Chiral Fluorescence Polyethers Based on BINOL for Enantioselective Recognition of Phenylalanine Anion

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ABSTRACT

Series of polyethers with different configurations were synthesized from chiral BINOL and optical epichlorohydrin. The optical behavior of the obtained polyethers is evaluated with specific optical rotation, UV-vis spectroscopy, circular dichroism (CD) and fluorescence spectroscopy. Thermogravimetric analysis (TGA) reveals the polyethers a good thermal stability. The fluorescence responses of the chiral polyethers on chiral phenylalanine anion were investigated. The sensors (*S,S*)-**4** and (*R,R*)-**4** showed high enantioselective fluorescent sensing ability to phenylalanine anion. The value of enantiomeric fluorescence difference ratio (*ef*) reached to 6.29.

KEYWORDS: chiral polyether, fluorescence enantioselective recognition, phenylalanine anion.

INTRODUCTION

Enantioselective recognition of chiral molecules by host compounds is an attractive topic for its vital role in asymmetric synthesis and biological systems.¹⁻⁴ Among the countless chiral substances, α -amino acids are the most common and basic enantiomers. Enantioselective recognition of α -amino acids attracted considerable interest due to their importance in nature.⁵⁻¹¹ Various techniques, including high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), UV/vis, circular dichroism (CD) and fluorescence spectroscopy have been applied to the discrimination and analysis of enantiomers.¹²⁻¹⁵ Enantioselective fluorescent sensors are receiving growing research attention as they potentially provide a real time technique to analysis the enantiomeric composition of chiral organic compounds.¹⁶⁻²² Although great development of fluorescent sensors has been achieved, enantioselective fluorescent sensors for structurally diverse chiral α -amino acids still remain challenges in this area due to the zwitterionic property of the α -amino acids, which results in their very slight solubility in organic solvents and little interaction with organic fluorophores in water.²³⁻²⁶ Series of fluorescent sensors, most of which are based on chiral small molecules, have been studied.²⁷⁻³¹ 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.³²⁻³⁵

In this work, we synthesized a series of polyethers derived from chiral BINOL and optical epichlorohydrin. The BINOL plays the role of fluorophore, scaffold and the chiral center. The long chain of ether band brings the polymers superior solubility, which allows us to conduct our research in a mixed solvent of THF and water. The fluorescence responses of the obtained polyethers on chiral phenylalanine anions were investigated by fluorescence spectra in THF/H₂O system, The sensors (*S,S*)-**4** and (*R,R*)-**4** were found to show high enantioselective fluorescent sensing ability to phenylalanine anion. The value of enantiomeric fluorescence difference ratio (*ef*) reaches to 6.29,

makes (*S,S*)-**4** and (*R,R*)-**4** practically useful sensors for the recognition of the chiral phenylalanine anion.

EXPERIMENTAL

Reagents and instrumentation

All solvents and reagents are commercially available and analytical-reagent-grade. Optically active epichlorohydrin (ECH) was purchased from Yueyang Branch Company, Shenzhen Yawangkang Technology Co., Ltd. Toluene were purified by distillation from sodium in the presence of benzophenone. NMR spectra were measured on Bruker ARX400 MHz spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. Optical rotation data were measured on a Perkin Elmer Model 341 LC Polarimeter at 365 nm. Elemental analyses were carried out on Elementar Vario EL instrument. GPC analyses were performed with a JASCO-GPC system consisting of DG-1580-53 degasser, PU-980 HPLC pump, UV-970 UV/Vis detector, RI-930 RI detector, and CO-2065-plus column oven (at 38 °C) using two connected Shodex GPC-KF-804L columns in THF (sample concentration = 1 wt%; flow rate = 1.0 mL/min). The molecular weight was calibrated with commercially available polystyrene. The fluorescence measurements were done on a Shimadzu RF-5301PC spectrofluorimeter. UV-vis spectra were obtained with a Shimadzu UV-2450 spectrophotometer. Thermal gravimetric analysis was conducted on a thermogravimetric analyzer (TGA Q50, TA instrumen, USA).

Synthesis of chiral 2-glycidyloxy-2'-methoxymethyloxy-1,1'-binaphthalene, (monomer **2**)

2'-(methoxymethoxy)-[1,1'-binaphthalen]-2-ol, (**1**) (*S* or *R*) (3.30 g, 10 mmol), powder potassium hydroxide (KOH) (1.12 g, 20 mmol), tetrabutylammonium bromide (TBAB) (0.32 g, 1 mmol) and 50 mL THF were added in a 100 mL round-bottom flask. The mixture was stirred for 10 minutes at room temperature. (*S*)-ECH or (*R*)-ECH or racemic ECH (1.39 g, 15 mmol) was added and the mixture was stirred at the same temperature for another 20 h. Solvent was evaporated under reduced pressure and the residue was diluted with ethyl acetate (50 mL). The ethyl acetate solution was washed with water. The water layer was extracted with ethyl acetate (3×20 mL) and the combined organic layer was dried over Na₂SO₄. Flash column chromatography (petroleum ether/ethyl acetate = 3/1) was performed carefully on silica gel to give compound **2** (colorless oil, yield 94–96%).

(*S,S*)-**2**, yield 94%. $[\alpha]_{365}^{20} = -669.0$ (*c* = 1.0, THF). ¹H NMR δ : 7.95 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.18 (s, 2H), 7.17 – 7.08 (m, 2H), 5.09 (d, *J* = 6.5 Hz, 1H), 4.98 (d, *J* = 6.7 Hz, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 4.00 (dd, *J* = 11.2, 4.7 Hz, 1H), 3.16 (s, 3H), 2.94 (s, 1H), 2.55 (s, 1H), 2.30 (s, 1H). ¹³C NMR δ : 154.25, 152.93, 134.21, 134.14, 130.01, 129.81, 129.67, 129.58, 128.10, 128.09, 126.57, 126.44, 125.69, 125.59, 124.16, 124.13, 121.12, 121.05, 117.37, 116.34, 95.35, 70.62, 55.94, 50.37, 44.50. Elem. Anal. Calcd. for C₂₅H₂₂O₄: C, 77.70; H, 5.74. Found: C, 77.75; H, 5.76.

(*S,R*)-**2**, yield 95%. $[\alpha]_{365}^{20} = -741.0$ (*c* = 1.0, THF). ¹H NMR δ : 7.97 – 7.94 (m, 2H), 7.88 (d, *J* = 6.2 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.22 – 7.12 (m, 4H), 5.08 (s, 1H), 4.97 (d, *J* = 6.4 Hz, 1H), 4.16 – 4.12 (m, 1H), 4.03 – 3.99 (m, 1H), 3.16 (s, 3H), 2.95 (s, 1H), 2.55 – 2.51 (m, 1H), 2.30 (s, 1H). ¹³C NMR δ : 154.14, 152.96, 134.24, 134.17, 130.33, 129.81, 129.69, 129.60, 128.13, 126.60, 126.50, 125.69, 125.62, 124.20, 124.15, 121.16, 121.01, 117.40, 116.23, 95.38, 69.95, 55.94, 50.39, 44.32. Elem. Anal. Calcd. for C₂₅H₂₂O₄: C, 77.70; H, 5.74. Found: C, 77.73; H, 5.78.

(*S*)-**2**, yield 95%. $[\alpha]_{365}^{20} = -513$ ($c = 1.0$, THF). ^1H NMR δ : 7.95 (dd, $J = 8.9, 3.1$ Hz, 2H), 7.87 (d, $J = 7.2$ Hz, 2H), 7.57 (dd, $J = 9.0, 1.5$ Hz, 1H), 7.44 (dd, $J = 9.0, 3.4$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.17 (ddd, $J = 20.9, 10.1, 5.4$ Hz, 4H), 5.08 (dd, $J = 6.7, 3.8$ Hz, 1H), 4.97 (dd, $J = 9.6, 6.8$ Hz, 1H), 4.16 – 4.05 (m, 1H), 4.00 (dd, $J = 11.3, 4.7$ Hz, 1H), 3.16 (d, $J = 5.5$ Hz, 3H), 2.94 (s, 1H), 2.54 (dt, $J = 9.0, 4.6$ Hz, 1H), 2.30 (dd, $J = 4.9, 2.5$ Hz, 1H). ^{13}C NMR δ : 154.05, 152.83, 134.14, 134.06, 129.96, 129.60, 129.52, 128.00, 126.51, 126.41, 125.63, 125.54, 124.10, 121.08, 117.38, 116.41, 116.28, 95.37, 70.66, 70.05, 55.94, 50.39, 50.36, 44.58, 44.41. Elem. Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_4$: C, 77.70; H, 5.74. Found: C, 77.72; H, 5.75.

(*R,R*)-**2**, yield 94%. $[\alpha]_{365}^{20} = +661$ ($c = 1.0$, THF). ^1H NMR δ : 7.95 (dd, $J = 8.9, 2.4$ Hz, 2H), 7.87 (d, $J = 7.7$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 1H), 7.45 – 7.42 (m, 1H), 7.34 (t, $J = 7.4$ Hz, 2H), 7.22 – 7.10 (m, 4H), 5.08 (dd, $J = 6.5, 3.8$ Hz, 1H), 4.99 – 4.97 (m, 1H), 4.07 (dd, $J = 11.4, 3.4$ Hz, 1H), 4.00 (d, $J = 6.4$ Hz, 1H), 3.16 (s, 3H), 2.94 (s, 1H), 2.56 – 2.53 (m, 1H), 2.31 – 2.28 (m, 1H). ^{13}C NMR δ : 154.03, 152.72, 133.99, 133.93, 129.80, 129.80, 129.59, 129.47, 129.38, 127.89, 126.37, 126.24, 125.47, 125.38, 123.96, 123.93, 120.88, 120.79, 117.14, 116.09, 115.99, 95.12, 70.39, 55.73, 50.16, 44.28. Elem. Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_4$: C, 77.70; H, 5.74. Found: C, 77.77; H, 5.77.

(*R,S*)-**2**, yield 96%. $[\alpha]_{365}^{20} = +735$ ($c = 1.0$, THF). ^1H NMR δ : 7.95 – 7.92 (m, 2H), 7.86 (d, $J = 6.4$ Hz, 2H), 7.56 (d, $J = 9.0$ Hz, 1H), 7.43 (dd, $J = 9.0, 3.4$ Hz, 1H), 7.33 (t, $J = 7.3$ Hz, 2H), 7.21 – 7.10 (m, 4H), 5.08 – 5.05 (m, 1H), 4.95 (t, $J = 4.7$ Hz, 1H), 4.14 (dd, $J = 11.6, 3.1$ Hz, 1H), 3.98 (d, $J = 6.7$ Hz, 1H), 3.14 (s, 3H), 2.93 (s, 1H), 2.52 (dd, $J = 9.5, 4.6$ Hz, 1H), 2.31 – 2.27 (m, 1H). ^{13}C NMR δ : 153.96, 152.75, 134.05, 133.97, 129.87, 129.87, 129.65, 129.53, 129.44, 127.93, 126.42, 126.33, 125.52, 125.47, 124.04, 124.00, 121.03, 120.89, 117.28, 116.14, 95.29, 69.91, 55.83, 50.29, 44.27. Elem. Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_4$: C, 77.70; H, 5.74. Found: C, 77.74; H, 5.78.

(*R*)-**2**, yield 95%. $[\alpha]_{365}^{20} = +526$ ($c = 1.0$, THF). ^1H NMR δ : 7.95 (d, $J = 8.7$ Hz, 2H), 7.87 (d, $J = 7.5$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.34 (t, $J = 6.7$ Hz, 2H), 7.24 – 7.10 (m, 4H), 5.08 (d, $J = 3.6$ Hz, 1H), 4.97 (t, $J = 7.6$ Hz, 1H), 4.13 (t, $J = 13.4$ Hz, 1H), 4.00 (dd, $J = 11.0, 4.4$ Hz, 1H), 3.15 (d, $J = 4.1$ Hz, 3H), 2.94 (s, 1H), 2.57 – 2.51 (m, 1H), 2.30 (s, 1H). ^{13}C NMR δ : 154.57, 154.44, 153.24, 134.53, 134.46, 130.35, 130.16, 130.13, 130.00, 129.91, 128.41, 126.90, 126.80, 126.77, 126.03, 126.01, 125.93, 124.50, 121.51, 121.39, 117.75, 117.73, 116.74, 116.62, 95.76, 95.73, 71.01, 70.38, 56.31, 50.76, 50.73, 44.92, 44.75. Elem. Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_4$: C, 77.70; H, 5.74. Found: C, 77.76; H, 5.75.

Preparation of poly-2-glycidyoxy-2'-methoxymethyloxy-1,1'-binaphthalene, (polyether 3)

A test tube with a stirrer bar was charged with 1.92 g (5.00 mmol) of epoxide monomer **2**, 0.2 mmol of KOH and 1 mL degassed toluene under an argon atmosphere, and then sealed with the flame of a Bunsen burner. The test tube was put into an oil bath thermostat at 110 °C. The reaction mixture was then stirred for 24 h. The reaction mixture was then cooled to room temperature and the tube was opened. Next, 10 mL THF was added to give a homogenous solution. The THF solution was poured into 100 mL methanol to precipitate the white polymer. The resulting polymer was filtrated and washed with methanol several times. The above mentioned process, that is, the solving and precipitating, was repeated, then the obtained precipitation was dried in vacuo at 50 °C to obtain polyether **3** (white powder, yield 74–77%). ^1H NMR δ : 7.90 – 6.76 (br, 12H, Ar-H), 5.01 – 4.43 (br, 2H, –O–CH₂–O–), 3.75 – 3.20 (br, 2H, O–CH₂–), 3.15 – 2.15 (br, 6H, –CH₂–O, –O–CH₃, >CH–O). ^{13}C NMR δ : 154.09, 152.62, 134.06, 129.68, 129.39, 129.24, 127.97, 126.33, 125.40, 123.98, 123.62, 121.22, 119.69,

117.07, 115.01, 94.90, 69.04, 55.67.

Preparation of poly-2-glycidyoxy-[1,1'-binaphthalen]-2-ol, (polyether 4)

1.05 g polyether **3** was dissolved in a mixture solvent (35 mL THF and 10 mL 12 M HCl). The mixture was stirred for 24 h at room temperature. Then the mixture was poured into 350 mL methanol to precipitate the white polymer. The resulting polymer was filtrated and washed with methanol several times. The obtained precipitation was dried in vacuo at 50 °C to obtain polyether **4** (white powder, yield 94–97%). ¹H NMR δ : 7.97 – 6.59 (br, 12H, Ar–H), 6.02 – 5.19 (br, 1H, –OH), 3.69 – 3.17 (br, 2H, –O–CH₂–), 2.89 – 2.08 (br, 3H, –CH₂–O, >CH–O). ¹³C NMR δ : 154.75, 151.46, 134.10, 130.44, 129.48, 128.96, 128.21, 128.06, 127.09, 126.44, 125.20, 125.01, 124.14, 123.24, 118.09, 115.87, 114.98, 77.60, 68.02.

Preparation of the test samples

The host compounds **4** were dissolved in a THF/H₂O system (1:1, 0.01 M Tris – HCl buffer, pH 7.4) as stock solutions. The tetrabutylammonium salts were prepared by adding 1 equiv. of tetrabutylammonium hydroxide to a solution of (*D*)- or (*L*)-phenylalanine the in methanol and stirred for 2 h. After removing the methanol under reduced pressure, the syrup was dried under high vacuum for 24 h and prepared as stock solutions in a THF/H₂O system (1:1, 0.01 M Tris – HCl buffer, pH 7.4). The test solutions were prepared by mixing desired volumes of anion solution to a series of stock solution of the host compound.

RESULTS AND DISCUSSION

Synthesis

Chiral polymer sensors were synthesized according to Scheme 1. The reaction of compound **1** and ECH catalyzed by KOH and TBAB gives monomer **2** with pretty high yields 94-96%. Polyether **3** was obtained with the yields varied from 74% to 77% by anionic polymerizations of **2** initiated by KOH. Polyether **4** were efficiently prepared by deprotection of **3** also with high yields 94-97%.

Scheme 1. The synthetic route for the monomers **2** and polyethers **3** and **4**.

The data of the synthesized compounds are shown in Table 1. The *M_n* of polyether **3** was 3300-3800, about 9 or 10 repeat units. The deprotection of MOM group made the *M_n* of polyether **4** normally decreased to 3000-3400. Both polyether **3** and **4** have narrow molecular weight distribution, the PDI changes from 1.24 to 1.30. The specific optical rotation of the obtained compounds **2**, **3** and **4** show that (*S*)-BINOL gives the obtained compounds negative rotation, when (*R*)-BINOL was used, the compounds all showed positive rotation. The rotation increased a little after deprotection when it compared of **3** and **4** with the same configuration.

Table 1. Anionic polymerizations of epoxide monomers ^a

Conf.	Monomers 2		Protected-polyether 3				Deprotected-polyether 4			
	Yield	[α] ₃₆₅ ^{20 b}	Yield	[α] ₃₆₅ ^{20 b}	<i>M_n</i>	PDI	Yield	[α] ₃₆₅ ^{20 b}	<i>M_n</i>	PDI

	/% ^a		/% ^a		(M _w /M _n) ^c		/% ^a		(M _w /M _n) ^c	
(S,S)	94	-669	75	-906	3357	1.25	96	-986	3076	1.24
(S,R)	95	-741	77	-716	3856	1.28	94	-776	3415	1.26
(S)	95	-513	76	-855	3413	1.29	96	-889	3024	1.27
(R,R)	94	+661	77	+896	3349	1.27	97	+979	2967	1.24
(R,S)	96	+735	74	+730	3783	1.25	94	+781	3352	1.24
(R)	95	+526	77	+838	3381	1.30	97	+878	2993	1.26

^a The polyethers were obtained by bulk polymerization for 24 h at 110 °C using KOH as an initiator, [M]/[I] = 25:1. ^b $c = 1.0 \text{ mg} \cdot \text{mL}^{-1}$ in THF. ^c Number-average molar mass (M_n), weight-average molar mass (M_w), and polydispersity (M_w/M_n) were determined by GPC in THF on the basis of standard polystyrene calibration.

The CD spectroscopy was used to further characterize the chiroptical properties of **2**, **3** and **4**. As is shown in *Supplementary Information Part 2*, all the compounds absorbed intensively at 244nm, indicating the electronic transitions of BINOL group. Another two opposite weak peaks were at 288nm and 319nm. Mirror images were observed in the CD spectra when different configuration of BINOL was used. Comparing with the same configuration compounds such as (S,S)-**2**, (S,S)-**3** and (S,S)-**4**, the CD spectra of **2**, **3**, **4** were almost the same, revealing that no other chiral centers were formed in the polymerization and deprotection process.

Thermogravimetric analysis (TGA) of (R,R)-**4** was carried out (*Supplementary Information Part 3*). The high decomposition temperature 325 °C reveals the polyether (R,R)-**4** excellent thermal stability.

Fluorescence spectra study

The fluorescence response behavior of the chiral polyether on (D)- or (L)-phenylalanine anions were investigated in a solution (1:1 THF/H₂O, 0.01 mol·L⁻¹ Tris-HCl buffer, pH=7.4) of **4** and enantiomers phenylalanine anions (as tetrabutylammonium salts). As expected, the dilute solution of (S,S)-**4** had low fluorescence at 364 nm. We first examined the fluorescent response of chiral polyether (S,S)-**4** on (D)- and (L)-phenylalanine anions. (D)-phenylalanine anion causes a large increase in the fluorescence intensity of (S,S)-**4** at 364 nm, (L)-phenylalanine anion has little effect on the fluorescence intensity of (S,S)-**4** under the same condition (Figure 1 (a)). (D)-phenylalanine anion enhanced the fluorescence intensity of (S,S)-**4** 6.29 times more than (L)-phenylalanine anion did, that is, $ef = 6.29$ ($ef = (I_D - I_0)/(I_L - I_0)$). I_0 represents the fluorescence emission intensity in the absence of the chiral substrate. I_D and I_L are the fluorescence intensities in the presence of (D)-substrate and (L)-substrate, respectively). Due to inherent chiral recognition, using the mirror sensor (R,R)-**4** instead of (S,S)-**4**, a contrasting result was obtained as being expected (Figure 1 (b)). The large fluorescence increasing could be attributed to the photoinduced electron transfer (PET) mechanism. In the absence of anion, the electron-withdrawing group -OH decreased fluorescence intensity, when the sensors interact with the anion, the interaction was expected to turn on the fluorescence by inhibiting the PET.^{5, 36, 37}

To get deep insight into the recognition system, (R)-**4**, (S,R)-**4** and (R,S)-**4** were applied to conduct the fluorescent recognition. (R)-**4** shows a selective recognition of (L)-phenylalanine anion, but the selectivity is weaker than that of (R,R)-**4** (Figure 1 (c)). When (S,R)-**4** and (R,S)-**4** were treated with (D)- or (L)-phenylalanine anion, as shown in Figure 1 (d) and (e), nearly the same weak fluorescence enhancement was observed, but the fluorescence enhancement did not indicate any enantioselectivity. We believe the configurations of both BINOL and ECH affect the selectivity, the building block of BINOL modified by ether and hydroxyl groups can well fit for the formation of a more stable complex of (R,R)-**4** + (L) and (S,S)-**4** + (D).

We also found that the hydroxyl groups of polyether **4** are necessary for the selective recognition of

phenylalanine anion. As can be seen in Figure 1 (f), when it comes to (R,R) -**3** (the hydroxyl group is protected), the fluorescence is much stronger than (R,R) -**4** at the same concentration. While only very small fluorescence enhancement is observed in the presence of (D) - or (L) -phenylalanine anion.

The effect of various concentrations of (D) - and (L) -phenylalanine anions on the fluorescence of (R,R) -**4** at 364 nm was investigated (Figure 2). It can be seen that the fluorescence intensity was enhanced within the scope of the investigated concentrations. (L) -phenylalanine anion led to 1.5–3.25-fold increase in the fluorescence intensity of (R,R) -**4**, while (D) -phenylalanine anion caused little change in the fluorescence. Thus, the sensor (R,R) -**4** proved to be highly enantioselective toward phenylalanine anion.

Figure 1. Fluorescence spectra of the polyethers ($1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ in 1:1 v/v THF/ H_2O , $0.01 \text{ mol} \cdot \text{L}^{-1}$ Tris-HCl buffer, pH=7.4) with (D) - and (L) -phenylalanine anion ($1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$). $\lambda_{\text{ex}} = 239 \text{ nm}$, ex/em slits = 3/5 nm.

Figure 2. Fluorescence spectra of (R,R) -**4** ($1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ in 1:1 v/v THF/ H_2O , $0.01 \text{ mol} \cdot \text{L}^{-1}$ Tris-HCl buffer, pH=7.4) with increasing amounts of (D) - and (L) -phenylalanine anion ($1, 2, 4, 8, 10 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$). $\lambda_{\text{ex}} = 239 \text{ nm}$, ex/em slits = 3/5 nm.

CONCLUSION

Herein we have synthesized a class of fluorescence-based polyether from chiral BINOL and optical ECH. The fluorescence response of the polyether on phenylalanine anion show that polyether (*S,S*)-**4** and (*R,R*)-**4** exhibit greater fluorescence enhancement response toward phenylalanine anion, the value of enantiomeric fluorescence difference ratio (*ef*) reaches as high as 6.29. These fluorescence sensitivity and enantioselectivity make (*S,S*)-**4** and (*R,R*)-**4** practically useful sensors for the recognition of the phenylalanine anion.

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SUPPORTING INFORMATION AVAILABLE

Supplementary material is available on the publisher's web site along with the published article. Charts of ¹H and ¹³C NMR, CD spectra, UV-vis spectroscopy and TGA are included.

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