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Synthesis and enantiomeric recognition studies of triazine-based chiral fluorescent compounds

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Abstract

In this study novel fluorescence active, two triazine based thiazole derivatives, (2R,2'R)-2,4,6-triamine-N^2-[2-(4-benzothiazolyl)phenyl]-N^4,N^6-[di(butan-1-ol)]-1,3,5-triazine and (1S,1'S,2R,2'R)-2,4,6-triamine-N^2-[2-(4-benzothiazolyl)phenyl]-N^4,N^6-[di(1,2-diphenylethanol)]-1,3,5-triazine with chiral aminoalcohol groups were synthesized conveniently. Their enantiomeric recognition abilities toward the enantiomers of carboxylic acids such as mandelic acid and 2-chloromandelic acid were examined in DMSO/H_2O (30:70) system using fluorescence spectroscopy. It was observed that DMSO solutions of chiral selectors showed no fluorescence emission while the emission increased 38 and 43 fold in 95% H_2O for butan-1-ol and diphenylethanol derivatives, respectively similar with the aggregation-induced emission (AIE) characterized compounds. In the light of the experiment results, it was determined that the R-isomers of carboxylic acids formed more favourable complexes with the chiral selectors when compared to S-isomers.

Keywords: *Chiral recognition, fluorescence, triazine, thiazole, hydrogen bonding, carboxylic acid, aggregation-induced emission.*

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Triazin bazlı kiral floresans bileşiklerin sentezi ve enantiyomerik tanınma çalışmaları

Özet

Bu çalışmada yeni floresans aktif, iki adet triazin bazlı tiyazol türevleri, (2R,2'R)-2,4,6-triamin-N^2-[2-(4-benzotiyazolil)fenil]-N^4,N^6-[di(bütan-1-ol)]-1,3,5-triazin ve (1S,1'S, 2R,2'R)-2,4,6-triamin-N^2-[2-(4-benzotiyazolil)fenil]-N^4,N^6-[di(1,2-difenil etanol)]-1,3,5-triazin uygun şekilde sentezlendi. İlgili bileşiklerin, mandelik asit ve 2-kloromandelik asit gibi karboksilik asit enantiyomerlerine karşı enantiyomerik tanıma yetenekleri, DMSO/H_2O (30:70) sisteminde floresans spektroskopisi aracılığıyla incelendi. Kiral seçicilerin DMSO çözeltileri floresans emisyonu göstermez iken, %95 su yüzdesine çıkıldığında, agregasyona bağlı emisyon karakterli bileşiklere benzer olarak emisyonun sırasıyla bütan-1-ol ve difeniletanol türevleri için 38 ve 43 kat arttığı gözlemlendi. Deney sonuçları ışığında, karboksilik asitlerin R-izomerlerinin, S-izomerleri ile karşılaştırıldığında kiral seçiciler ile daha uygun kompleksler oluşturduğu saptandı.

Anahtar kelimeler: *Kiral tanınma, floresans, triazin, tiyazol, hidrojen bağı, karboksilik asit, kümelenmeye dayalı emisyon.*

1. Introduction

Chiral receptor designing and synthesis for molecular recognition studies of chiral guests such as carboxylic acids, amines, amino alcohols and amino acids have become increasingly an important topic in chiral recognition [1, 2]. Since the significance of chiral recognition is inevitable for the biomolecules such as proteins, carbohydrates and nucleic acids that play a vital role in nature and thereby our life, the development of chiral receptors has drawn attention in agrochemical, pharmaceutical, food and fragrance industries to ensure the quality of the end products by eliminating undesired enantiomers with useless/harmful activities [3, 4]. Among several techniques proposed for discrimination of enantiomers such as circular dichroism (CD) [5], high-performance liquid chromatography (HPLC) [6], capillary zone electrophoresis (CZE) [6], ultraviolet-visible (UV/Vis) [7, 8], fluorescence [9-13] and nuclear magnetic resonance (NMR) [14, 15] spectroscopy, the best technique considered for this purpose has been fluorescence spectroscopy due to its easy, rapid, accurate, selective, sensitive, cost-effective and high-throughput features [16].

Fluorescence-based chiral discrimination has been studied in the past three decades. Fluorescent sensors generally consist of a fluorophore and a binding site. By means of introducing chirality into the binding site, the derived fluorescent sensor could carry out the enantioselective recognition of chiral organic molecules. Many structural features of these host molecules including structural rigidity, hydrogen bonding, hydrophilic, hydrophobic and π-π interactions and also electronic transitions directly differentiate the fluorescence efficiency [17]. In this direction, fluorescent sensor development is encouraged the new ideas with very diverse structures as well as specific responses for substrate detection.

Through the fluorescence-based studies, a unique phenomenon called aggregation-induced emission (AIE) has come to the light and lead to many applications in the fields of organic light emitting diodes (OLEDs), cell imaging, chemosensors and biosensors [18]. AIE-characterized compounds showing induced emission by aggregation have received considerable interest in development of sensors for chiral discrimination [19]. In recent years, although some papers have been published about enantioselective recognition of carboxylic acids within the scope of host-guest chemistry, chiral fluorescent sensors for α-hydroxycarboxylic acids are fairly rare and still highly needed due to their synthetic utility and biological significance as being structural unit of many natural products and drug molecules [20, 21]. Recently, we have reported chiral hosts for α-racemic carboxylic acids such as 2-chloropropionic acid, 2-chloromandelic acid, mandelic acid, α-methoxyphenylacetic acid and 2-phenylpropionic acid utilizing triazine backbone as the binding site in the design [22]. As well as very rare using of chiral hosts, their capability of hydrogen bonding made us focus on triazine group with different substituents.

With reference to the interesting results obtained from our previous work, we decided to make further examination of different thiazole groups. From this point of view, in this work, we tried to combine fluorescent property and chirality in one skeleton and develop novel, effective and utilizable materials. By this way, we will have chance to conceive an idea about comparative fluorescence capacity of target thiazole derivatives. We hope that our novel compounds may shed new light on the mechanism of enantioselective recognition of chiral α-hydroxycarboxylic acids by leading to more far-reaching applications and developments.

2. Materials and methods

All relevant chemicals and common organic solvents obtained from commercial sources (Merck and Sigma Aldrich) were used without further purification. Besides, all the reactions were carried out under a nitrogen atmosphere. Melting points were determined on a Gallenkamp electrothermal WA11373 instrument and are uncorrected. Optical rotations were detected on a Rudolph Research Analytical Autopol II automatic polarimeter. FT-IR spectra were recorded on a Perkin Elmer Spectrum Two spectrophotometer equipped with ATR apparatus. The ^{1}H and ^{13}C NMR spectra were performed on an Agilent 600 MHz spectrometer using deuterated dimethyl sulphoxide (DMSO-d_6) as the solvent. Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) and with the solvent resonance as the internal standard. Fluorescence spectra were obtained with an Agilent Cary Eclipse Spectrophotometer and emission spectra were corrected by the spectrophotometer software using quartz cuvettes with the path length of 1 cm. For reaction monitoring, thin layer chromataography (TLC) were performed on pre-coated silica gel 60 F_{254} aluminum plates and spots were visualized under UV light (254 and 366 nm) while silica gel (230 × 400 mesh) was used for flash chromatographic studies.

2.1. Synthesis of triazine based intermediate (Tr)

2,4,6-Trichloro-1,3,5-triazine (4 mmol) and disopropylethyl amine (DIPEA) (4.8 mmol) were stirred in THF (100 mL) for an hour and the solution cooled to 0 °C. Afterwards, 2-(4-aminophenyl)benzothiazole (4.1 mmol) dissolved in 50 mL THF was added dropwise over a period of an hour. The reaction mixture left stirring at 0 °C for 8 hours

with the assistance of TLC monitoring (Hexane:Ethyl acetate, 6:1). After the filtration of DIPEA hydrochloride salt, the solvent was evaporated under reduced pressure affording crude residue. The crude residue redissolved in CH_2Cl_2 and washed with HCl (0.5 M, 60 mL), brine (60 mL) and water (60 mL), respectively. The organic layer was dried over anhydrous sodium sulfate, subsequently evaporated the solvent. The resulting white solid was used in the next steps without any purification process.

2.2. General procedure for the syntheses of host molecules Tr1 and Tr2

To a well stirred solution of intermediate compound **Tr** (0.6 mmol) and DIPEA (1.5 mmol) in THF (50 mL) at 0 °C, a mixture of amino alcohol derivatives (R)-(–)-2-amino-1-butanol or (1S,2R)-(+)-2-amino-1,2-diphenyl ethanol (1.38 mmol) in THF (30 mL) was added dropwise. Then, it was refluxed for 8 hours for **Tr1** and for 10 hours for **Tr2**. After the completion of the reaction along with TLC monitoring (Hexane:Ethyl acetate, 5:2 for **Tr1** and 4:1 for **Tr2**), the solvent was removed in vacuo, and the crude product was purified by means of flash chromatography over silica gel using Hexane:Ethyl acetate (from 10:1 to 3:1) as eluent to obtain pure product **Tr1** and **Tr2** as white solids.

2.3. (2R,2'R)-2,4,6-triamine-N^2-[2-(4-benzothiazolyl)phenyl]-N^4,N^6-[di(butan-1-ol)]-1,3,5-triazine (Tr1)

198 mg **Tr1** (yield 65%) was obtained as white solid. mp: 220–221 °C, $[\alpha]_D^{20}$ +6.68 (*c* 0.25, DMSO), IR (ATR, cm^{-1}): 3363, 3275 (NH), 2962, 2932 and 2873 (CH), 1613 (C=N), 1573 (C=C), 1378 (C-N), 1239 (NH), ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 10.36 (*NH*-Ar, s, 1H), 10.26 (*NH*-CH, s, 2H), 8.09 (Ar*H*, d, *J* = 8.4 Hz, 1H), 8.04-7.99 (Ar*H*, m, 3H), 7.91 (Ar*H*, d, *J* = 7.8 Hz, 2H), 7.52-7.49 (Ar*H*, m, 1H), 7.42-7.40 (Ar*H*, m, 1H), 5.01-4.96 (-OH, m, 2H), 4.72 (C*H*-NH, td, J = 6.0 Hz, 2H), 3.92-3.84, 3.79-3.38 (CH_2-OH, m, 4H), 1.50-1.37 (CH_2-CH_3, m, 4H), 0.88 (CH_3, td, *J* = 7.4, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 171.2, 165.9, 163.7, 152.7, 140.9, 134.5, 128.9, 126.3, 125.8, 124.6, 121.4, 121.1, 112.8, 65.4, 55.1, 23.7, 10.7. Anal. Calcd for $C_{24}H_{29}N_7O_2S$ (479.21): C, 60.10%; H, 6.09%; N, 20.44%; S, 6.69%; Found: C, 60.15%; H, 6.10%; N, 20.46%; S, 6.69%.

2.4. (1S,1'S,2R,2'R)-2,4,6-triamin-N^2-[2-(4-benzotiyazolil)fenil]-N^4,N^6-[di(1,2-difenil etanol)]-1,3,5-triazin (Tr2)

553 mg **Tr2** (yield 76%) was obtained as white solid. mp: 224–226 °C, $[\alpha]_D^{20}$ -109.73 (*c* 0.25, DMSO), IR (ATR, cm^{-1}): 3323 (NH), 1723 (C=O), 1605 (C=N), 1571 (C=C), 1389 (C-N), 1239 (NH), ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 10.35 (*NH*-Ar, s, 1H), 8.74 (*NH*-CH, s, 2H), 8.09 (Ar*H*, dd, *J* = 8.4 Hz, 4H), 8.03 (Ar*H*, d, *J* = 7.8 Hz, 2H), 7.82 (Ar*H*, d, *J* = 8.4 Hz, 4H), 7.43 (Ar*H*, dd, *J* = 7.2 Hz, 6H), 7.28 (Ar*H*, dt, *J* = 7.8 Hz, 8H), 7.21 (Ar*H*, dd, *J* = 7.8 Hz, 4H), 5.51 (C*H*-OH, dd, *J* = 5.4 Hz, 2H), 5.15-5.19 (-OH, m, 2H) 4.84 (C*H*-NH, dd, J = 5.4 Hz, 2H), ^{13}C NMR (150 MHz, DMSO-d_6) δ (ppm): 167.1, 156.2, 151.9, 142.3, 136.8, 135.1, 134.7, 132.2, 131.1, 128.7, 128.3, 128.1, 128.0, 127.7, 127.5, 127.2, 127.0, 125.6, 122.6, 123.0, 120.7, 75.1, 61.3. Anal. Calcd for $C_{44}H_{37}N_7O_2S$ (727.27): C, 72.60%; H, 5.12%; N, 13.47%; S, 4.41%; Found: C, 72.63%; H, 5.13%; N, 13.49%; S, 4.42%.

2.5. Preparation for the fluorescence study

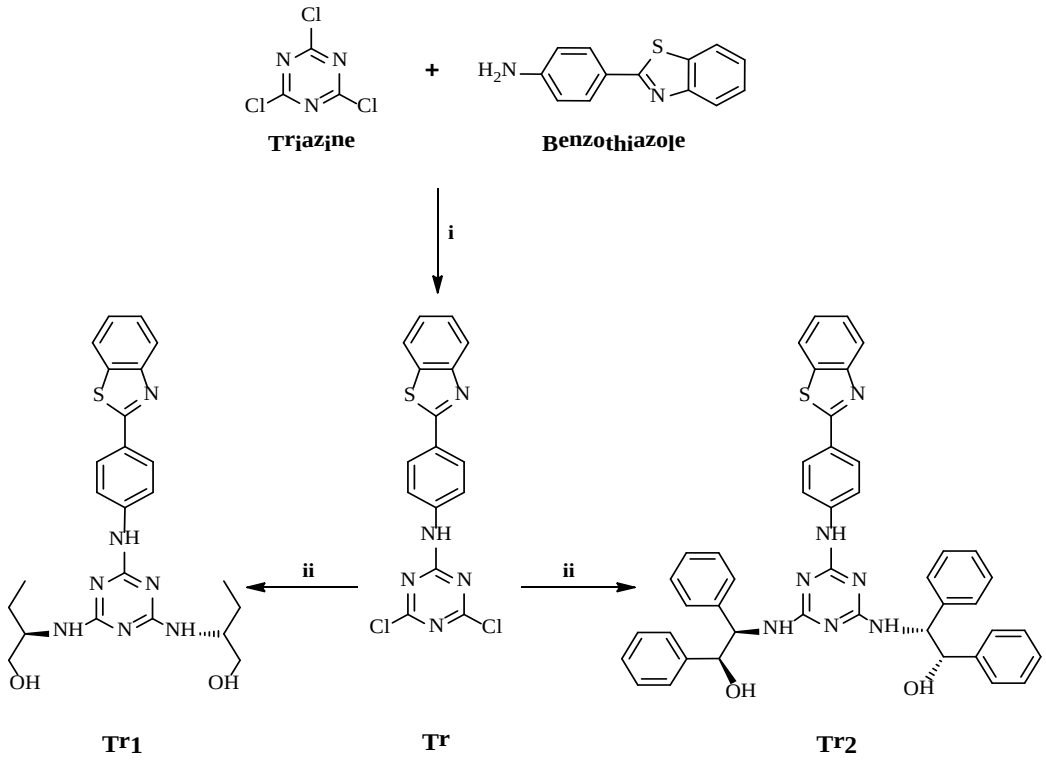
Enantiomeric purity determination of *α*-racemic carboxylic acids (**a**, **b**) was carried out according to the reported technique in our former work [22]. Fluorescence

spectrophotometer was used for the determination of recognition abilities of chiral and fluorescent thiazoles, **Tr1** and **Tr2** in DMSO:H_2O (20:80). 7.5×10^{-4} mol L^{-1} stock solutions of carboxylic acid derivatives **a**, **b** and chemosensor candidates **Tr1**, **Tr2** were prepared in absolute DMSO and the prepared solutions of **Tr1** and **Tr2** were diluted (1.88×10^{-5} M). Afterwards, diluted **Tr1** and **Tr2** solutions and 1 equivalent of *R* or *S*-carboxylic acid solutions were stirred vigorously in DMSO:H_2O (20:80) for 5 min. The fluorescence spectra of those obtained solutions were then recorded instantly.

3. Results and discussion

3.1. Synthesis and structural analysis

The target compounds were synthesized by a two step reaction. Synthetic routes are shown in Scheme 1. Initially, monosubstituted triazine derivative, compound **Tr** was synthesized via nucleophilic substitution reaction between triazine and benzothiazole at 0°C in the presence of DIPEA as a base. Next, the target compounds **Tr1** and **Tr2** were obtained through the same type of reaction using aminobutanol or diphenyl aminoethanol, however binding to two positions were performed by refluxing at this time. The chemical structures of both two target products were characterized by FTIR, ^{1}H NMR, ^{13}C NMR and elemental analysis.



Scheme 1. Synthesis of the fluorescent sensor candidate molecules **Tr1** and **Tr2**.

^{1}H NMR spectrum of **Tr1** showed that C<u>H</u>-NH and C<u>H</u>$_2$-OH protons of amino alcohol group gave signals at 4.72 (td) and 3.92-3.84 (m) ppm, respectively while N<u>H</u> protons resonated at 10.36 (N<u>H</u>-Ar) and 10.26 (N<u>H</u>-CH). In the ^{13}C spectrum of the related compound, <u>C</u>H$_3$, <u>C</u>H$_2$, <u>C</u>H$_2$-OH and <u>C</u>H-NH carbons along with thiazole S-<u>C</u>=N carbon

gave their specific peaks at 10.7, 23.7, 55.1, 65.4 and 171.2, respectively. For the receptor **Tr2**, ^{1}H NMR gave specific peaks of 5.51 (dd) and 4.84 (dd) for the C$\underline{H}_2$-OH and C$\underline{H}$-NH protons, respectively while N$\underline{H}$ protons were observed at 10.35 (N$\underline{H}$-Ar) and 8.74 (N$\underline{H}$-CH). Besides, ^{13}C spectrum showed details of diphenyl aminoalcohol group with the peaks of 61.3 (C$\underline{H}$-NH) and 75.1 (C$\underline{H}$-OH) along with thiazole skeleton details, S-C=N and bridge carbons (C-N, C-S) at 167.1, 142.3 and 132.2, respectively.

3.2. Fluorescence and aggregation-induced emission (AIE) properties

These target final products possessed excellent solubility in DMSO along with showing poor solubility in ordinary organic solvents including dichloromethane, chloroform, tetrahydrofuran, toluene, methanol etc, and no solubility in water.

Both two compounds showed strong solid-state fluorescence, but when we dissolved them in proper solvent stated above there was no fluorescence emission. After the fluorescence characteristic identification of these two sensor candidates, the AIE properties were confirmed by adding ineffective solvent water into the series of their DMSO solutions. As shown in Figure 1, while chiral receptors **Tr1** or **Tr2** dissolved in DMSO with the concentration of 1.88×10^{-5} mol L^{-1} did not emit fluorescence, they began giving emission due to turbidity formation upon addition of large amounts of water.

Figure 1. Fluorescence photograph of **Tr1** in pure DMSO (cell on the left) and in DMSO/H_2O mixture (cell on the right).

In both experiments with **Tr1** and **Tr2**, when water fraction was increased step by step (with ten percent increments), so slight enhancement in fluorescence intensity occurred and we determined that the DMSO/H_2O ratio at which fluorescence intensity showed a sharp increase was 20:80 by naked eye (Figure 2).

Figure 2. Fluorescence photograph of **Tr2** in DMSO/H_2O mixtures with 0% and 95% H_2O fraction.

To further confirm the best fluorescence intensity for the enantiomeric recognition studies, fluorescence spectroscopy was performed in a wide concentration range with the water fraction (f_w) increasing from 0% to 95%. Estimated fluorescence quantum yield (Φf) of **Tr1** and **Tr2** in DMSO/H_2O mixtures compared to the corresponding reference material quinine sulphate supported us to prove the AIE properties of these luminogens. Φf value of **Tr1** and **Tr2** in pure DMSO was calculated as 0.0010 and 0.0012, respectively. Values of Φf remain unchanged for solvent mixtures with H_2O < 70 vol %, but with further increase of H_2O content in the solvent mixtures, the Φf values increased rapidly. Basically, because of these experiments based on the formation of aggregate upon addition of water into the **Tr1**/**Tr2** DMSO solution and fluorescence quantum yield calculations, it was determined that when compared with no water added solution, adding 95% water to the DMSO solutions caused to 38-fold and 43-fold increase in the fluorescence intensity of **Tr1** and **Tr2**, respectively. Thus, the AIE characteristics of **Tr1** and **Tr2** were proven by determining and observing aforesaid features of the related sensors along with literature findings of similar works [18, 19, 23-25].

More importantly, it was determined that the best DMSO/H_2O ratio would be 30:70 during the enantioselective fluorescent recognition studies for the observations of increase in intensity due to host/guest interactions or hydrogen bonding capacities of molecules including water (Figure 3).

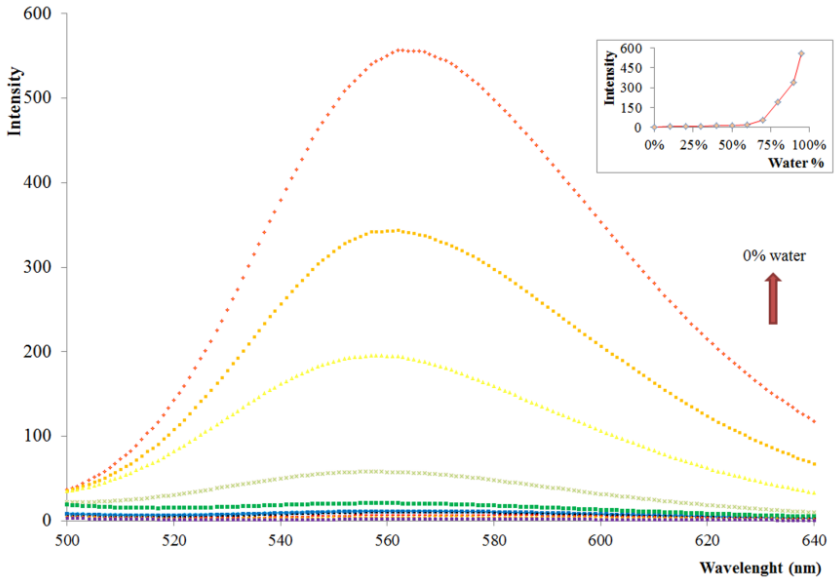


Figure 3. Fluorescence spectrum of **Tr2** with the various of water content (λ_{ex} 350 nm, ex/em slits 5/5 nm), inset: curve of fluorescent intensity vs water percentage in DMSO measured at 562 nm.

3.3. Enantioselective fluorescent recognition studies

The fluorescence response behavior of the triazine based chiral receptors **Tr1** and **Tr2** on *α*-racemic carboxylic acids shown in Figure 4 were investigated in a solution (30:70 DMSO/H_2O) of **Tr1** or **Tr2** hosts and mandelic acid (**a**) or 2-chloromandelic acid (**b**) guest enantiomers.

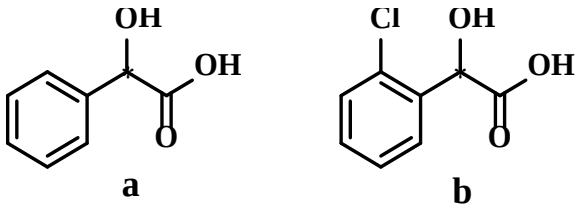


Figure 4. Chemical structures of the guest molecules employed.

We first examined the fluorescence response of chiral ligands on *R*- or *S*-carboxylic acids. *R* and *S* enantiomers of both carboxylic acids caused a large increase in the fluorescence intensity of **Tr1** and **Tr2** except for the fewer effect of (*S*)-2-chloromandelic acid on the fluorescence intensity of **Tr1** under the same condition. However, it does not change the result that the receptors are selective towards the enantiomers of both carboxylic acid enantiomers. Based on the change of fluorescence intensity associated with the addition of guest molecules, fluorescence intensity ratio/enantioselectivity were calculated and compiled in Table 1. By the way, as seen in the spectrums, both **Tr1** and **Tr2** showed a selective recognition of *R* isomers, but the selectivity was weaker for the *S* isomers based on the emission intensities.

Table 1. Fluorescence intensities and intensity ratio of host/guest mixtures in DMSO/H_2O (30:70).

	Tr1		Tr2	
	R	*S*	*R*	*S*
2-ClMA	162.6	100.2	305.9	192.6
	1.62		1.59	
MA	249.2	163.0	301.2	210.9
	1.53		1.43	

If we get deep insight into the recognition system (Figure 5), when ligands **Tr1** and **Tr2** were treated with the individual enantiomers of 2-chloromandelic acid, the fluorescence intensity was strongly induced by *R*-enantiomer and slightly induced by *S*-enantiomer for both ligands. Besides, selectivity of 2-chloromandelic acid *R*- and *S*- enantiomers which were identified with the fluorescence intensity ratio as 1.62 and 1.59 resulted that receptor **Tr1** was a little better than **Tr2** (Table 1). Similar phenomena were found when mandelic acid enantiomers interacted with **Tr1** and **Tr2** hosts, which resulted in better fluorescence intensity for *R*-mandelic acid than *S*-mandelic acid (Figure 6). In addition, while enantiomeric discrimination was good for both receptors, enantioselectivity of **Tr1** was better than **Tr2** against mandelic acid.

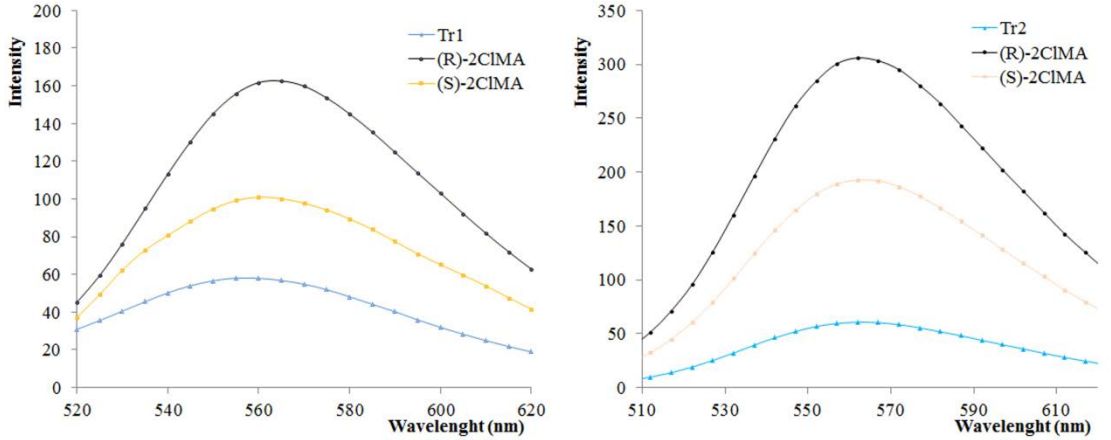


Figure 5. Fluorescence spectra of a mixture of 2-chloromandelic acid enantiomers and **Tr1** and **Tr2** receptors in 1.88×10^{-5} mol L^{-1} with 30:70 DMSO/H_2O ratio.

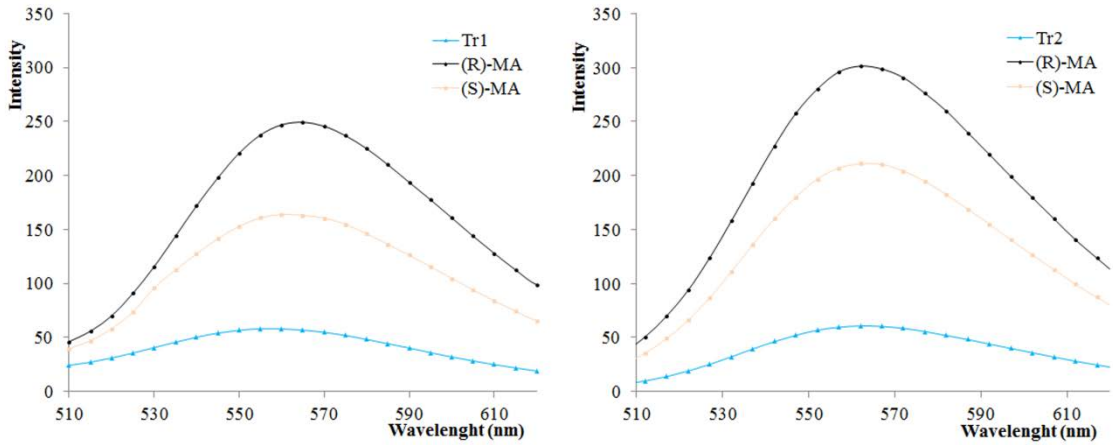


Figure 6. Fluorescence spectra of a mixture of mandelic acid enantiomers and **Tr1** and **Tr2** receptors in 1.88×10^{-5} mol L^{-1} with 30:70 DMSO/H_2O ratio.

We believe that the configuration and so inhibited rotation of benzothiazole derivatives affected the selectivity, the building block of triazine modified by thiazole group could well fit for the formation of a more stable complex between receptors and (*R*)-2-chloromandelic acid or (*R*)-mandelic acid [14, 22].

4. Conclusion

In summary, two novel chiral fluorescent sensors based on triazine bearing thiazole and amino alcohol units were synthesized and characterized. These receptors showed good sensitivity and selectivity in enantiomeric recognition of α-racemic carboxylic acids such as mandelic acid and 2-chloromandelic acid. Also, we demonstrated that DMSO soluble sensors **Tr1** and **Tr2** studied in the work exhibits typical AIE luminogen character upon addition of water into the DMSO solution. Consequently, the present work enriches our investigations toward thiazole-derived fluorescent sensors and provides new insight into the molecular design for fluorescent sensor development. In this way, a valid molecular design strategy to construct high performance light-emitting

material with promising discrimination capability is provided for the scientists working in the field where the use of such compounds is important. We believe that these findings will be helpful for further exploration.

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