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Salen-Based Enantiomeric Polymers for Enantioseletive Recognition

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This paper describes how the spatial arrangement of the building block in a polymer chain influences the recognition property of polymers. Here, we have designed and synthesized a series of fluorene based $(A\text{-}B)_n$ type salen polymers where A-part is fluorophore and B-part is recognition site using the condensation reaction of fluorene based di(salicyclaldehyde) compound (**FSal**) with diamines. Among the polymers, two are chiral (**P1** and **P2**) which are enantiomer (1*R*,2*R* vs 1*S*,2*S*) to each other and three are achiral polymers (**P3**, **P4** and **P5**). Circular dichroism studies of two chiral polymers reveal more or less equal and opposite CD intensity, indicating the induction of handedness in the polymer backbone. All polymers (**P1**-**P5**) contain same recognition site but the spatial arrangement of the recognition sites are different from one to another. We have studied recognition property of the polymers towards phenylglycinol. Only **P1** and **P2** exhibit good enantioselective recognition towards phenylglycinol through"turn-on" fluorescence enhancement because the microenvironment of recognition sites is well organized to accommodate guest molecule. Three achiral polymers **P3**, **P4** and **P5** have no capacity to capture guest molecules due to lack of suitable microenvironment of recognition sites. This observation supports the phenomena that the spatial arrangement of building blocks in a main chain polymer determines its recognition property. Moreover, **P1** and **P2** recognize guest molecules through "turn-on" fluorescence (bright blue) in solution which opens a good platform for real application purpose.

Introduction

Recently, enantioselective recognition achieves a significant progress as it is one of the most important and basic properties of natural system.[1] Sometimes, chirality at the molecular level influences the structures and properties of molecules, thus molecular chirality is of great importance in biological and artificial systems. It has also great application in optical spectroscopy (circular dichroism, the basis of optical rotation etc.), for asymmetric catalysis, sugar industry (sugars are D isomers), and pharmaceuticals (amino acids that naturally occurs are L type isomers). Numerous efforts have been employed to design fluorescence based enantioselective sensors which are of great interest because of their high selectivity, quick determination of enantiomeric composition and provide high throughput screening (HTS).[2]

1,2-Diaminocyclohexane (optically active) is an important C_2 symmetric compound which is extensively used to synthesize chiral salen or salen based ligand for asymmetric catalysis purpose.[3] Nowadays, there is a growing interest to use these molecule in the field of chiral recognition systems. Pu and co-workers used this technique for recognition of structurally diverse α-hydroxycarboxylic acids.[4] Several small molecular receptors have also been developed for chiral recognition purpose.[5,6] A growing interest is to insert chiral moiety into polymeric system for chiral recognition purpose as it provides several advantages compared with small molecule, such as fluorescence efficiency enhancement and a probable cooperative effects from multiple chiral segments.[7] Particularly, these conjugated polymers can show high affinity towards external structural perturbations and there is a change of electron density in to the conjugated polymer backbone on their interaction and complexsation with analytes.[8]

Keeping these advantages in mind, we report a series of fluorene based polymers. Two of them are chiral enantiomeric polymers (**P1** and **P2**) and remaings are achiral. All polymers contain same type of building block for interaction with analytes, however, spatial arrangement of the building blocks are not similar. This dissimilar spatial arrangement has been intricately incorporated into polymer back-bone by using different diamines. The chiral polymers have been used for enantioselective recognition towards phenylglycinol. Selectivity studies have been performed with (*S*)-/(*R*)-phenylglycinol. Upon guest molecule binding both polymers, surprisingly, show bright blue fluorescence color which is clearly observed in naked eye under 365 nm UV irradiation. Even chiral polymers have no sensitivity towards other amino alcohol like valinol or chiral molecules with different functional

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group like mandelic acid. Attempts have been taken to explain the selectivity of guest molecules in the polymer and the proper orientation of binding site using remaining three achiral polymers. To the best of our knowledge, this is the first report, showing successfull incorporation of building block with different spatial arrangement in a very simple way into polyfluorene chain and their effect towards chiral molecule recognition.

Experimental section

Materials

All commercial grade reagents (2,7-dibromo-9,9-dioctylfluorene, 5-bromosalicylaldehyde, n-BuLi, tri-methylborate, 1,3-propanediol, $Pd(PPh_3)_4$, (1*R*,2*R*)-1,2-diaminocyclohexane, (1*S*,2*S*)-1,2-diaminocyclohexane, (*cis* and *trans*)-1,2-diaminocyclohexane, ethylenediamine, and *o*-phenylenediamine were from Sigma-Aldrich Co. Ltd. and rest from Merck India Pvt. Ltd. All experiments were performed at room temperature (25 °C). Solvents (dichloromethane (DCM), chloroform ($CHCl_3$), toluene etc.) were from Merck India Pvt. Ltd., used after distillation under N_2 environment. HPLC grade tetrahydrofuran (THF) was used for spectroscopic measurement.

Instruments

Polymers were characterized by ^{1}H-NMR, ^{13}C-NMR, and MALDI-TOF techniques. NMR spectra were acquired on 500 MHz Bruker DPX spectrometer (Bruker using $CDCl_3$ as solvent and tetramithylsilane(TMS, Me_4Si) as standard reference at room temperature, with chemical shift given in parts per million (ppm). UV–Vis spectra of all samples were studied with Hewlett–Packard UV–Vis spectrophotometer (model 8453). Emission studies of solution were performed with a Horiba Jobin Yvon Fluoromax 3 spectrometer at an excitation wavelength 360 nm with the slits of 5nm/5nm. Thermogravimetric analysis (TGA) was done with TA thermal analysis system at heating rate 10 °C/min under N_2 environment. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass measurement were performed with Bruker Ultra flextreme (Bruker Daltonik GmbH, Germany) and diathranol was used as a matrix. The FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu, Japan) using the KBr pellets of the samples. The CD spectra of all the samples were taken in a spectropolarimeter (JASCO, Japan, model J-815) in a 1 mm quartz cuvette.

Synthesis of polymers

Polymers **P1**, **P4** and **P5** were synthesized according to our previous report.[9] Following the similar procedure, herein **P2** and **P3** were synthesized.

Synthesis of polymer P2

A mixture of FSal (100 mg, 0.16 mmol) and (1*S,2S*)-1,2-diaminocyclohexane (18.2 mg, 0.16 mmol) was dissolved in 6 mL of chloroform. The obtained solution was stirred at 50 °C for 24 hrs and it was cooled to room temperature. The solution was poured into 20 ml methanol and stirred for half an hour to get the solid yellow polymer (90 mg, 76%).
^{1}H-NMR (500 MHz, $CDCl_3$, δ): 13.39 (s, 2H), 8.44 (s, 2H), 7.72–7.68 (m, 2H), 7.65–7.43 (m, 8H), 7.02–6.99 (d, 2H), 3.42 (m, 2H), 1.99 (m, 8H), 1.79 (m, 4H), 1.16 -0.66 (m, 30H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 164.8, 160.5, 151.7, 139.7, 139.2, 132.6, 131.2, 130.1, 125.5, 121.0, 120.0, 118.9, 117.3, 73.1, 55.4, 40.5, 33.4, 31.9, 30.1, 29.8, 29.3, 24.3, 23.9, 22.7, 14.2. FT-IR (KBr): ν = 1632 cm^{-1} (C=N), ν = 3430 cm^{-1} (–OH).

Synthesis of polymer P3

A mixture of FSal (100 mg, 0.16 mmol) and (*cis* and *trans*)-1,2-diaminocyclohexane (18.2 mg, 0.16 mmol) was dissolved in 6 mL of chloroform. The obtained solution was stirred at 50 °C for 24hrs and it was cooled to room temperature. The solution was poured into 20 ml methanol and stirred for half an hour to get the solid yellow polymer (94 mg, 79%).
^{1}H-NMR (500 MHz, $CDCl_3$, δ): 13.56 (s, 2H), 13.38 (s, 2H), 8.51 (s, 2H), 8.44 (s, 2H), 7.74–7.42 (m, 20H), 7.06-6.99 (m, 4H), 3.70 (m, 2H), 3.41 (m, 2H), 2.00 (m, 16H), 1.79 (m, 8H), 1.09-0.68 (m, 60H). ^{13}C-NMR (125 MHz, $CDCl_3$, δ): 164.8, 164.3, 160.8, 160.5, 151.7, 139.7, 139.3, 139.2, 132.6, 132.5, 131.3, 131.2, 130.1, 130.0, 125.5, 121.0, 120.0, 119.9, 118.9, 117.6, 117.3, 73.1, 69.7, 55.3, 40.5, 33.3, 31.9, 30.1, 29.3, 24.3, 23.9, 22.7, 14.1. FT-IR (KBr): ν = 1631 cm^{-1} (C=N), ν = 3433 cm^{-1} (–OH).

Results and discussion

The synthesis procedure for monomer (**FSal**) and polymers are outlined in **Scheme 1**. **FSal**, **P1**, **P4** and **P5** were prepared from 2,7-dibromo-9,9-dioctylfluorene according to our previous reports.[9] Polymers were synthesized from the condensation reaction of **FSal** and corresponding diamine using Schiff-base chemistry according to **Scheme 1**. Following the similar procedure, **P2** and **P3** were synthesized from **FSal** with (1*S*,2*S*)-1,2-diaminocyclohexane and (*cis* and *trans*)-1,2-diaminocyclohexane to receive 76% and 79% yield, respectively. Their formation and purity were checked with the help of NMR and the absence of chemical shift at 10.03 ppm in NMR spectra for aldehyde proton of FSal in NMR spectra (Fig. S1-S4) primarily indicated the formation of polymer. The degree of polymerization (DP) value observed by MALDI-TOF study was 9 for **P2** (M_W ~6400), and **P3** (M_W ~ 6400) (Fig. S5 and Fig. S6). All Polymers are yellow solid, air stable and soluble in DCM, $CHCl_3$, toluene, THF etc.

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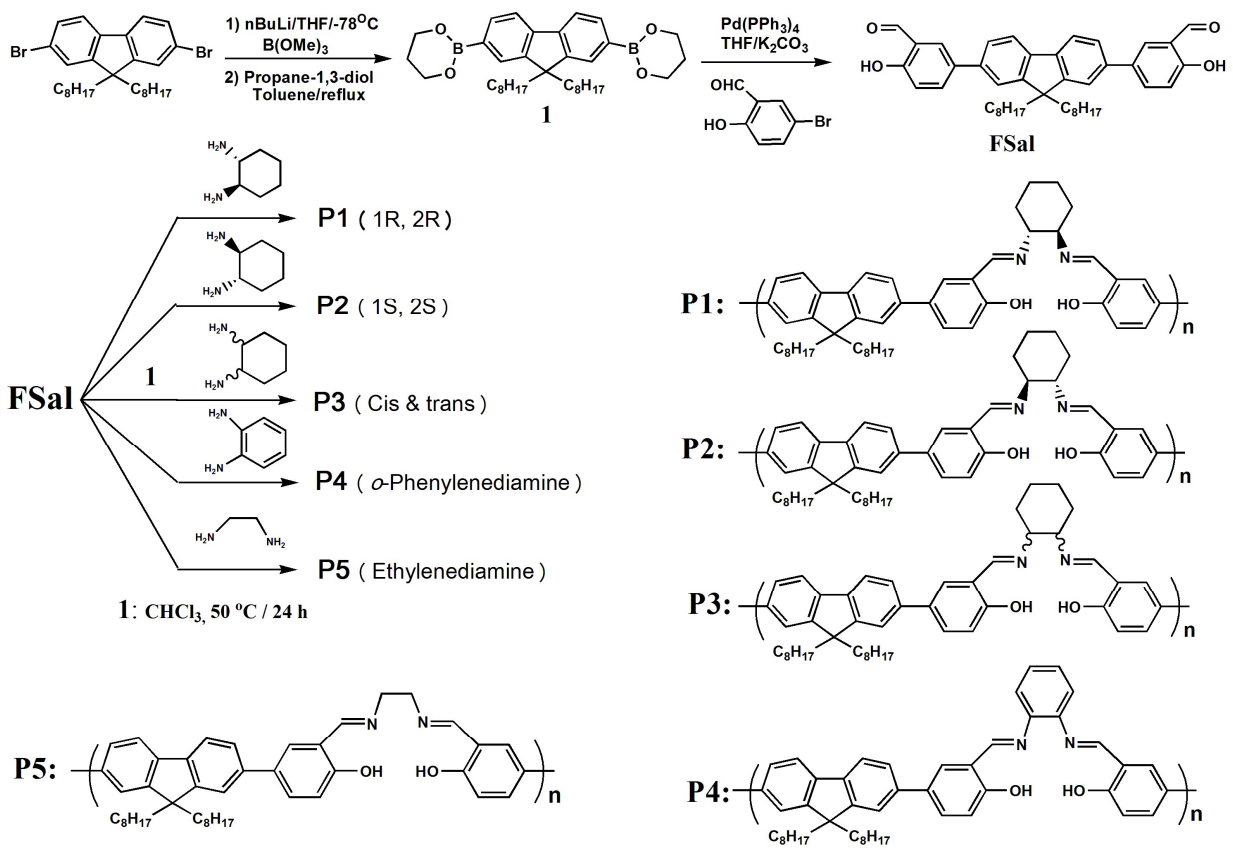

Scheme 1 Synthesis of fluorene based chiral and achiral polymers.

FTIR studies of **P2** and **P3** (**Fig. 1**) have revealed the characteristic stretching vibration of C=N ranging from 1620-1634 cm^{-1} and phenolic –OH from 3430-3491 cm^{-1} for all polymers. The stretching vibration of C=O at 1709 cm^{-1} that is present in **FSal**, is completely vanished in all polymers, supporting the formation of polymers.

Among the polymers, **P1** and **P2** are chiral and they are enantiomer to each other (*1R,2R* vs *1S,2S*). Remaining **P3**, **P4**

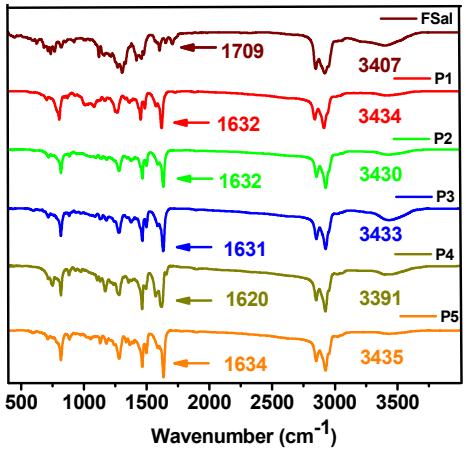

Fig. 1 IR spectra of **FSal**, **P1**, **P2**, **P3**, **P4** and **P5**.

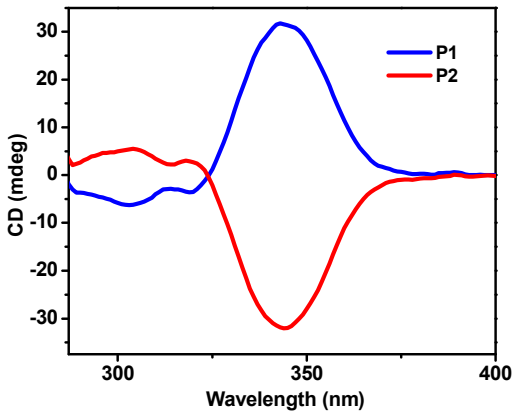

Fig. 2 CD spectra of **P1** amd **P2** (10 μM in THF).

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and **P5** are achiral in nature. The chiral nature of these two polymers (**P1** and **P2**) is confirmed by CD studies (**Fig. 2**) that produce positive Cotton effect at 342 nm for **P1** and negative Cotton effect at the same wavelength for **P2** due to the presence of helical chain structures of the repeating units in the polymer backbone. The Kuhn's factor (g) for **P1** and **P2** are 1.30×10^{-3} and 1.29×10^{-3} respectively.

Thermal stabilities of **P1** and **P2** are relatively high without loss of weight below 330°C. All of them show two step degradations: first step degradation is observed at 330 °C which probably arises from the degradation of the side chains of polyfluorene, second step degradation is observed at 400 °C and tend to complete decomposition at 700 °C (Fig. S7) due to degradation of the main chain of polyfluorene.[10]

Fluorescence studies of polymer **P1** and **P2** towards guest molecules were done in THF (10 μM, corresponding to the salen moiety/building block). Both polymers show very weak fluorescence with broad and low emission intensity at 540 nm (λ_{ex}= 333 nm) in addition to a peak at 370 nm (**Fig. 3a** and **Fig. 4a**). The emission band near 370 nm of **P1** and **P2** may be assigned as for π-π* transition of fluorene unit and 550 nm is due to extended conjugation of fluorene and salen unit. Upon addition of (*R*)- or (*S*)-phenylglycinol to the THF solution of **P1** or **P2**, a remarkable difference in their fluorescence response has been observed. (*S*)-phenylglycinol increases the fluorescence intensity of **P1** at 452 nm with 13 fold increase in intensity (**Fig. 3a**), whereas (*R*)-phenylglycinol shows very little effect towards fluorescence response of **P1** with only 4 fold increase in intensity (**Fig. 3b**). A plot of I/I_0 (where I_0 is the intensity of **P1** without guest at 540 nm and I is the intensity with guest at 452 nm for **P1**-guest complex; guest = phenylglycinol) against [phenylglycinol] showed gradual enhancement of intensity up to 600 equiv. of (*S*)-phenylglycinol (**Fig. 3c**) and a deep blue fluorescence colour

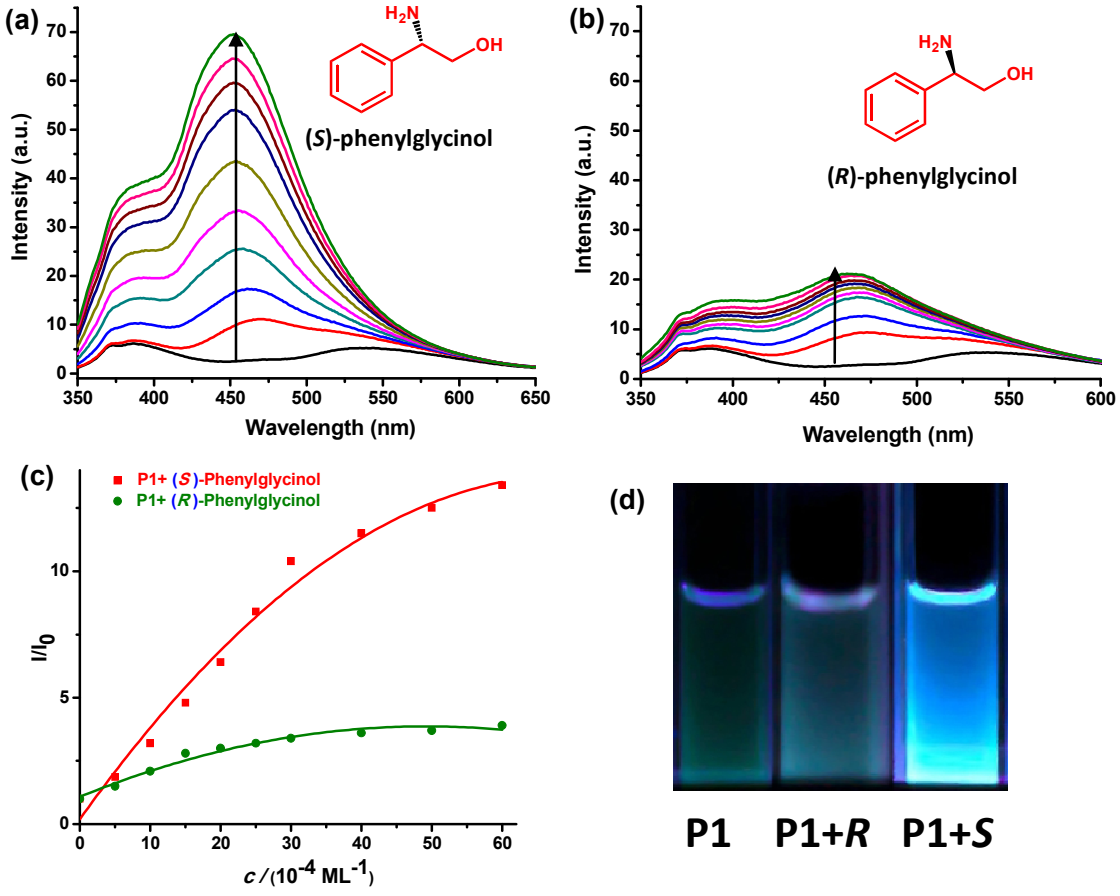

Fig. 3 (a) Fluorescence spectra of **P1** (10 μM in THF) with increasing amount (0-600 equiv.) of a) (*S*)- phenylglycinol and (b) (*R*)-phenylglycinol in THF, Excitation at 333 nm (slit 5 nm/5 nm). (c) Fluorescence enhancement (I/I_0) of **P1** with concentration of (*S*)- and (*R*)-phenylglycinol. (d) Fluorescence color of **P1** in presence of (*S*)- and (*R*)-phenylglycinol under 365 nm UV light.

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of solution (**P1**) after addition for (*S*)-phenylglycinol is observed by naked eye under UV irradiation at 365 nm (**Fig. 3d**). On the contrary, (*R*)-phenylglycinol increases the fluorescence intensity of **P2** by 11 fold (**Fig. 4a**), whereas (*S*)-phenylglycinol shows very little effect (**Fig. 4b**). Plot of I/I_0 against [guest molecule] revealed a gradual increment of intensity up to 600 equiv. of (*R*)-phenylglycinol (**Fig. 4c**) with a deep blue fluorescence colour of **P2** solution (**Fig. 4d**).

Both polymers have a tendency to form enantiomeric complex with guest molecule (i.e. *R,R*-polymer complex with *S*-analyte) than diastereomeric complex (i.e. *R,R*-polymer complex with *R*-analyte). Now the selective recognition of guest molecule by a chiral host polymer depends on the enantiomeric fluorescence difference ratio (*ef*), where $ef = (I_S\text{-}I_0)/(I_R\text{-}I_0)$ for polymer **P1** and $ef = (I_R\text{-}I_0)/(I_S\text{-}I_0)$ for polymer **P2** in which I_0 represents emission intensity of polymer in the absence of a chiral substrate and I_S and I_R are the fluorescence intensities in the presence of (*S*)- and (*R*)- phenylglycinol. A representative bar plot (Fig. S8) is shown to compare recognition behaviour of **P1** and **P2**. The *ef* values are 3.95 for polymer **P1** and 3.22 for polymer **P2**, reflecting significant enantioselective fluorescence response of **P1** towards (*S*)-phenylglycinol and **P2** towards (*R*)-phenylglycinol.

This selective recognition of the polymer may be considered as inherent chiral recognition in the microenvironment of binding cavity that generates from the steric repulsion between (*R,R*)- or (*S,S*)-salen precursor and guest molecule.[7] The binding cavity of polymer, which is composed of hydroxyl and imine group, may provide a rigid and helical chain arrangement in the polymer backbone and well accommodate the guest molecule for the formation of more stable enantiomeric complex rather than less stable diastereomeric complex. The rigid and helical chain arrangement in the polymer backbone is overwhelmingly manifested by CD spectra showing strong positive and negative Cotton effect (Fig. 2). However, upon the inclusion of guest molecule into the polymer solution, small decrease of the intensity in CD signals (Fig. S9) suggest a very little structural change upon complex formation between

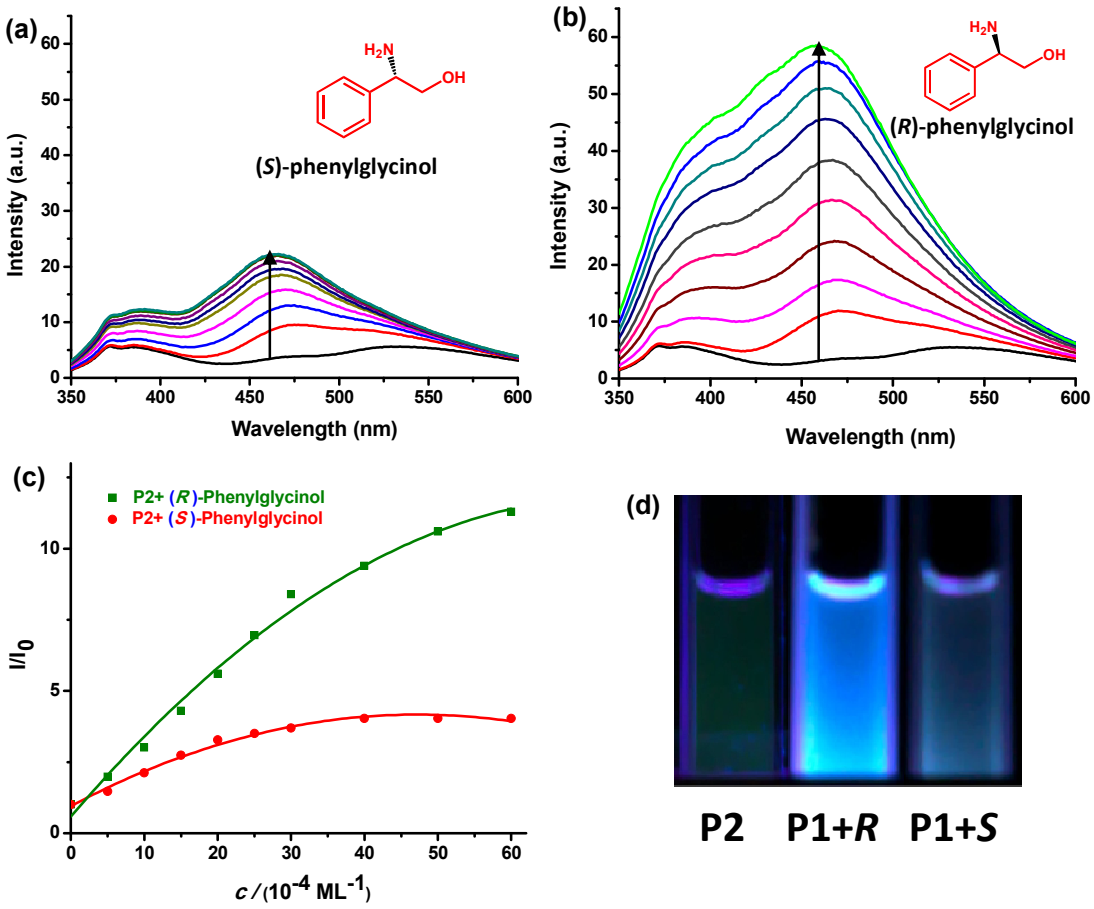

Fig. 4 (a) Fluorescence spectra of **P2** (10 μM in THF) with increasing amount (0-600 equiv.) of a) (*S*)- phenylglycinol and (b) (*R*)-phenylglycinol in THF, Excitation at 333 nm (slit 5 nm/5 nm). (c) Fluorescence enhancement (I/I_0) of **P2** with concentration of (*S*)- and (*R*)-phenylglycinol. (d) Fluorescence color of P2 in presence of (*S*)- and (*R*)-phenylglycinol under 365 nm UV light.

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polymer and guest molecule. We have calculated anisotropy factor/ Kuhn factor (g), the values are as in similar trend a like CD signal change (Fig.S13 & Table ST1). To support preferential forming of enantiomeric complexes rather than diastereomeric, binding constants of **P1** and **P2** towards (*S*)-phenylglycinol and (*R*)-phenylglycinol have been calculated from fluorescence titration measurement by using Benesi-Hildebrand equation.[11] Binding constant of **P1** towards (*S*)-phenylglycinol is 10.9 x 10^3 M^{-1} and towards (*R*) phenylglycinol is 3.7 x 10^2 M^{-1} and for **P2** towards (*R*)-phenylglycinol is 8.8 x 10^3 M^{-1} and towards (*S*)-phenylglycinol is 2.8 x 10^2 M^{-1} (Table ST2). So both polymers show enantiomeric complexes formation preferentially rather than diastereomeric ones.

In order to examine whether this recognition of chiral polymer is due to well-defined spatial arrangement of building block or not, we compare the results with three achiral polymers (**P3**, **P4** and **P5)** where the orientation of the binding cavities are different that we have shown in our previous report (In **P3**, the binding cavity is not planar; in **P4**, the binding cavity is planar and in **P5**, the definite spatial arrangement of binding cavity is absent).[9b] Addition of (*S*)- / *(R)*-phenylglycinol to the solution of these polymers, the fluorescence intensities of these polymer solutions (Fig. S10-S12) are practically unchanged. They have no tendency to capture the guest molecules. These results suggest that the host should have a definite spatial arrangement of binding cavity to recognize a chiral molecule.

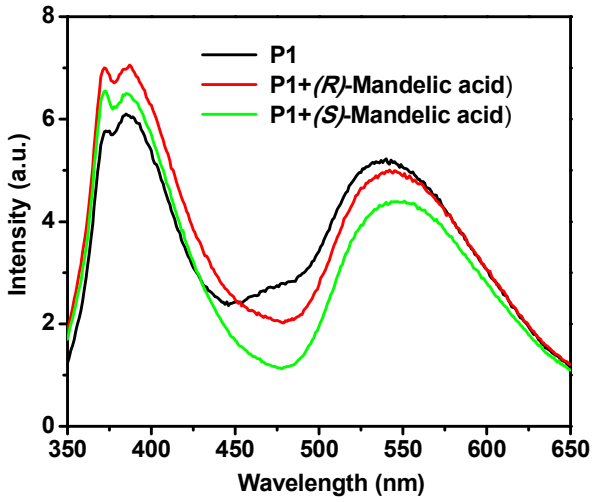

Fig. 5 Fluorescence spectra of **P1** (10 μM in THF) with and without 600 equiv. (*S*)- and (*R*)-mandelic acid in THF. Excitation at 333 nm (slit 5 nm/5 nm).

Both **P1** and **P2** recognize phenylglycinol by enhancement of fluorescence owing to suppressed PET (photoinduced-electron-transfer) quenching by the interaction of protons of phenylglycinol with nitrogen atoms of imine moieties through intramolecular hydrogen bonding.[12] Upon complexation, the lone pair of electrons on the nitrogen atom of imine moiety, is no longer available for PET leading to the enhancement of emission. Due to this PET inhibition, we have observed blue shift of emission maxima, i.e. from 550 nm to 452 nm for P1 and 458 nm for P2. However, in all cases the peak position at 370 nm remains almost unaltered, only the emission maxima corresponding to extended conjugation is blue shifted.

To support the hydrogen bonding between polymer and analyte, ^{1}H-NMR titration of polymer with analytes have been studied. These results are showing that upon gradual addition of analyte, OH proton peak of the polymer becomes gradually broden (Fig. S14). The interaction of the chiral polymer with the two enantiomers of phenylglycinol generates two different diastereomers that show different extent of fluorescence enhancement. It is possible that diastereomers are characteristically different in their physical properties, such as solubilities, heats of formation, etc.

Sometimes, α-hydroxyl carboxylic acid (**Fig. 6a**) has a tendency to interact with nitrogen atoms of imine moiety. To cross check this probability, in a comparable experiment we studied the fluorescence response of **P1** in presence of enantiomers of mandelic acid separately (**Fig. 5**). Also we have investigated the fluorescence behaviour of **P1** with other amino alcohol like enantiomers of valinol (**Fig. 6a-b**).

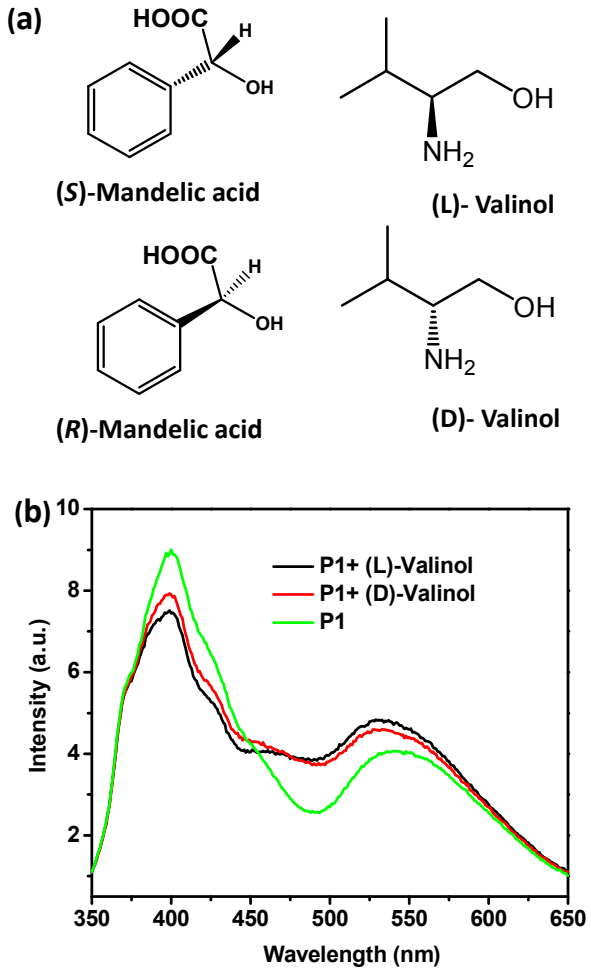

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Fig. 6 (a) Structure of enantiomers of mandelic acid and valinol. (b) Fluorescence spectra of **P1** (10 μM in THF) with and without 600 equiv. (D)- and (L)-Valinol in THF. Excitation at 333 nm (slit 5 nm/5 nm).

Interestingly, no enantioselective recognition has been noticed towards these guest molecules. This may be due to non-adjustment of microenvironment of building block of the polymer. So, our designed polymers **P1** and **P2** are highly selective and sensitive towards enantiomeric phenylglycinol only.

Conclusions

In summary, a series of fluorene based chiral and achiral polymers (**P1**-**P5**) have been designed, synthesized and well characterized. Each polymer has same building block, however, spatial arrangement of the building blocks are different in all polymers. In a very simple way, we are able to tune the spatial arrangement of the polymers chains. Among the polymers, only chiral polymers (**P1** and **P2**) show very nice enantioselective recognition behavior through "turn-on" fluorescence enhancement towards (*S*)- and (*R*)-phenylglycinol. For each enantioseletive complex a bright blue color is observed in presence of a commercially available UV lamp. Achiral polymer have no tendency to accommodate guest molecule. In case of chiral polymers, spatial arrangement of the recognition site of polymer and guest molecule is well matched as it is compared to achiral polymers. The chiral polymers are only selective towards phenylglycinol not other amino alcohol or other chiral small molecules having different functional groups. Again, as the recognition is captured through an instant "turn-on" fluorescence, the present study offers a very easy, quick and sensitive method for chiral phenylglycinol recognition.

Acknowledgements

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Salen-Based Enantiomeric Polymers for Enantioseletive Recognition

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In a simple way, spatial arrangement of building blocks in a main chain polymer determines its recognition property.