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Fluorescence sensors based on chiral polymer for highly enantioselective recognition of phenylglycinol

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ABSTRACT

Chiral polymer **P-1** incorporating (*R*,*R*)-salen-type unit was synthesized by the polymerization of (*R*,*R*)-1,2-diaminocyclohexane with 2,5-dibutoxy-1,4-di(5-*tert*-butylsalicyclaldehyde)-phenylene (**M-1**) *via* nucleophilic addition–elimination reaction, and chiral polymer **P-2** incorporating (*R*,*R*)-salan-type unit could be obtained by the reduction reaction of **P-1** with $NaBH_4$. The fluorescence response of two chiral polymers **P-1** and **P-2** on (*R*)- or (*S*)-phenylglycinol were investigated by fluorescence spectra. The fluorescence intensities of two chiral polymers **P-1** and **P-2** show gradual enhancement upon addition of (*R*)- or (*S*)-phenylglycinol and keeps nearly linear correlation with the concentration molar ratios of (*R*)- or (*S*)-phenylglycinol. But both **P-1** and **P-2** exhibited more sensitive response signals for (*S*)-phenylglycinol. The values of enantiomeric fluorescence difference ratio (***ef***) are 1.84 and 2.05 for **P-1** and **P-2**, respectively. The results also showed that two chiral polymers **P-1** and **P-2** can also be used as fluorescence sensors for enantiomer composition determination of phenylglycinol.

Fluorescence-based enantioselective sensors are of great practical value because of their high sensitivity and potential applications in analytical, biological, and clinical biochemical environments [1–5]. They can effectively provide a real-time analytical tool for chiral compound assay. Using these 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 [6–9]. To date, reports of successful enantiodiscriminating sensors have included a variety of chiral macrocycles (fluorophore-modified calixarenes, cyclodextrins, and crown ethers), dendrimers, and oligomers [1,2,10–13].

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 due to the potentially tetradentate N_2O_2 donor with metal ions [14–16]. Recently, these molecules are getting increasing attention in chiral recognition area. Pu and his coworkers reported that the bisbinaphthyl macrocycles containing chiral diamine were useful for the enantioselective fluorescence recognition for amino acid derivatives and *R*-hydroxycarboxylic acids [11,17]. Banerjee and his coworkers synthesized a chiral Schiff-base compound which showed highly enantioselective recognition of mandelic acid [18]. Many fluorescence sensors for enantioselective recognition of amines, amino alcohols and hydroxycarboxylic acids have been reported, but most of them are based on chiral small molecules, and fluorescent polymer-based sensors are very few [19–23]. Chiral polymers used as fluorescence-based enantioselective sensors for chiral molecule recognition offer several advantages over small molecule sensors, such as fluorescence efficiency enhancement and possible cooperative effects of multiple chiral units [19]. Moreover, these fluorescent chiral polymers can be systematically modified by the introduction of the functional groups based on steric and electronic property at well-defined molecular level.

In this paper, we first reported the synthesis of two novel (*R*,*R*)-salen/salan-based polymers **P-1** and **P-2** used as fluorescence sensors for chiral discrimination of phenylglycinol. The (*R*,*R*)-salen or salan moieties can orient a well-defined spatial arrangement in the regular polymer backbone. Both **P-1** and **P-2** exhibited highly chiral discrimination of phenylglycinol. The results also indicated that the two chiral polymers **P-1** and **P-2** can be used for enantiomer composition determination of phenylglycinol.

The synthesis procedures of chiral polymers **P-1** and **P-2** are shown on Scheme 1. 2,5-dibutoxy-1,4-phenylene diboronic acid was synthesized from hydroquinone according to literature [24–27]. The monomer 2,5-dibutoxy-1,4-di(5-*tert*-butylsalicyclaldehyde)phenylene could be obtained from 2-*tert*-butylphenol by a 3-step reaction according to reported literature [28–30] and needed to be kept in the

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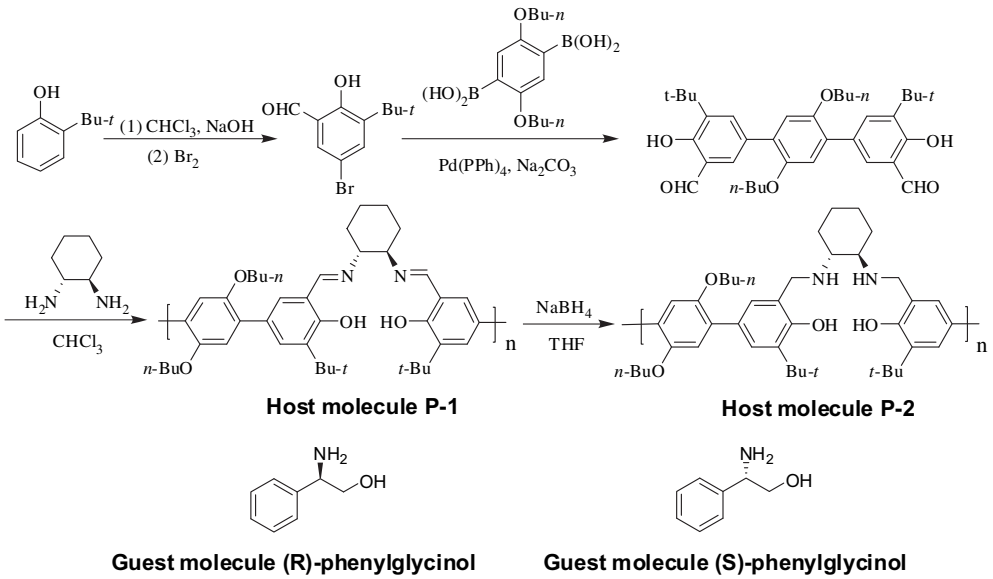

Scheme 1. Synthesis procedures of chiral polymers **P-1** and **P-2**.

dark at −4 °C before using. Chiral polymer **P-1** incorporating (*R*,*R*)-salen-type unit was synthesized by the polymerization of (*R*,*R*)-1,2-diaminocyclohexane with the monomer 2,5-dibutoxy-1,4-di(5-*tert*-butylsalicyclaldehyde)phenylene *via* nucleophilic addition–elimination reaction, and chiral polymer **P-2** could be obtained by reduction of **P-1** with $NaBH_4$. The GPC results of two chiral polymers show moderate molecular weight (Table 1). The two polymers are air stable solid and show good solubility in common solvents, such as toluene, THF, $CHCl_3$, and CH_2Cl_2, which can be attributed to the nonplanarity of the twisted polymer backbone and the flexible *n*-butoxy substitutents. The fluorescence response behavior of two chiral polymers **P-1** and **P-2** on (*R*)- or (*S*)-phenylglycinol have been investigated by fluorescence spectra. Fig. 1 shows the fluorescence spectra of the chiral polymers **P-1** and **P-2** (1.0×10^{-5} mol L^{-1} corresponding to salen-based or salan-based unit in $CHCl_3$ solution) upon addition of (*R*)- or (*S*)-phenylglycinol (0.1 mol L^{-1} in $CHCl_3$) at 1:800 M ratio. Remarkable differences in fluorescence enhancement were observed as demonstrated in Fig. 1, (R)-phenylglycinol has little effect on the fluorescence of **P-1** or **P-2**. But (*S*)-phenylglycinol causes a large increase in the fluorescence intensity of **P-1** or **P-2** under the same conditions. As shown in Fig. 1, highly enantioselective fluorescence differences were observed as expected when **P-1** and **P-2** were treated with (*R*)- or (*S*)-phenylglycinol, respectively. Herein, remarkable fluorescence differences indicate that (*R*)-phenylglycinol caused little change on the fluorescence enhancement of **P-1** and **P-2**, on the contrary, **P-1** and **P-2** can show more pronounced fluorescence response for (*S*)-phenylglycinol under the same conditions. The selective recognition effect on the guest of the chiral molecular isomers is related to the enantiomeric fluorescence difference ratio, *ef* [$ef = (I_S - I_0)/(I_R - I_0)$]. I_0 represents the fluorescence emission intensity in the absence of the chiral substrate, I_S and I_R are the fluorescence intensities in the presence of (*S*)-substrate and (*R*)- substrate, respectively [31]. The values of *ef* are 1.84 and 2.05 for **P-1** and **P-2**, which indicates that **P-1** and **P-2** can exhibit highly enantioselective response toward (*S*)-phenylglycinol, and **P-2** incorporating (*R*,*R*)-salan-type receptors shows more sensitive effect than **P-1** incorporating (*R*,*R*)-salen-type receptors. The reason may be attributed to an inherent chiral recognition based on the steric repulsion of (*R*,*R*)-salen or salan precursor for *S*-phenylglycinol. The building block of (*R*,*R*)-salen or salan receptor can well fit for the formation of a more stable complex of *R*–*S* complex as compared to the *R*–*R* diastereomeric complex. In addition, the interaction of **P-1** and **P-2** with phenylglycinol was studied at a much broader concentration range of the substrate. In regard to the fluorescence signal changes of the chiral polymers **P-1** and **P-2** on (*R*)- or (*S*)-phenylglycinol, the fluorescence intensities of both **P-1** and **P-2** appear the obvious gradual enhancement upon the addition of (*R*)- and (*S*)-phenylglycinol from the molar ratios of 1:50 to 1:800. It can also be found that the addition curves of both **P-1** and **P-2** keep nearly linear correlation with the molar ratio of (*R*)- and (*S*)-phenylglycinol (Fig. 2). The obvious fluorescence enhancement can be attributed to suppressed PET (photoinduced-electron-transfer) quenching [32–35] when the protons of phenylglycinol interacts with the nitrogen atoms of (*R*,*R*)-salen/salan-based moieties in the chiral polymer main chain. On complexation, the lone pair of electrons on the nitrogen atom is no longer available for PET, leading to the fluorescence enhancement. In the same way, salen-based polymer **P-1** should show the weaker H-bonding interaction with phenylglycinol than salan-based polymer **P-2**, and lead to the reduced enantioselective fluorescence response due to the p-π conjugation of the lone pair electrons of the nitrogen atoms in salen moieties. In a set of comparable experiments, we also studied the interaction of these two polymers **P-1** and **P-2** with (*R*)-/(*S*)-2-amino-1-propanol and (*R*)-/(*S*)-mandelic acid, but no enantioselective fluorescence responses were observed.

In this paper, we further investigated the fluorescence response of the chiral polymers **P-1** and **P-2** on different enantiomeric compositions of phenylglycinol. The fluorescence intensities of both **P-1** and **P-2** based on various molar ratios of (*R*)- and (*S*)-phenylglycinol revealed a fair linear relationship between I/I_0 and the percent of the (*S*)-phenylglycinol component (Fig. 3). This

Table 1
Polymerization results and characterization of **P-1** and **P-2**.

	Yield (%)	M_w[a]	M_n[a]	PDI	$[\alpha]_D$[b]
P-1	72.4	9860	4100	2.4	+220.0
P-2	85.3	13,530	5880	2.3	+63.5

[a] *M*w, *M*n and PDI of **P-1** and **P-2** were determined by gel permeation chromatography using polystyrene standards in THF.
[b] Temperature at 25 °C and solvent in $CHCl_3$.

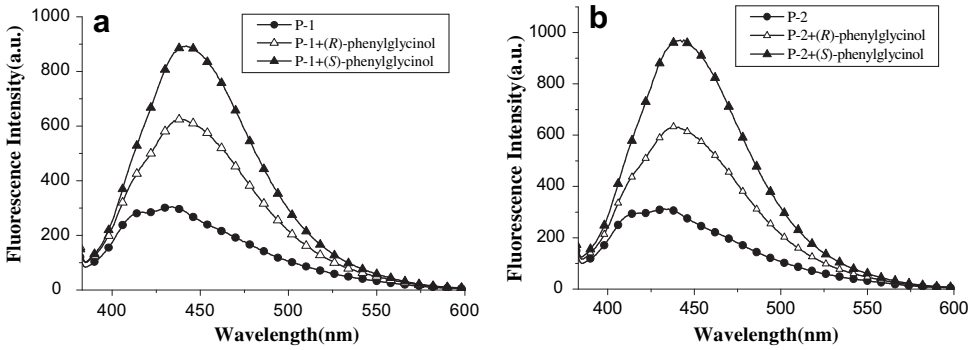

Fig. 1. Fluorescence spectra of **P-1** (a) and **P-2** (b) (1.0×10^{-5} mol L^{-1} corresponding to salen-based or salan-based unit) both with and without (*R*)- and (*S*)-phenylglycinol at 1:800 M ratio ($\lambda_{ex} = 367$ nm) in $CHCl_3$.

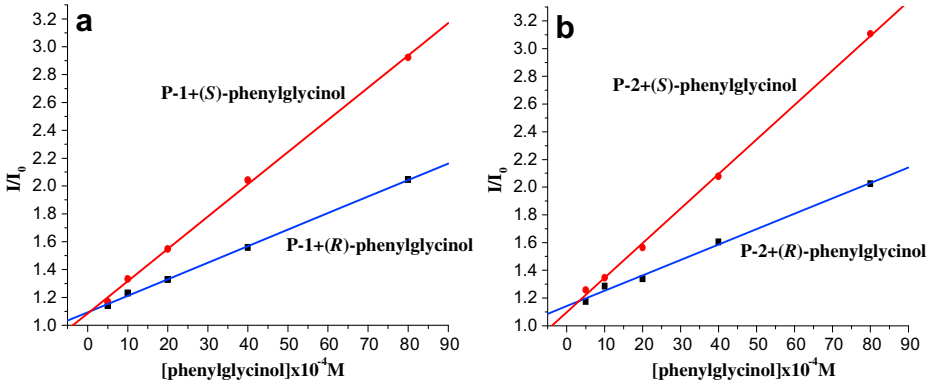

Fig. 2. Fluorescence enhancement of **P-1** (a) and **P-2** (b) (1.0×10^{-5} mol L^{-1} in $CHCl_3$) vs molar ratios of (*R*)- and (*S*)-phenylglycinol from 1:50 to 1:800.

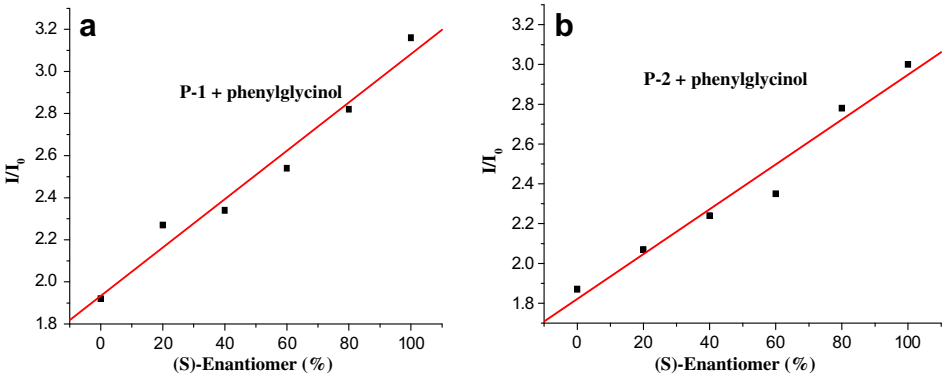

Fig. 3. Fluorescence enhancement of **P-1** (a) and **P-2** (b) (1.0×10^{-5} mol L^{-1}) vs the enantiomeric composition of phenylglycinol (8.0×10^{-3} mol L^{-1}) in $CHCl_3$.

indicated that the enantioselective fluorescence sensors **P-1** and **P-2** can be effectively applied for enantiomer composition determination of phenylglycinol.

In summary, two fluorescence-based polymers **P-1** and **P-2** incorporating (*R*,*R*)-salen and salan moieties as chiral receptors can exhibit as excellent fluorescence sensor for enantioselective recognition of (*S*)-phenylglycinol, and can also be used in ascertaining the enantiomeric composition of (R)- and (S)-phenylglycinol.

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Appendix. Supplementary data

The supplementary data associated with this article can be found, in the online version at doi:10.1016/j.polymer.2010.01.038.

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