JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Salen-Based Chiral Fluorescence Polymer Sensor for Enantioselective Recognition of α-Hydroxyl Carboxylic Acids

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Supporting Information

ABSTRACT: (*R*,*R*)-Salen-based chiral 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 (1*R*,2*R*)-cyclohexane-1,2-diamine (**M-2**) via nucleophilic addition− elimination reaction, and (*R*,*R*)-salan-based polymer **P-2** could be obtained by the reduction reaction of **P-1** with $NaBH_4$. (*R*,*R*)-Salen-based chiral polymer **P-1** can exhibit greater fluorescence enhancement response toward (L)-α-hydroxyl carboxylic acids, and the value of enantiomeric fluorescence difference ratio (*ef*) can reach as high as 8.41 for mandelic acid and 6.55 for lactic acid. On the contrary, (*R*,*R*)-salan-based chiral polymer **P-2** shows obvious fluorescence quenching response toward α-hydroxyl carboxylic acids. Most importantly, (*R*,*R*)-salen-based polymer **P-1** can display bright blue fluorescence color change in the presence of (L)-α-hydroxyl carboxylic acids under a commercially available UV lamp, which can be clearly observed by the naked eyes.

INTRODUCTION

More and more attention has been paid to highly selective and sensitive fluorescence sensors for enantioselective recognition because chiral molecular recognition is one of the most fundamental and significant processes in nature systems. Chiral recognition has great potential applications in analytical, biological, and clinical biochemical environments, and it also effectively provides a real-time analytical tool for chiral compound assay.[1] Using chiral fluorescence-based sensors can not only greatly facilitate rapid determination of enantiomeric composition of chiral compounds, but also allow a rapid screening of high-throughput catalysts for their asymmetric synthesis.[2] In the past several years, there has been a growing interest in the enantioselective recognition of α-hydroxycarboxylic acids due to their biological significance and synthetic utility.[1c,3,4] Pu and co-workers developed several highly enantioselective fluorescence sensors bearing the scaffold of BINOL-amino alcohol for α-hydroxycarboxylic acids, α-amino acid, and their derivatives.[3d,e,5] Zhao also reported that enantioselective recognition of mandelic acid could be detected by using the boronic acid-based chiral fluorescence sensors via the relay mechanism of the D-PET effect.[4b,f,i]

Although there have been some reports on enantioselective recognition of chiral hydroxycarboxylic acids, most of them are based on chiral small molecules,[3,4] and fluorescent polymer-based sensors are very few.[6] Chiral polymers used as fluorescence-based sensors for enantioselective recognition of chiral molecules offer several advantages over small molecule sensors, such as fluorescence efficiency enhancement and possible cooperative effects of multiple chiral units. In particular, they can make use of the high sensitivity of conjugated polymers to external structural perturbations and to electron density changes of the conjugated polymer backbone, when they interact and form complexes with analytes.[7,8] Swager reported that the delocalizable π-electronic conjugated "molecular wire" polymer can greatly amplify the fluorescence response signal due to facile energy migration along the polymer backbone upon light excitations.[7a,b] Moreover, these chiral fluorescence polymers can be systematically modified by the introduction of the different functional groups based on steric and electronic property at well-defined molecular level.

Optically active 1,2-diaminocyclohexane is one of the most important C_2 symmetric compounds. The chiral salen/salan-based ligands have been extensively used in asymmetric catalysis because of the potentially tetradentate N_2O_2 donor with metal ions.[9] Recently, these molecules are getting increasing attention in chiral recognition area. In our previous work, we first reported salen-based and salan-based chiral polymers as fluorescence sensors for enantioselective recognition of phenylglycinol.[8b] In this paper, we further designed (*R*,*R*)-salen-based and salan-based chiral fluorescence polymers by introduction of the piperidyl group as the side chain of the conjugated polymer backbone to systematically adjust the microenvironment of (*R*,*R*)-salen/salan moieties and improve

Received: March 15, 2012
Published: April 29, 2012

Scheme 1. Synthesis Procedures of M-1, the Chiral Polymer Sensors P-1 and P-2

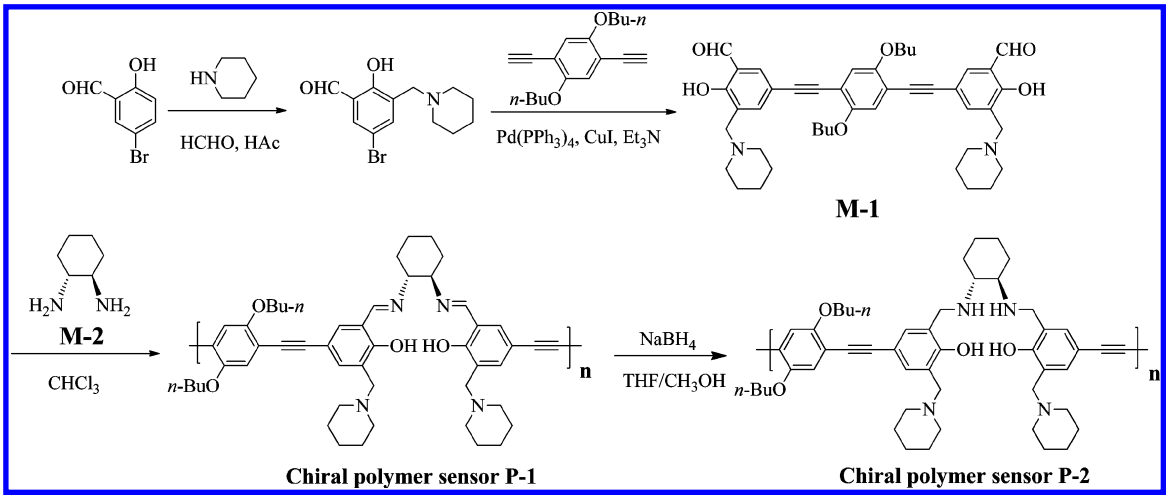


Table 1. GPC, Thermal Properties, and Fluorescence Quantum Yields of P-1 and P-2

	yield (%)	$[\alpha]_D^{20}$ (c 0.2, THF)	M_w[a] (g/mol)	M_n[a] (g/mol)	PDI[a] (M_w/M_n)	T_d[b] (°C)	fluorescence quantum yield[c]
P-1	72	+316.0	13040	4800	2.72	400	0.087
P-2	83	+57.0	14080	8800	1.60	380	0.30

[a]Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump, and THF was used as solvent and relative to polystyrene standards. [b]Temperature at 5% weight loss estimated using TGA under N_2. [c]The fluorescence quantum yields of **P-1** and **P-2** were determined using quinine bisulfate in 0.05 M H_2SO_4 solution as the standard.

enantioselective recognition effect of α-hydroxyl carboxylic acids. The results show that (*R*,*R*)-salen-based chiral fluorescence polymer can exhibit great fluorescence enhancement response toward (L)-α-hydroxyl carboxylic acids. More importantly, (*R*,*R*)-salen-based chiral polymer can display bright blue fluorescence color change in the presence of (L)-α-hydroxyl carboxylic acids under a commercially available UV lamp, which can be clearly observed by the naked eye. To the best of our knowledge, this is the first example of the polymer-based fluorescence sensor for enantioselective recognition of α-hydroxyl carboxylic acids.

RESULTS AND DISCUSSION

The synthesis procedures of **M-1** and chiral polymer sensors **P-1** and **P-2** are outlined in Scheme 1. 1,4-Dibutoxy-2,5-diethynylbenzene was synthesized according to the reported literature.[8f] 5-Bromo-2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde could be synthesized by Mannich reaction from the starting material 5-bromosalicylaldehyde in 77% yield.[10] The monomer **M-1**, 5,5′-((2,5-dibutoxy-1,4-phenylene)bis-(ethyne-2,1-diyl))bis(2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde, could be synthesized by the reaction of 1,4-dibutoxy-2,5-diethynylbenzene with 5-bromo-2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde via a typical Pd-catalyzed Sonogashira cross-coupling reaction. (*R*,*R*)-Salen-based polymer **P-1** was synthesized by the polymerization of **M-1** with (1*R*,2*R*)-cyclohexane-1,2-diamine (**M-2**) in 72% yield. (*R*,*R*)-Salan-based polymer **P-2** could be obtained by reduction of **P-1** with $NaBH_4$ in 83% yield. **P-1** and **P-2** were further purified by MeOH and collected as yellow and gray solids, respectively. As evident from ^{1}H NMR spectra of the polymers **P-1** and **P-2**, **P-1** has one well-resolved peak at 8.29 ppm corresponding to the imine group adjacent to the phenyl (—CH═N—). But 8.29 ppm in ^{1}H NMR spectra of the polymer **P-2** disappears, which indicates the complete reduction of imine group of **P-1** (see Supporting Information, Figure S6). (*R*,*R*)-Salen/salan moieties of **P-1** and **P-2** as the chiral sites can orient a well-defined spatial arrangement in the regular polymer main chain backbones. Furthermore, (*R*,*R*)-salen/salan moieties modified by two piperidyl groups can effectively activate and improve the building block microenvironment of (*R*,*R*)-salen or salan receptors, while the chiral polymer hosts interact with chiral guests.

Both **P-1** and **P-2** can dissolve in common organic solvents, such as toluene, CH_2Cl_2 and THF, which can be attributed to the nonplanarity of the polymer backbone and the flexible *n*-butoxy substitutents on phenyl units as side chains of the polymers. gel permeation chromatography (GPC), thermal properties, and quantum yields of **P-1** and **P-2** are showed in Table 1. According to Table 1, GPC results of both **P-1** and **P-2** show moderate molecular weights. But the molecular weight of **P-1** is higher than **P-2**, which could be attributed to the changes of conformational mobility. TGA of **P-1** and **P-2** were carried out under a N_2 atmosphere at a heating rate of 10 °C/min (see Supporting Information, Figure S1). The result shows that **P-1** and **P-2** have high thermal stability without loss weight before 380 °C and tend to complete decomposition at 700 °C. Therefore, the two polymers can provide a desirable thermal property for practical application as fluorescence sensors. The CD spectra of **P-1** and **P-2** have been investigated in THF solution (see Figure 3). The molecular ellipticities of **P-1** are as follows: $[\theta]_{\lambda(max)}$ = +2.83 × 10^5 (245.8 nm), −2.15 × 10^5 (265.4 nm), +1.27 × 10^5 (322.4 nm), −5.98 × 10^4 (347.6 nm), +3.28 × 10^5 (384.0 nm); and **P-2**: +4.33 × 10^4 (384.0 nm).

The fluorescence spectra of **P-1** and **P-2** were carried out in a mixed solution of toluene and DME (v/v, 0.4%). The (*R*,*R*)-salen-based chiral polymer **P-1** host shows a weak fluorescence emission with lower fluorescence quantum yield of 0.087 at 465 nm on excitation at 420 nm due to the strong and ordered intramolecular hydrogen bonding between imine and hydroxyl

dx.doi.org/10.1021/jo3005233 | J. Org. Chem. 2012, 77, 4759−4764

of phenol, which leads to nonradiative transition. But the (*R*,*R*)-salan-based chiral polymer **P-2** can show a strong fluorescence emission with higher fluorescence quantum yield of 0.30 at 465 nm on excitation at 385 nm, which may be attributed to the weak and disordered intramolecular hydrogen bonding between hydroxyl of phenol and amine or piperidyl. Figure 1 shows the fluorescence spectra of the chiral polymer **P-1** (1.0×10^{-5} mol/L corresponding to salen-based unit) upon addition of (L)- or (D)-mandelic acid (1.0×10^{-2} mol/L in toluene, 10% v/v DME). Obvious fluorescence enhancement response could be observed as demonstrated in Figure 1a, on the contrary, (D)-mandelic acid (MA) has little effect on the fluorescence intensity of **P-1** under the same condition (Figure 1b). In addition, in the spectra of **P-1**, a new shoulder peak at 440 nm can be observed upon addition of MA. As the molar ratio of (L)-MA increases from 1 to 15, the fluorescence intensities of **P-1** also appear to have gradual enhancement and reach as high as 8.79-fold, compared to 2.59-fold of (D)-MA (Figure 1c). The selective recognition effect on the guest of the chiral molecular isomers is related to the enantiomeric fluorescence difference ratio, *ef* [$ef = (I_L - I_0)/(I_D - I_0)$]. I_0 represents the fluorescence emission intensity in the absence of the chiral substrate. I_L and I_D are the fluorescence intensities in the presence of (L)-substrate and (D)-substrate, respectively.[3k] The value of *ef* is 8.41 for **P-1**, which indicates that this polymer can exhibit highly enantioselective response toward (L)-MA. The reason may be attributed to an inherent chiral recognition based on the steric repulsion of (*R*,*R*)-salen precursor for (L)-MA. The building block of (*R*,*R*)-salen receptor modified by the piperidyl groups can well fit for the formation of a more stable complex of *R*−*L* complex as compared to the *R*−*D* diastereomeric complex. Interestingly, the fluorescent color of **P-1** solution turns bright blue upon the addition of (L)-MA, which can be clearly observed by the naked eyes (Figure 1c, inset). In this experiment, the fluorescence image of a solution of the polymer (5×10^{-5} mol/L) plus 15.0 equiv of MA were excited by a commercially available UV lamp (λ = 365 nm). Meanwhile, we also found that free-**P-1** solution appears to have the similar fluorescent color to (D)-MA-polymer.

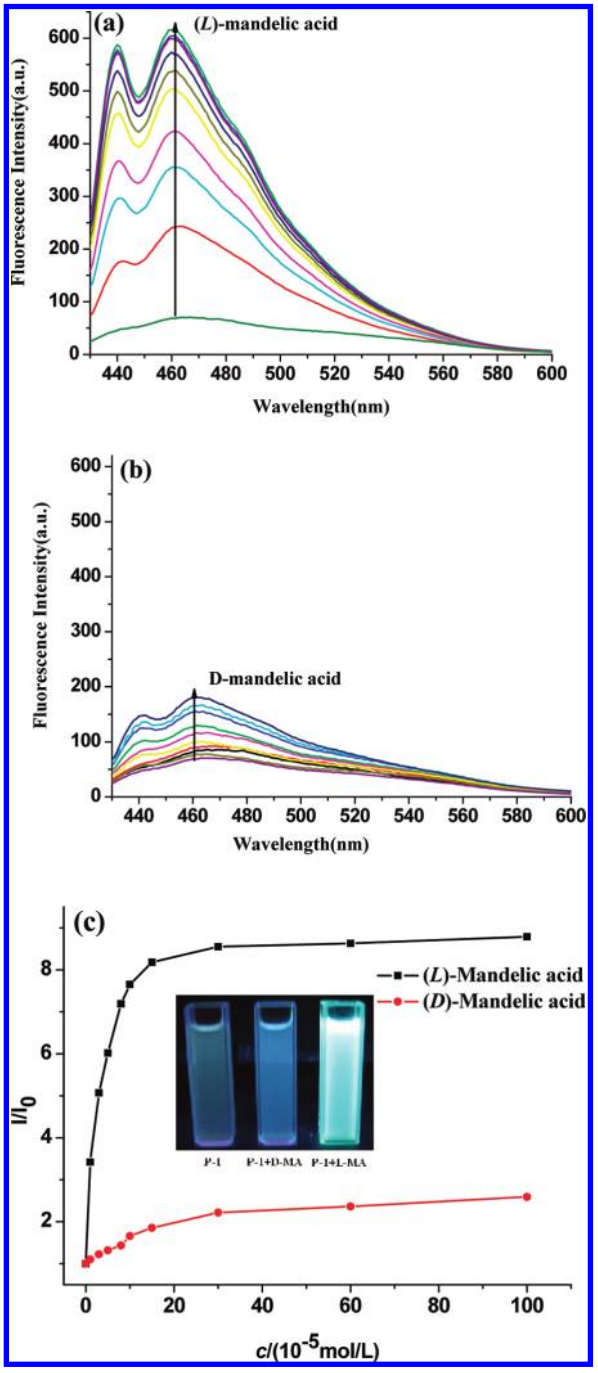


Figure 1. Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to salen moiety in toluene, 0.4% v/v DME) with increasing amounts of (L)-MA (a) and (D)-MA (b) (0, 1, 3, 5, 8, 10, 15, 30, 60, 100×10^{-5} mol/L, 1.0×10^{-2} mol/L in toluene, 10% v/v DME). (c) Fluorescence enhancement of **P-1** (1.0×10^{-5} mol/L) with (D)- and (L)-MA (λ_{em} = 465 nm; λ_{ex} = 420 nm) (inset: left, **P-1**; middle, **P-1** + (D)-MA; right, **P-1** + (L)-MA).

In a set of comparable experiments, we also studied the fluorescence response behavior of polymer **P-2** on (D)- and (L)-MA. As is evident from Figure 2, the interesting results show that both (L)- or (D)-MA can lead to gradual and obvious fluorescence quenching of salan-based chiral polymer **P-2** as the molar ratio increase of the guest MA. Fluorescence quenching ratios of **P-2** are 60.6% for (D)-MA and 83.4% for (L)-MA, the 1:30 molar ratio addition of MA, respectively. The obvious fluorescence enhancement of **P-1** with MA can be attributed to the suppressed photoinduced-electron-transfer (PET) quenching[11] when the protons of MA interact with the nitrogen atoms of imine moieties in the salen-based chiral polymer main chain through the intramolecular hydrogen bond.[12] On complexation, the lone pair of electrons on the nitrogen atom is no longer available for PET, leading to the fluorescence enhancement.[8b,c] Compared to the rigid and helical chain backbone structure of salen-based polymer **P-1**, the chain backbone of the salan-based polymer **P-2** becomes flexible and twisted, and the intramolecular hydrogen bond is in disorder. It is evident from CD spectra of **P-1** and **P-2** (Figure 3) that the rigid and stable chain configuration of salen-based polymer **P-1** appears to have strong positive and negative Cotton effect since the (*R*,*R*)-salen moieties can orient a well-defined spatial arrangement in the regular polymer backbone. On the contrary, salan-based polymer **P-2** appears to have almost no Cotton effect at short wavelengths in the CD spectra. It may be attributed to the chiral salan-based repeating unit in the disordered state and the irregular chain backbone. It can be further demonstrated by specific rotation values from the great difference of two chiral polymers (Table 1). While the flexible salen-based polymer **P-2** reacts with the guest MA, formation of the unstable complex will produce a relaxation channel for the excited state to decay.

dx.doi.org/10.1021/jo3005233 | J. Org. Chem. 2012, 77, 4759−4764

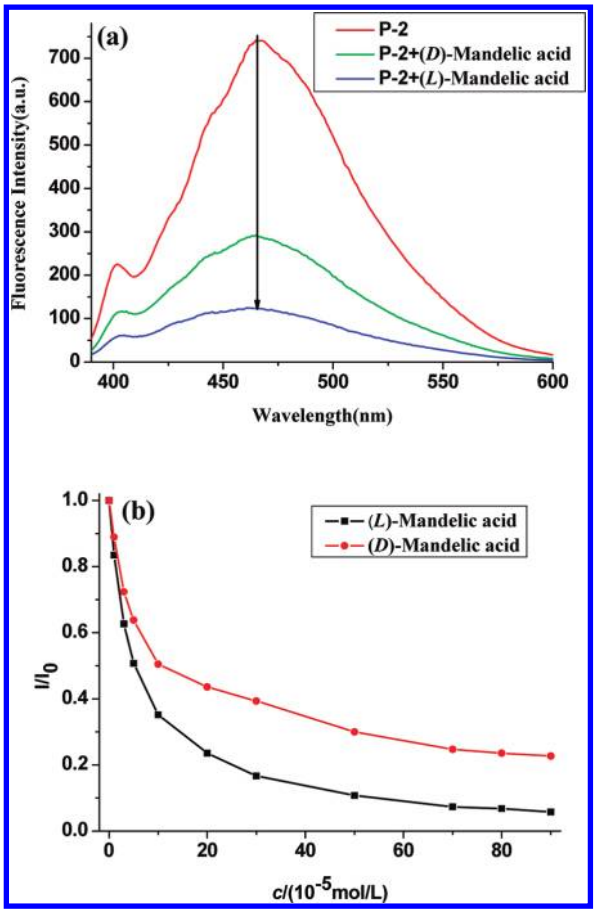


Figure 2. (a) Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to salan moiety in toluene, 0.4% v/v DME) with and without (D)- and (L)-MA (1.0×10^{-2} mol/L in toluene, 10% v/v DME) at 1:30 molar ratio. (b) Fluorescence enhancement of **P-2** (1.0×10^{-5} mol/L) with (D)- and (L)-MA (λ_{em} = 465 nm; λ_{ex} = 385 nm).

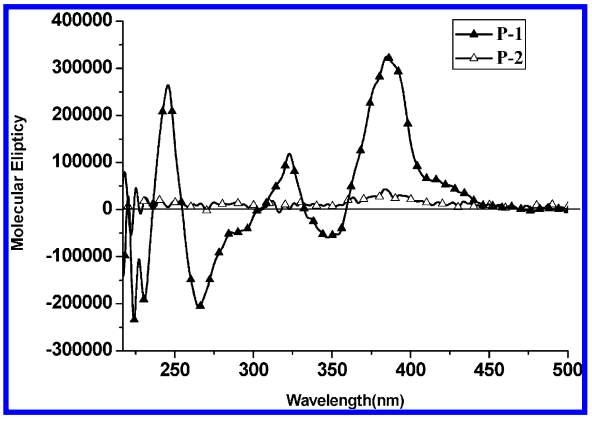


Figure 3. CD spectra of **P-1** and **P-2** (1.0×10^{-4} mol/L in THF).

As a result, the initial excitation leads to formation of an exciton, which can rapidly migrate between isoenergetic sites along the π-electronic conjugated system to a low energy acceptor site, which blocks the radiative decay and activates the nonradiative path.[7d,13]

To further understand the fluorescence response behavior of the interaction mechanism between host **P-1** and guest MA, we studied the fluorescence change of **P-1** in the presence of the derivatives of MA by esterified protection of either the acid group or the hydroxyl group (Scheme 2). Whether **P-1** was treated with 2-acetoxy-2-phenylacetic acid or methyl 2-hydroxy-2-phenylacetate (1.0×10^{-2} mol/L in toluene, 5% v/v DME), **P-1** displays a little fluorescence enhancement response, but almost no enantioselective effect can be observed (see Supporting Information, Figures S2 and S3). These studies demonstrate that both the carboxylic acid group and the hydroxyl group of MA play important role in the enantioselective recognition of salen-based chiral fluorescence sensor. Inspired by the preliminary results, we further investigated the enantioselectivity of **P-1** toward other α-hydroxyl carboxylic acids, such as lactic acid and tartaic acid. As is evident from Figure 4, the chiral polymer sensor can exhibit obvious enantioselective response toward (L)-lactic acid, and the value of *ef* is 6.55 at 1:20 molar ratio. While using (D)-/(L)-tartaic acid as guest molecules, no obvious fluorescence enhancement responses on the enantioselectivity of tartaic acid were observed (see Supporting Information Figure S4).

CONCLUSION

In summary, two novel chiral fluorescence polymers incorporating functional (*R*,*R*)-salen/salan moieties were designed. And (*R*,*R*)-salen-based chiral polymer can exhibit a greater fluorescence "turn-on" response toward (L)-α-hydroxyl carboxylic acids and appear bright blue fluorescence color change under a commercially available UV lamp, which can be clearly observed by the naked eyes. The value of enantiomeric fluorescence difference ratio (*ef*) can reach as high as 8.41 for mandelic acid and 6.55 for lactic acid. On the contrary, (*R*,*R*)-salan-based chiral polymer shows an obvious fluorescence "turn-off" response toward α-hydroxyl carboxylic acids.

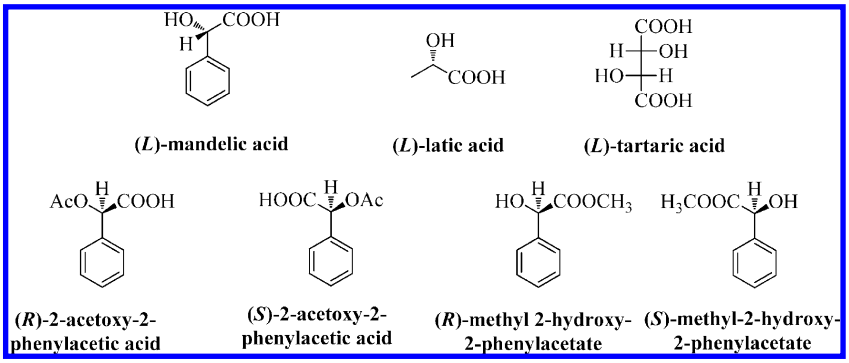
EXPERIMENTAL SECTION

5-Bromo-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde. Piperidine (2.0 mL, 20 mmol) was added to a solution of paraformaldehyde (0.6 g, 20 mmol) dissolved in HAc (30 mL) and stirred for 12 h at room temperature. Then 5-bromo-2-hydroxybenzaldehyde (4.02 g, 20 mmol) was added, and the mixture was heated at reflux for 24 h. After cooling to rt, the mixture was brought to pH ~ 8 with saturated Na_2CO_3, extracted with $CHCl_3$, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 2:1, v/v) to yield 4.61 g (77%) of the product as a pale yellow solid after removal of the solvent: mp 70 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.78 (d, J = 2.1 Hz, 1H), 7.32 (d, J = 2.1 Hz, 1H), 3.72 (s, 2H), 2.58 (br, 4H), 1.73 −1.65 (m, 4H), 1.55 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2, 161.3, 136.7, 129.7, 125.4, 124.4, 110.7, 60.6, 53.7, 25.5, 23.5; ESI-MS 298.17; FT-IR (KBr, cm^{-1}) 3417, 2935, 2864, 1674, 1594, 1448, 1385, 1238, 1110, 989. Anal. Calcd for $C_{48}H_{59}N_4O_3$: C, 77.91; H, 8.01; N, 7.57. Found: C, 76.59; H, 7.69; N, 7.80. Anal. Calcd for $C_{13}H_{16}BrNO_2$: C, 52.36; H, 5.41; N, 4.70. Found: C, 52.29; H, 5.41; N, 4.80.

5,5′-((2,5-Dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis-(2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde. 1,4-Dibutoxy-2,5-diethynylbenzene could be synthesized from hydroquinone by a four-step reaction according to reported literature.[8f] The mixture of 1,4-dibutoxy-2,5-diethynylbenzene (0.87 g, 3.2 mmol), 5-bromo-2-hydroxy-3-(piperidin-1-ylmethyl)benzaldehyde (2.01 g, 6.7 mmol), $Pd(PPh_3)_2Cl_2$ (121.2 mg, 0.17 mmol), and CuI (33.1 mg, 0.17 mmol) was dissolved in 50 mL of anhydrous Et_3N. The reaction mixture was stirred for 24 h at 70 °C under N_2. After cooling to room temperature, the solvent was removed by a rotary evaporator. The residue was purified by flash chromatography on silica gel (ethyl acetate/triethylamine, 1:1, v/v) and then dichloromethane as eluent on a short plug of silica gel. The solvent was removed and then washed by ethyl acetate to afford 5,5′-((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(2-hydroxy-3-(piperidin-1-ylme-thyl)benzaldehyde (**M-1**)

dx.doi.org/10.1021/jo3005233 | J. Org. Chem. 2012, 77, 4759−4764

Scheme 2. Chiral Guests Used in the Enantioselective Recognitions with the P-1 and P-2



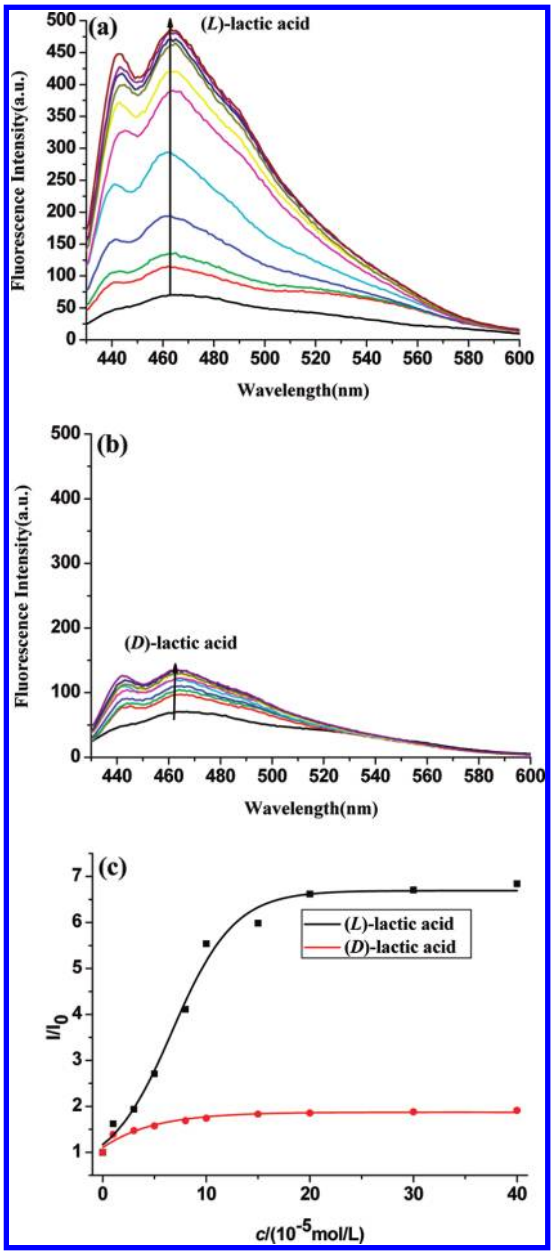


Figure 4. Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L in toluene, 0.4% v/v DME) with increasing amounts of (L)-LA (a) and (D)-LA (b) (0, 1, 3, 5, 8, 10, 15, 20, 30, 40×10^{-5} mol/L, 1.0×10^{-2} mol/L in toluene, 5% v/v DME). (c) Fluorescence enhancement of **P-1** (1.0×10^{-5} mol/L) with (D)- and (L)-LA (λ_{em} = 465 nm; λ_{ex} = 420 nm).

as a yellow powder (975 mg, 43%): mp > 300 °C; ^{1}H NMR (300 M Hz, $CDCl_3$) δ 10.41 (s, 2H), 7.87 (s, 2H), 7.40 (s, 2H), 6.99(s, 2H), 4.05 (t, J = 6.6 Hz, 4H), 3.76 (s, 4H), 2.60 (br, 8H), 1.88−1.53 (m, 20H), 1.04 (t, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.9, 162.4, 153.4, 137.0, 131.2, 123.4, 123.1, 116.8, 113.8, 113.7, 93.8, 85.0, 69.3, 60.8, 53.7, 31.3, 25.5, 23.6, 19.2, 13.9; ESI-MS 705.33; FT-IR (KBr, cm^{-1}) 3422, 2931, 2857, 2360, 1671, 1603, 1465, 1383, 1208, 1113. Anal. Calcd for $C_{44}H_{52}N_2O_6$: C, 74.97; H, 7.44; N, 3.97. Found: C, 75.18; H, 7.42; N, 3.80.

Chiral Polymer Sensor P-1. A mixture of **M-1** (705.0 mg, 1.0 mmol) and (1*R*,2*R*)-cyclohexane-1,2-diamine (114.2 mg, 1.0 mmol) was dissolved in THF (60 mL) and kept refluxing for 12 h. The solvent was removed under reduced pressure, the residue was dissolved in a small quantity of THF, and 100 mL of methanol was added to precipitate the polymer. A yellow solid was filtered off and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 to precipitate in methanol again. The polymer was dried under vacuum at room temperature for 24 h. The final yield was 72% (563.2 mg): $[\alpha]_D^{25}$ = +316.0 (c 0.2, THF); M_w = 13040, M_n = 4800, PDI = 2.72; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.52 (s, 2H), 7.34 (s, 2H), 6.96 (s, 2H), 4.02 (t, J = 6.3 Hz, 4H), 3.66−3.53 (m, 4H), 3.36 (br, 2H), 2.50 (br, 8H), 1.85−1.44 (m), 1.00 (t, J = 6.9 Hz, 6H); FT-IR (KBr, cm^{-1}) 3418, 2926, 2857, 2200, 1625, 1497, 1456, 1380, 1266, 1197, 1021, 852. Anal. Calcd for $C_{48}H_{59}N_4O_3$: C, 77.91; H, 8.04; N, 7.57. Found: C, 77.59; H, 7.69; N, 7.80.

Chiral Polymer Sensor P-2. Polymer **P-1** (200 mg) was dissolved in the mixed solvents of 10 mL of THF and 10 mL of MeOH, and then 80 mg $NaBH_4$ was added in batches to the above solution. The reaction mixture was stirred at room temperature for 2 h, and 10 mL of water 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 **P-2** as a gray powder (167 mg, 83% yield): $[\alpha]_D^{25}$ = +57.0 (c 0.2, THF); GPC M_w = 14080; M_n = 8800; PDI = 1.60; ^{1}H NMR (300 Hz, $CDCl_3$) δ = 7.33 (s, 2H), 7.12 (s, 2H), 6.97 (s, 2H), 4.02 (s, 4H), 3.92−3.74 (m, 4H), 3.60 (s, 4H), 2.47−2.34 (m, 8H + 2H), 2.11 (s, 4H), 1.82−1.27 (m), 1.00 (s, 6H); FT-IR (KBr, cm^{-1}) 3424, 2925, 2358, 1601, 1463, 1381, 1194, 1107, 854. Anal. Calcd for $C_{48}H_{63}N_4O_3$: C, 77.48; H, 8.53; N, 7.53. Found: C, 77.36; H, 8.58; N, 7.03.

■ ASSOCIATED CONTENT

Supporting Information

Fluorescence and data mentioned in above paragraphs and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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dx.doi.org/10.1021/jo3005233 | J. Org. Chem. 2012, 77, 4759−4764

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Natural Science Foundation of China (No. 21074054, 51173078, 21172106), National Basic Research Program of China (2010CB923303), and Zhejiang Provincial Natural Science Foundation (No. Y4110141) for their financial support.

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