Electronic Supplementary Material (ESI) for Polymer Chemistry.

'Click'-BINOL Based Chiral Ionic Polymers for Highly Enantioselective Recognition of Tryptophan Anion

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Measurements and Materials:

All solvents and reagents were commercially available and 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 spectrometerand reported as parts per million (ppm) from the internal standard TMS. MS was determined on a SHIMADZU LCMS-2020 Instrument. Fluorescence spectra were obtained from an Perkim ls-55 spectrometer. The circular dichroism (CD) spectrum was determined with a Jasco J-810 spectropolarimeter. Specific rotation was determined with a Ruololph Research Analyfical Autopol I. C, H, and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Thermogravimetric analyses (TGA) were performed on a PerkinElmer Pyris-1 instrument under a N_2 atmosphere. Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as solvent relative to polystyrene standards.

The selective recognition response on the guest of the chiral molecular isomers is related to the enantiomeric fluorescence difference ratio, *ef* [$ef = (I_D - I_0)/(I_L - I_0)$]. Here, 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.

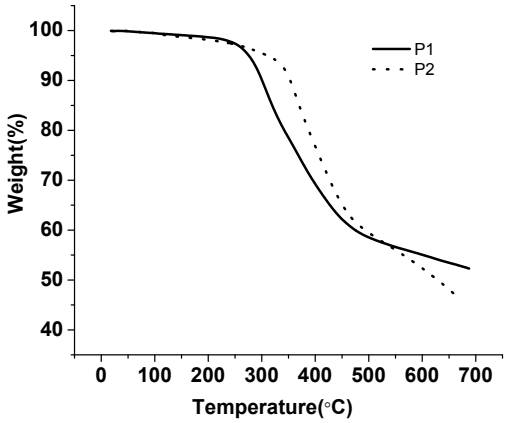


Figure S1. TGA curve of the chiral polymers

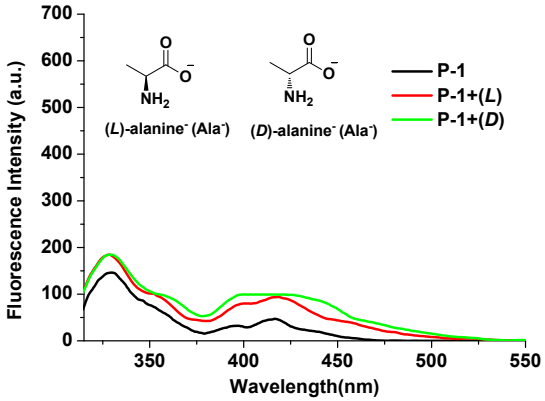


Fig. S2 Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-alanine anion and (*D*)-tryptophan anion (100×10^{-5} mol/L). (λ_{ex} = 300 nm; slit: 2.5 nm, 2.5 nm).

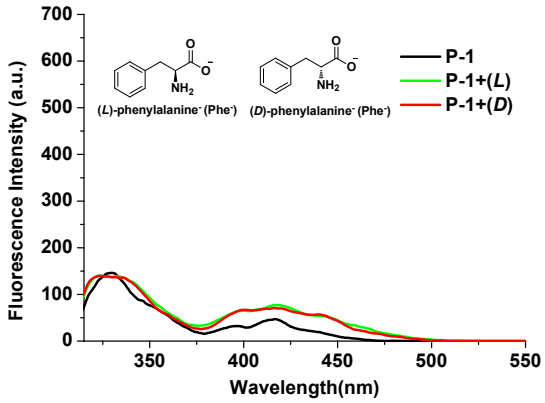


Fig. S3 Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-phenylalanine anion and (*D*)-phenylalanine anion (100×10^{-5} mol/L). (λ_{ex} = 300 nm; slit: 2.5 nm, 2.5 nm).

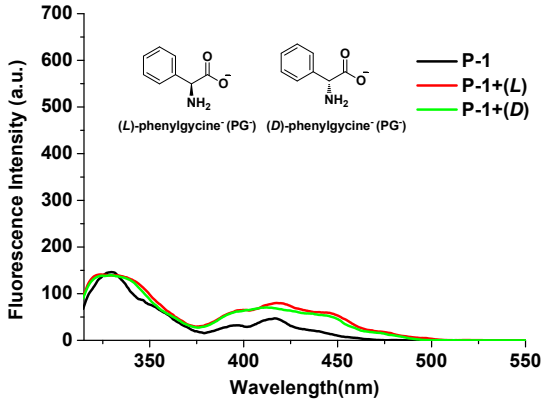


Fig. S4 Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-phenylgycine anion and (*D*)-phenylgcine anion (100×10^{-5} mol/L). (λ_{ex} = 300 nm; slit: 2.5 nm, 2.5 nm).

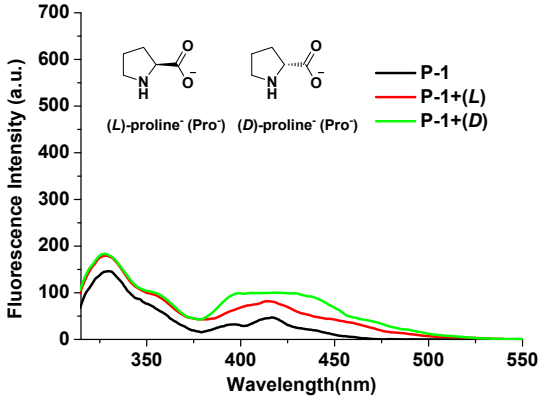


Fig. S5 Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-proline anion and (*D*)-proline anion (100×10^{-5} mol/L). (λ_{ex} = 300 nm; slit: 2.5 nm, 2.5 nm).

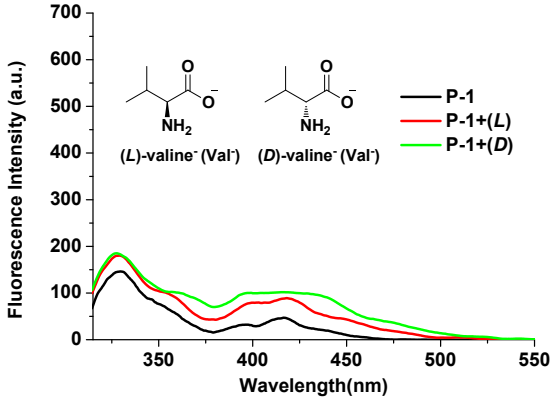


Fig. S6 Fluorescence spectra of **P-1** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-valine anion and (*D*)-valine anion (100×10^{-5} mol/L). (λ_{ex} = 300 nm; slit: 2.5 nm, 2.5 nm).

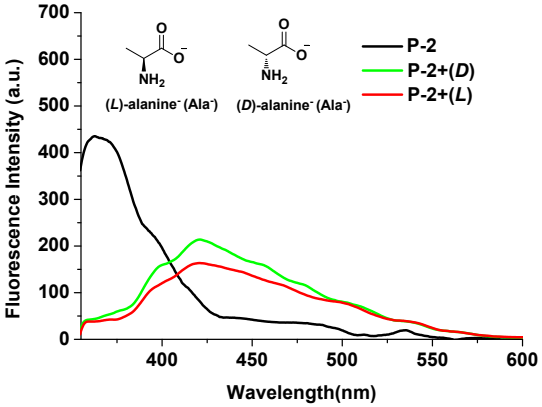


Fig. S7 Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-alanine anion and (*D*)-alanine anion (100×10^{-5} mol/L). (λ_{ex} = 335 nm; slit: 5.0 nm, 5.0 nm).

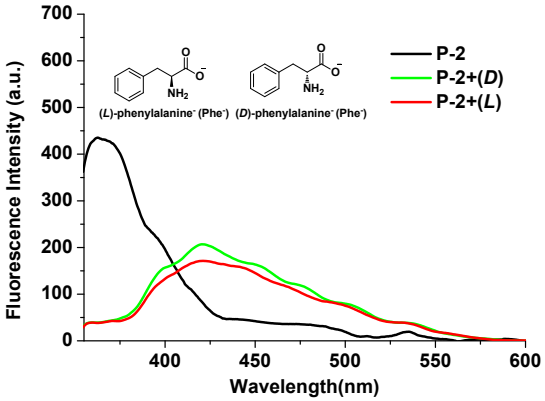


Fig. S8 Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-phenylalanine anion and (*D*)-phenylalanine anion (100×10^{-5} mol/L). (λ_{ex} = 335 nm; slit: 5.0 nm, 5.0 nm).

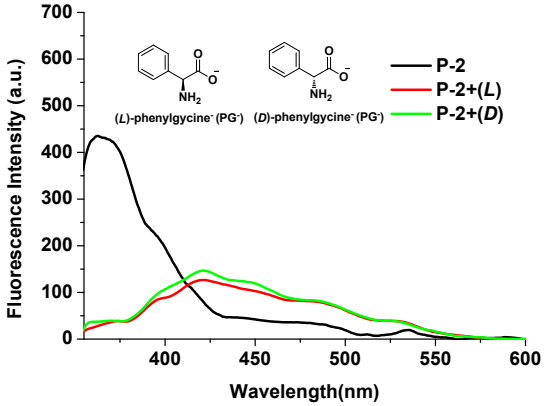


Fig. S9 Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-phenylgcine anion and (*D*)-phenylgcine anion (100×10^{-5} mol/L). (λ_{ex} = 335 nm; slit: 5.0 nm, 5.0 nm).

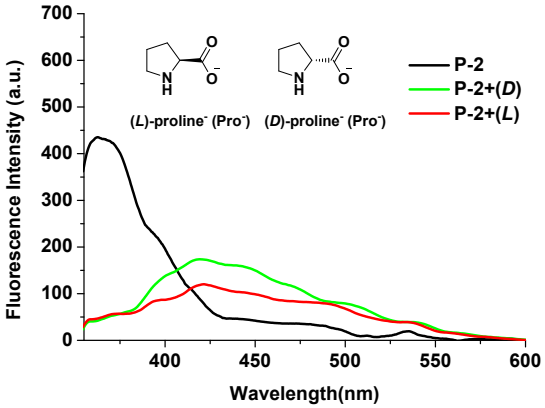


Fig. S10 Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-proline anion and (*D*)-proline anion (100×10^{-5} mol/L). (λ_{ex} = 335 nm; slit: 5.0 nm, 5.0 nm).

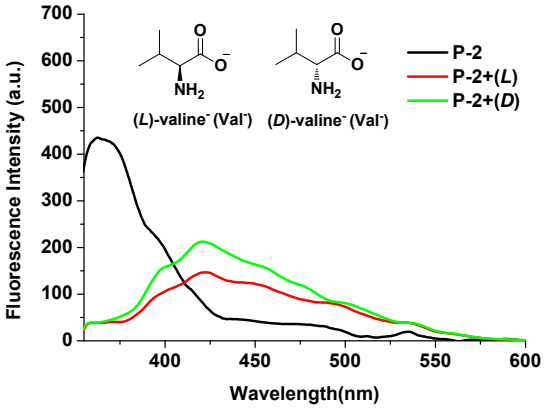


Fig. S11 Fluorescence spectra of **P-2** (1.0×10^{-5} mol/L corresponding to BINOL moiety in THF containing 0.1% DMSO) with (*L*)-valine anion and (*D*)-valine anion (100×10^{-5} mol/L). (λ_{ex} = 335 nm; slit: 5.0 nm, 5.0 nm).

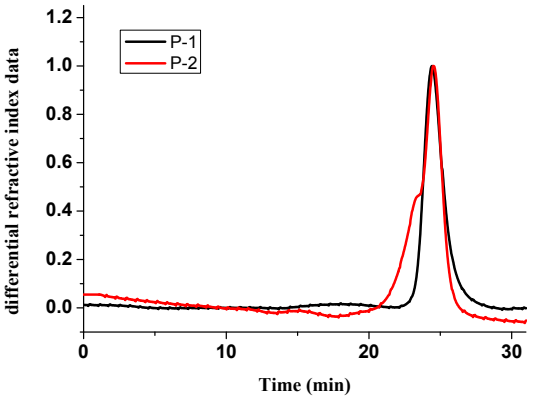
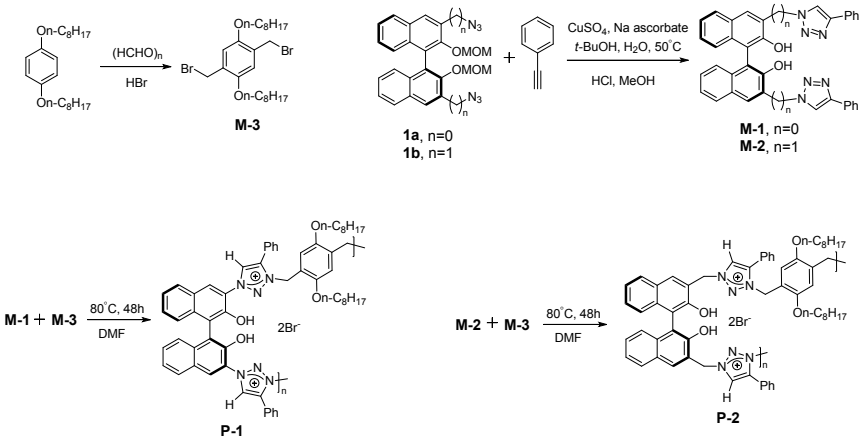


Figure S12. GPC curves of polymers **P-1** and **P-2**.



Scheme S2. Synthesis procedures of the chiral ionic polymer and model compound.

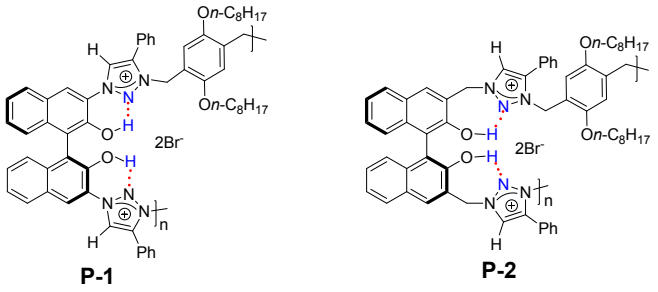
Compound **M-3** was synthesized according to the reported literature.[1]

Compound **M-1**, **M-2** were synthesized according to the reported literature.[2]

Preparation of P-1. A mixture of Compound **M-1** (0.1 g, 0.17 mmol) and **M-3** (45.42 mg, 0.17

mmol) was dissolved in 10 mL of anhydrous DMF. The obtained solution was stirred at 100 °C for 7 days under N_2 atmosphere. The solution was then cooled to room temperature. The solvent was removed under reduced pressure. 20 mL Methanol was added to precipitate the polymer. The resulting polymer was filtrated and washed with methanol (5 mL × 2) ， Et_2O (5 mL × 2)，and dried in the yield of 61% (91.6 mg). GPC results: M_w=28710, M_n=19800, PDI=1.45; $[\alpha]_D^{25}$= -74.0 (*c* 0.10, THF); FT-IR (KBr, cm^{-1}): 3416, 2905, 2797, 2408, 1603, 1522, 1334, 1211, 1155, 1060, 922, 829, 752. Anal. Calcd for $C_{60}H_{64}N_6O_4Br_2$: C, 66.03; H, 5.87; N, 7.70. Found: C, 66.10; H, 5.86; N, 7.68.

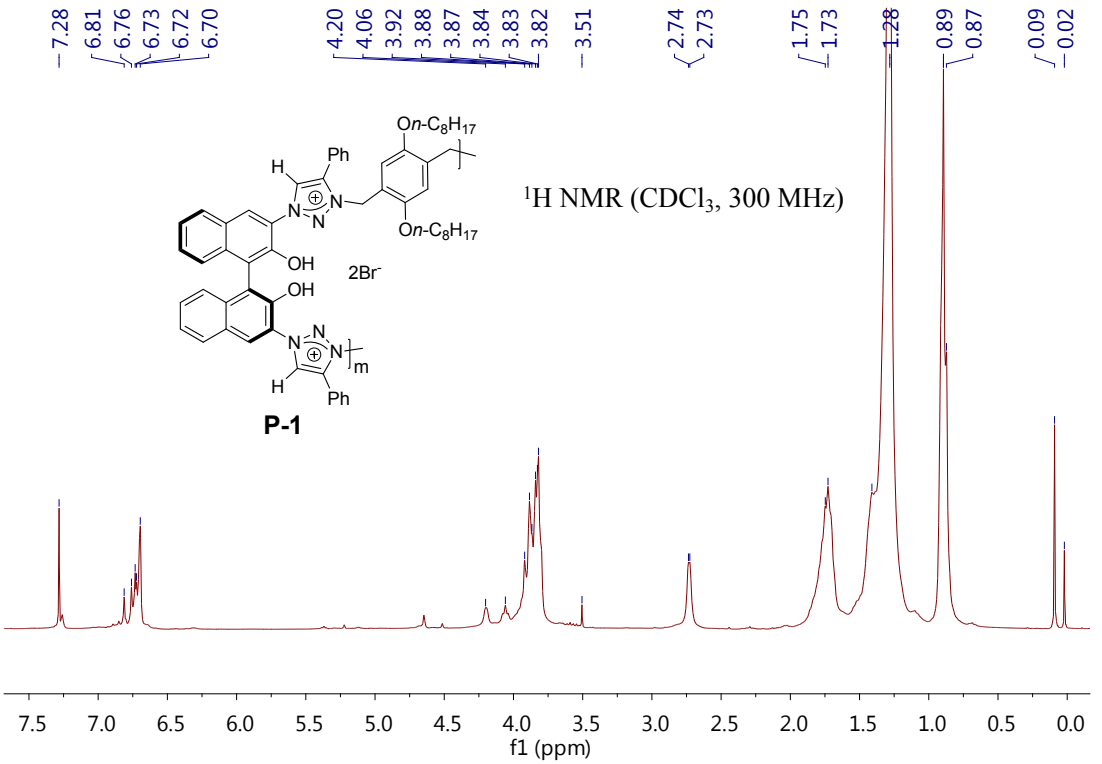
Preparation of P-2. A mixture of Compound **M-2** (0.1 g, 0.17 mmol) and **M-3** (43.30 mg, 0.17 mmol) was dissolved in 10 mL of anhydrous DMF. The obtained solution was stirred at 100 °C for 7 days under N_2 atmosphere. The solution was then cooled to room temperature. The solvent was removed under reduced pressure. 20 mL Methanol was added to precipitate the polymer. The resulting polymer was filtrated and washed with methanol (5 mL × 2) ， Et_2O (5 mL × 2)，and dried in the yield of 69% (96.0 mg). GPC results: M_w=28650, M_n=18130, PDI=1.58; $[\alpha]_D^{25}$= -66.0 (*c* 0.10, THF); FT-IR (KBr, cm^{-1}): 3405, 2938, 2811, 2607, 1623, 1514, 1388, 1220, 1151, 1046, 955, 833, 766. Anal. Calcd for $C_{62}H_{68}N_6O_4Br_2$: C, 66.52; H, 6.08; N, 7.51. Found: C, 66.48; H, 6.01; N, 7.55.

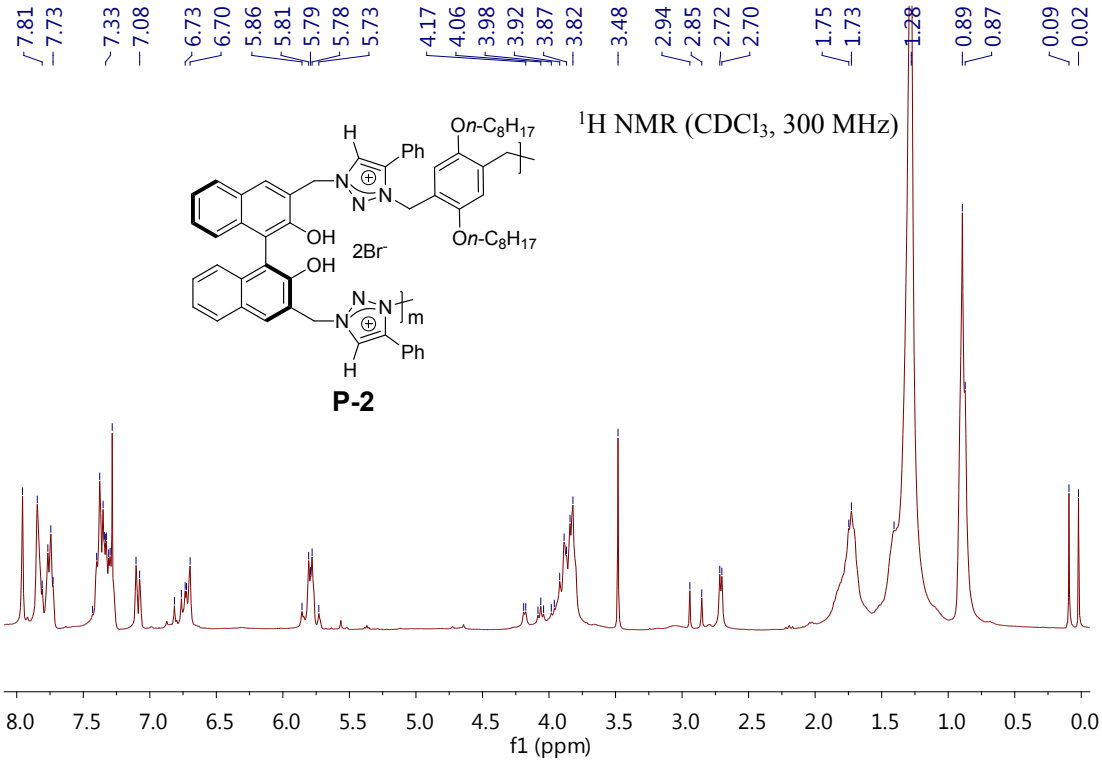


Strong intromolecular hydrogen bond (six membered ring)

Weak intramolecular hydrogen bond (seven membered ring)

Scheme S3. Intramolecular hydrogen bonds of chiral ionic polymers **P-1** and **P-2**





Reference:

1. Y. C. Zhang, W. H. Zhu, W. J. Wang, H. Tian, J. H. Sua and W. C. Wang, *J. Mater. Chem*., 2002, **12**, 1294-1300.

2. S. Beckendorf, O. G. Mancheno, *Synthesis*, 2012, **44**, 2162-2172.