene-based fluorescence polymer sensors are scarce.[6] Compared with chiral small organic molecules, polymer-based chiral fluorescence sensors can offer several advantages for the enantioselective recognition of chiral molecules, such as enhancement of fluorescence efficiency and possible cooperative effects between multiple chiral units.[7] In particular, these versatile conjugated polymers

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201302726.

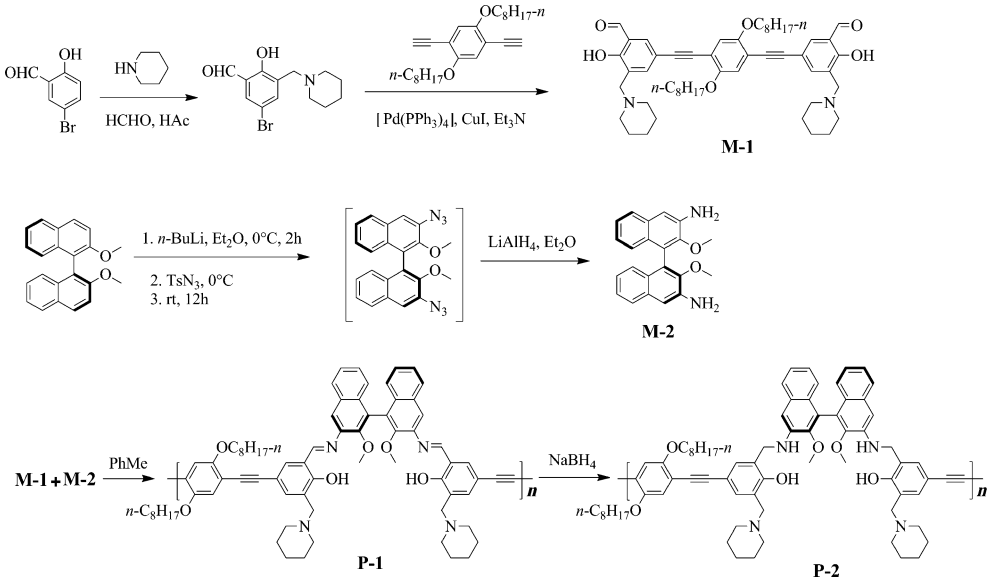
can exhibit high sensitivity towards external structural perturbations and electron-density changes of the delocalizable π-electron chain backbone on their interaction and complex formation with analytes.[6a,b]

Recently, we reported a chiral ionic BINOL-based polymer sensor and an in-situ-generated 1:1 Zn^{II}-containing BINAP-based polymer complex sensor for the highly enantioselective recognition of α-amino-acid anions and *N*-Boc-protected alanine (Boc = *tert*-butoxycarbonyl), respectively.[6c,e] Herein, we report the design and synthesis of a new (*S*)-binaphthalene-based polymer sensor that exhibited excellent enantioselective behavior and a remarkable "turn-on" fluorescence-enhancement response towards (D)-phenylalaninol. More importantly, this kind of chiral (*S*)-type polymer sensor displayed a bright blue color change in the presence of (D)-phenylalaninol under a commercially available UV lamp, which could be clearly observed by the naked eye for the direct detection of the enantiomers of phenylalaninol in a low-concentration solution.

Results and Discussion

The procedures for the synthesis of chiral polymer sensors **P-1** and **P-2** are outlined in Scheme 1. Monomer **M-1** was synthesized according to our previously reported procedure.[6e] Monomer **M-2** was first reported by Koeckelbergh and co-workers[8] from the starting material (*S*)-2,2′-dimethoxy-1,1′-binaphthalene in an overall yield of 5%. Herein, we have significantly improved the synthesis procedures. Thus, (*S*)-2,2′-dimethoxy-1,1′-binaphthalene as the starting reagent was first treated with *n*BuLi and then TsN_3 was added to afford the intermediate 3,3′-diazido-2,2′-dimethoxy-1,1′-binaphthalene. The azide group could be easily transformed into a NH_2 group through a reduction reaction with $LiAlH_4$. Monomer **M-2** could be obtained in good overall yield (as high as 53%). Chiral polymer **P-1** was synthesized by the polymerization of monomers **M-1** with **M-2** through a nucleophilic-addition/elimination process to afford a red solid in 71% yield; the corresponding polymer (**P-2**) could be obtained as a yellow solid by the reduction reaction of polymer **P-1** with $NaBH_4$ in 73% yield. These two polymers, **P-1** and **P-2**, were further purified by washing withMeOH and collected as red and yellow solids, respectively. As shown in the ^{1}H NMR spectra of chiral polymers **P-1** and **P-2** (see the Supporting Information, Figure S1), polymer **P-1** afforded one well-resolved peak, centered at $\delta = 8.99$ ppm, which corresponded to the imine group adjacent to the phenyl ring (C(*H*)=N); however, this peak disappears in the ^{1}H NMR spectrum of polymer **P-2**, which indicated the almost-complete reduction of the imine group in polymer **P-1**. Both polymers **P-1** and **P-2** could be easily dissolved in common organic solvents (THF, toluene, CH_2Cl_2, MeCN), owing to the non-planarity of the twisted polymer chain backbone and the flexible *n*-octyl substituents. As listed in Table 1, GPC results of both polymers **P-1** and **P-2** show moderate molecular weights. TGA results of polymers **P-1** and **P-2** show that both polymers have high thermal stability, with no weight loss before 400 °C, and tend to completely decompose at 700 °C, thus indicating that these two polymers can provide desirable thermal properties for practical applications as fluorescence sensors.

Herein, the resulting (*S*)-binaphthalene-based polymer **P-1** was quite different from our previous (*R*,*R*)-salen- and (*S*)-BINAM-based chiral polymers (BINAM = 1,1′-binaphthyl-2,2′-diamine), although a similar monomer **(M-1)** was employed as the linker unit in the conjugated polymer main chain. In addition, the microenvironments around the chiral receptors in the building block were also modified by two piperidyl groups as a molecular wall to tune the chiral bind-



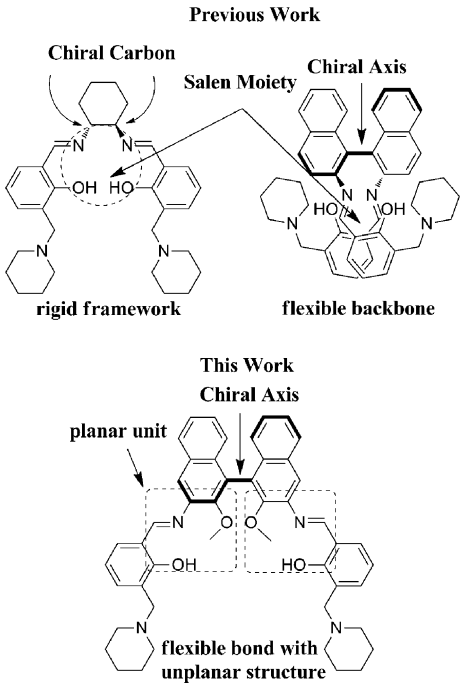
Scheme 1. Synthesis of compounds **M-1**, **M-2**, **P-1**, and **P-2**.

Table 1. GPC data, thermal properties, and fluorescence quantum yields of polymers **P-1** and **P-2**.

	Yield [%]	$[\alpha]_D^{25}$ (c=0.1, THF)	M_w[a] [g mol^{-1}]	M_n[a] [g mol^{-1}]	PDI[a] (M_w/M_n)	T_d[b] [°C]	Quantum yield[c]
P-1	66	+68.0	17890	6400	2.80	420	0.096
P-2	78	−14.0	18010	9700	1.86	400	0.33

[a] The molecular weight was determined by gel-permeation chromatography (GPC) with a Waters-244 HPLC pump; THF was used as the solvent, relative to polystyrene standards. [b] Temperature at 5% weight loss, as estimated by using TGA under a N_2 atmosphere. [c] The fluorescence quantum yield was determined by using quinine bisulfate in a 0.05 M solution of H_2SO_4 as a standard.

ing sites for enantioselective recognition, although clear differences in the chiral units, the main polymer backbone, and the chiral building block structures could be observed as shown in Scheme 2. (*R*,*R*)-Salen-based chiral polymer is



Scheme 2. Differences in the structures of the chiral building blocks.

linear and has a rigid backbone with a stable steric space from a tetradentate N_2O_2 donor for chiral recognition, whilst the chiral (*S*)-binaphthalene- or (*S*)-BINAM-based polymers have a flexible backbone, owing to free rotation around the C–C axis. The building block in the 1:1 Zn^{II}-containing complex of the (*S*)-BINAM-based polymer receptor was composed of a Zn^{II} complex of a Schiff base and the piperidyl groups were controlled by the dihedral angle of the binaphthalene group. Herein, (*S*)-binaphthalene-based polymer **P-1** is comprised of two independent building blocks that contain a Schiff base and methoxy and hydroxy groups of phenol and piperidyl moieties, respectively, but the free rotation around the C–C axis of the binaphthalene doesn't change the chiral binding sites in the building block for enantiomer recognition (Scheme 2).

The CD spectra of compounds **M-2**, **P-1**, and **P-2** have been investigated in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}, which corresponded to the binaphthalenyl moiety). The molecular ellipticities of these compounds were as follows **M-2**: $[\theta]_{\lambda(max)}=-1.19\times10^5$ (268.0 nm), $+1.65\times10^6$ (251.0 nm), -9.98×10^5 (237.0 nm); **P-1**: $[\theta]_{\lambda(max)}=+3.48\times10^5$ (392.5 nm), $+1.38\times10^5$ (333.0 nm), -5.37×10^5 (266.0 nm); **P-2**: $[\theta]_{\lambda(max)}=+6.35\times10^5$ (269.0 nm), -9.32×10^5 (234.5 nm). As is evident from Figure 1, the conjugated chiral polymer **P-1** appears to show a strong positive Cotton effect that is centered at 392 nm, which can be attributed to the rigid and stable chain and the well-defined

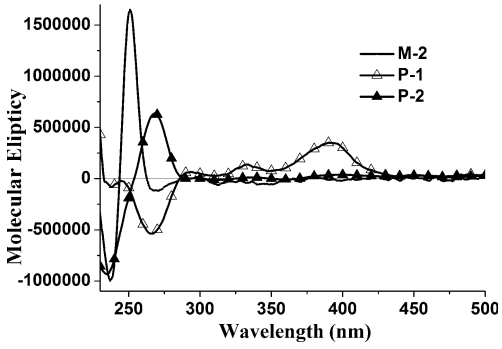


Figure 1. CD spectra of compounds **M-2**, **P-1**, and **P-2** (1.0×10^{-5} mol L^{-1} in CH_2Cl_2).

spatial arrangement of the repeating unit in the regular polymer backbone. Moreover, polymer **P-2** does not have a conjugated backbone and exhibits no Cotton effect around 392 nm because of the disordered state of the repeating unit and the irregular backbone. Compared with conjugated chiral polymer **P-1**, polymer **P-2** shows a reverse Cotton effect at about 268 nm. In addition, polymer **P-2** appears to show similar Cotton effects to monomer **M-2** at short wavelengths, but has a clear red-shift to 234.5 nm. Because polymer **P-2** does not contain a conjugated structure between the chiral moiety and the conjugated linker, we assume that the Cotton effects mainly arise from chiral monomer **M-2**, consistent with the similar specific rotations of monomer **M-2** and polymer **P-2** (Table 1).

The fluorescence responses of polymers **P-1** and **P-2** towards various guest molecules were investigated in toluene (1.0×10^{-5} mol L^{-1}). As shown in Figure 2, polymer **P-1** shows very weak fluorescence emission with a low quantum yield ($\Phi_f=0.092$) at 471 nm, which is attributed to strong and ordered intramolecular hydrogen-bonding interactions between the imine moiety and the hydroxy group of the phenol moiety and leads to nonradiative transition.[9,10d] On the contrary, polymer **P-2** exhibits a strong emission, with a high fluorescence quantum yield ($\Phi_f=0.33$), at 427 nm, owing to the weak and disordered intramolecular

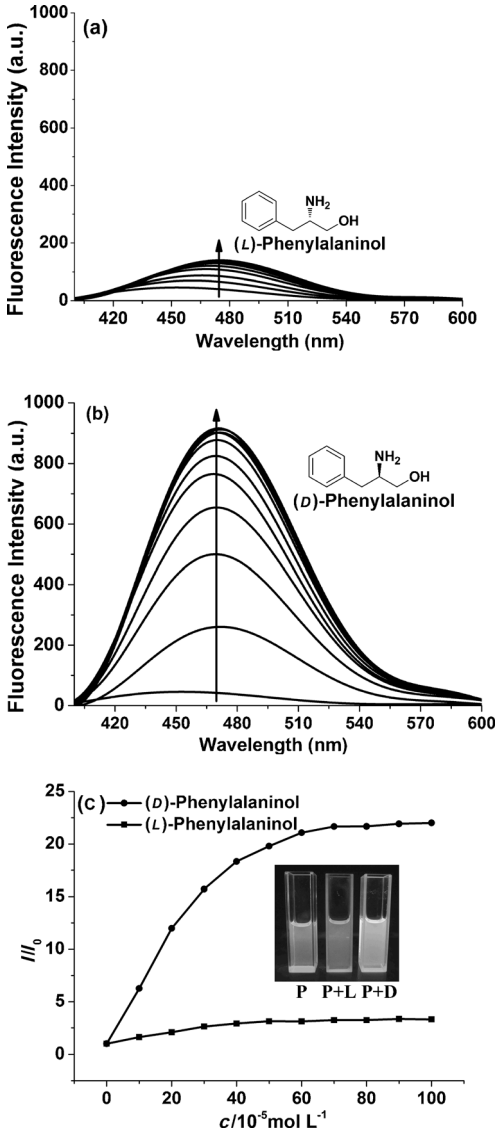
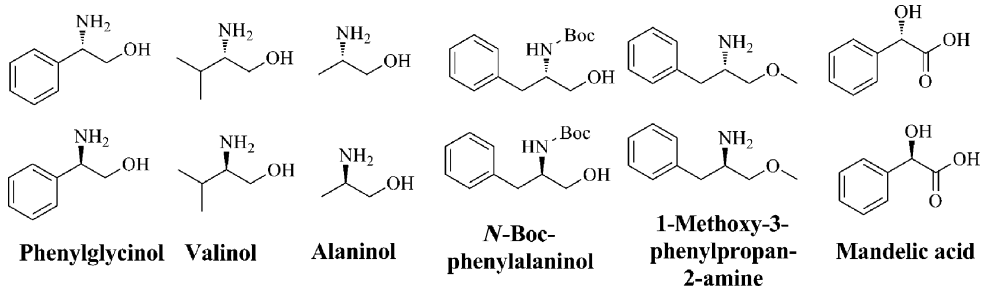


Figure 2. Fluorescence spectra of polymer **P-1** (1.0×10^{-5} mol L^{-1} in toluene) with increasing amounts of a) (L)-phenylalaninol and b) (D)-phenylalaninol (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100×10^{-5} mol L^{-1}). c) Fluorescence enhancement of polymer **P-1** (1.0×10^{-5} mol L^{-1}) with (D)- and (L)-phenylalaninol ($\lambda_{em}=471$ nm, $\lambda_{ex}=371$ nm; slit: 3 nm, 4 nm).

hydrogen-bonding interactions between the hydroxy group of the phenol moiety and the amine or piperidyl moieties.[9] As shown in Figure 2, (L)-phenylalaninol has little effect on the fluorescence intensity of polymer **P-1** (Figure 2a), whereas (D)-phenylalaninol leads to a clear fluorescence enhancement (Figure 2b). Compared to an only 3.32-fold increase upon the addition of (L)-phenylalaninol, the fluorescence intensity of polymer **P-1** showed an obvious gradual enhancement as high as 22.0-fold upon the addition of (D)-phenylalaninol from molar ratios of 1:10 to 1:100 (Figure 2c). The selective recognition of chiral molecular isomers of a guest is related to the enantiomeric fluorescence difference ratio, *ef*, according to $ef=(I_D-I_0)/(I_L-I_0)$, in which I_0 represents the fluorescence emission intensity in the absence of a chiral substrate and I_D and I_L are the fluorescence intensities in the presence of (D)- and (L)-substrates, respectively. The *ef* value for polymer **P-1** is as high as 8.99, which indicates excellent enantioselective fluorescence ability of polymer **P-1** towards (D)-phenylalaninol. The fluorescent-enhancement response of polymer **P-1** for the enantiomers of phenylalaninol as a guest molecule can be attributed to suppressed photoinduced-electron-transfer (PET),[9] through interactions of the protons of phenylalaninol with the nitrogen atoms of the imine moieties through intramolecular hydrogen-bonding interactions.[10] Upon the formation of host–guest complexes, the lone pair of electrons on the nitrogen atom (imine group) is no longer available for PET, thus leading to a fluorescence enhancement. (*S*)-Binaphthalene-based chiral polymer **P-1** has a rigid and stable configuration of the main chain and can exhibit remarkable "turn-on" fluorescence-enhancement response and excellent enantioselective recognition behavior towards (D)-phenylalaninol, which can be attributed to the inherent chiral interactions in the microenvironments in the building blocks, based on the steric repulsion between chiral receptors and chiral guest molecules. The building block of the (*S*)-binaphthalene receptor, which is composed of imine and hydroxy groups that are controlled by the dihedral angle of binaphthalene, can orient a well-defined spatial arrangement in the regular polymer backbone and well-accommodate the formation of a more-stable *S*-D complex compared to the diastereomeric *S*-L complex. Most interestingly, a solution of chiral polymer **P-1** has very weak blue fluorescence under a commercially available UV lamp ($\lambda_{ex}=365$ nm), but the color of the solution is bright blue upon the addition of (D)-phenylalaninol, which can be clearly observed by the naked eye (Figure 2c, inset). Moreover, this kind chiral polymer (**P-1**) can act as a highly sensitive and selective fluorescence sensor for the direct visual discrimination of the enantiomers of phenylalaninol at a lower concentration.

Herein, we further investigated the enantioselective fluorescence response of polymer **P-2** towards the D and L enantiomers of phenylalaninol. Interestingly, both (D)- and (L)-phenylalaninol caused almost the same fluorescence enhancement after the addition of 10 equivalents of a chiral guest, but the fluorescence intensity of polymer **P-2** gradually decreased with increasing molar ratio of the enantiomers of phenylalaninol from 10:1 to 100:1 (see the Supporting Information, Figures S2–S4). No highly enantioselective recognition could be observed, which may be ascribed to the disordered state of the chiral binding sites, unlike the stable building block in the chiral receptor of polymer **P-1** and the irregular chiral chain backbone, owing to its freely rotating, flexible C–N bond.[11]

In a set of comparable experiments, we also studied the fluorescence-response behavior of polymer **P-1** on other guest enantiomers, as shown in Scheme 3. Neither a clear fluorescence-enhancement response nor enantioselective recognition behavior could be detected (see the Supporting Information, Figures S5–S8), thus demonstrating that the designed (*S*)-binaphthalene-based polymer sensor (**P-1**) could



Scheme 3. Chiral guests that were used in the enantioselective recognition.

only exhibit highly selective fluorescence response towards the enantiomers of phenylalaninol. To further understand the enantioselective recognition mechanism towards phenylalaninol, we carried out the fluorescence change of polymer **P-1** in the presence of phenylalanine derivatives of by protection of either the amino group or the hydroxy group. On treatment with *N*-Boc-phenylalaninol or 1-methoxy-3-phenylpropan-2-amine at a molar ratio of 1:100, neither fluorescence-enhancement response nor clear enantioselectivity for chiral polymer **P-1** could be observed (see the Supporting Information, Figures S9 and S10), thus indicating that both the amino group and the hydroxy group of phenylalaninol played an important role in the enantioselective recognition process.

Conclusions

In summary, a new (*S*)-binaphthalene-based polymer sensor, which is comprised of two independent and stable building blocks with chiral binding sites, exhibits a remarkable "turn-on" fluorescence enhancement response towards (D)-phenylalaninol and excellent enantioselective recognition behavior. More interesting, this chiral (*S*)-type polymer sensor can display a bright blue color change in the presence of (D)-phenylalaninol under a commercially available UV lamp, which can be clearly observed by the naked eye for the direct detection of the individual enantiomers of phenylalaninol at low concentrations.

Experimental Section

General: All of the solvents and reagents were commercially available and of analytical reagent grade. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. NMR spectra were collected on a Bruker 300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) and are reported in parts per million (ppm) relative to TMS as an internal standard. Mass spectrometry was performed on a SHIMADZU LCMS-2020 Instrument. FTIR spectra were recorded on a Nexus 870 FTIR spectrometer. Fluorescence spectra were recorded on a Perkin–Elmer ls-55 spectrometer. Circular dichroism (CD) spectroscopy was performed on a Jasco J-810 spectropolarimeter. Specific rotation was determined on a Ruololph Research Analyfical Autopol I. Elemental analysis was performed on an Elementar Vario MICRO analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris-1 instrument under a N_2 atmosphere. Molecular weights were determined by gel-permeation chromatography (GPC) with a Waters 244 HPLC pump; THF was used as the solvent relative to polystyrene standards.

Synthesis of 2,2′-dimethoxy-[1,1′-binaphthalene]-3,3′-diamine (M-2): (*S*)-2,2′-Dimethoxy-1,1′-binaphthalene (4.21 g, 13.4 mmol, 1.0 equiv) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, 8.00 mL, 53.4 mmol, 4.0 equiv) were dissolved in Et_2O (300 mL) and the solution was cooled to 0 °C. *n*BuLi (14.7 mL, 2.5 M in *n*-hexane, 36.7 mmol, 2.75 equiv) was added dropwise and the resulting mixture was stirred for 2 h at RT. The reaction mixture was cooled to 0 °C and TsN_3 (7.90 g, 40.1 mmol, 3.0 equiv, Ts = 4-toluenesulfonyl) was added dropwise. The resulting mixture was stirred for 1 h at 0 °C and for a further 12 h at RT. The reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was used directly in the next step. A suspension of $LiAlH_4$ (1.5 g, 40 mmol) in Et_2O (10 mL) was cooled to 0 °C, a solution of the crude product in Et_2O (25 mL) was added dropwise, and the resulting mixture was stirred for 12 h at RT. The reaction mixture was cooled to 0 °C, water (1.5 mL), NaOH (15%, 1.5 mL), and water (4.5 mL) were added sequentially, and the mixture was stirred for 0.5 h. Filtration through diatomaceous earth filter aid and flash column chromatography on silica gel (EtOAc/petroleum ether, 1:2 v/v) afforded the desired product (2.45 g, 7.10 mmol, 53% yield over two steps) as a slightly brown solid. M.p. 79–82 °C; $[\alpha]_D^{25} = -14.0$ ($c = 0.10$, THF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.65$ (d, $J = 8.2$ Hz, 2H), 7.29 (d, $J = 6.8$ Hz, 2H), 7.21 (s, 2H), 7.10–7.00 (m, 4H), 3.35 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.8$, 139.5, 131.8, 128.2, 125.8, 125.5, 125.0, 124.6, 122.7, 109.8, 59.8 ppm; MS (ESI): *m*/*z*: 345.10 $[M+H]^+$; elemental analysis calcd (%) for $C_{22}H_{20}N_2O_2$: C 76.66, H 5.81, N 8.13; found: C 76.59, H 5.83, N 8.15.

Synthesis of polymer P-1: Compounds **M-1** (0.13 g, 0.22 mmol) and **M-2** (75.8 mg, 0.22 mmol) were dissolved in toluene (10 mL). The obtained solution was stirred at 80 °C for 48 h. MeOH (20 mL) was added to precipitate the red polymer. The resulting polymer was filtered, washed several times with MeOH, and dried (0.14 g, 71% yield). $[\alpha]_D^{25} = +68.0$ ($c = 0.10$, THF); ^{1}H NMR (300 Hz, $CDCl_3$): $\delta = 8.99$ (s, 2H), 7.95–7.88 (m, 2H), 7.74–7.67 (m, 2H), 7.60 (s, 2H), 7.47–7.39 (m, 2H), 7.25–7.20 (m, 4H), 7.06–6.99 (m, 4H), 4.07 (dd, $J = 6.32$, 11.34 Hz, 6H), 3.73 (d, $J = 10.89$ Hz, 4H), 3.64 (s, 4H), 3.56 (s, 2H), 2.57 (br s, 10H), 1.88 (m, 6H), 1.69–1.29 (m, 24H), 0.85 ppm (m, 6H); FTIR (KBr): $\tilde{\nu} = 3422$, 2971, 2866, 2354, 1611, 1532, 1521, 1399, 1374, 1272, 1094, 1011, 809 cm^{-1}; GPC: $M_w = 17890$, $M_n = 6400$, PDI = 2.80; elemental analysis calcd (%) for $C_{58}H_{52}N_4O_6$: C 77.24, H 5.77, N 6.22; found: C 77.07, H 6.00, N 6.34.

Synthesis of polymer P-2: Polymer **P-1** (0.15 g) was dissolved in a mixed solvent of THF (10 mL) and MeOH (10 mL) and $NaBH_4$ was added in batches to the solution. The reaction mixture was stirred at RT until the red color turned yellow. Then, the solution was stirred for a further 30 min and water (10 mL) was added to stop the reduction reaction. The mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and evaporated under reduced pressure to afford polymer **P-2** as a yellow solid (0.11 g, 73% yield).

$[\alpha]_D^{25} = -14.0$ ($c = 0.10$, THF); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 9.3$ Hz, 2H), 7.53 (s, 2H), 7.14–7.08 (m, 6H), 7.01–6.96 (m, 6H), 4.01–3.97 (m, 4H), 3.71 (s, 4H), 3.36 (s, 5H), 2.30 (s, 3H), 1.67–1.25 (24H), 0.87–0.83 ppm (m, 6H); FTIR (KBr): $\tilde{\nu} = 3528$, 3412, 2963, 2927, 1619, 1598, 1511, 1262 cm^{-1}; elemental analysis calcd (%) for $C_{58}H_{56}N_4O_6$: C 76.91, H 6.19, N 6.19; found: C 77.05, H 6.64, N 6.27.

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (21074054, 21174061, 51173078, and 21172106) and the National Basic Research Program of China (2010CB923303) for their financial support.

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Received: July 12, 2013
Published online: October 10, 2013

